DIRECT OXIDATION OF HYDROGEN TO HYDROGEN PEROXIDE

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CERTIFICATE AS PER FORM 'A'

Certified that the work incorporated in the thesis **"Direct Oxidation of Hydrogen to Hydrogen Peroxide"** submitted by **Mr. Chanchal Samanta** was carried out by the candidate under my guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. Vasant R. Choudhary)
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SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Hydrogen peroxide (H_2O_2) is a versatile and environmentally clean oxidizing agent. H_2O_2 is used for seemingly converse applications, which proves its versatility. For example, it can inhibit microbial growth (as in the biofouling of water circuits) and encourage microbial growth (as in the bioremediation of contaminated groundwaters and soils). Similarly, it can treat both easy-to-oxidize pollutants (iron and sulfides) and difficult to oxidize pollutants (solvents, gasolines and pesticides). Global sales of H_2O_2 amount to £1 billion per annum, and demand is rising at a rate of about 10% per annum. Already among the top 15 inorganic chemicals, H_2O_2 may soon overtake elemental sulphur and phosphorus. A major factor in this growth is its increasing application in the paper pulping and water treatment industries where it is being used as an environmentally friendly alternative to chlorine. In some parts of the world, the use of chlorine as a bleaching agent/disinfection has been prohibited by law. Hydrogen peroxide is also a very attractive oxidant for liquid–phase oxidation reactions. It can oxidize organic compounds with high atom efficiency and with the generation of water as the only theoretical co-product. The H_2O_2 oxidation is particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals or agrochemicals and electronic materials, requiring high chemical purity. It may also be used for improving the environment by oxidative removal of very small amounts of toxic compounds. We can make our household cleaner and safer just by substituting H_2O_2 for those caustic chemicals we are currently using.

Presently, H_2O_2 is mainly produced by the anthraquinone process, which is based on the indirect oxidation of hydrogen. This multi-step process suffers from several limitations, such as the use of costly complex solvent system to keep the reactant and product in the solution, the loss of quinone due to non-selective hydrogenation, the elaborate treatments to remove degradation products and organic matters, the deactivation of hydrogenation catalyst and also the need for effluent treatment. The H_2O_2 production cost in this process is therefore high enough to use H_2O_2 for the production of bulk organic chemicals and also for the wastewater treatment. It is, therefore, of great practical interest to develop a more economical and environmentally clean process for the production of H_2O_2, which is based on the direct oxidation of H_2.

Efforts have been made for the H_2O_2 production by the direct oxidation of H_2 to H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$, which is often considered as a 'Dream Reaction'), using palladium-based catalysts. In the direct oxidation of H_2 by O_2 to H_2O_2, the only undesired product formed is water, and hence the process is environ-friendly. Also since the process is based on direct oxidation of H_2, it is expected to be more economical. This process is covered in several patents, but it is not yet commercialized mainly because of its hazardous nature and poor selectivity for H_2O_2. Until recently, the information available on this process in open literature was very little. Recently, a few publications appeared on this practically important reaction. The H_2O_2 selectivities reported are, however, quite low.

The present work for the Ph.D thesis was undertaken as a part of the comprehensive R & D in our laboratory to develop a highly active and selective catalysts and non–(or less hazardous) catalytic process for the direct oxidation of H_2 to H_2O_2 by thoroughly investigating the factors affecting the H_2 conversion activity and H_2O_2 selectivity of supported Pd catalyst in the H_2-to-H_2O_2 oxidation and/or to develop new route for the H_2O_2 production.

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 decomposition over supported metal catalysts,

and also the objectives and scope of the present work has presented.

CHAPTER-2 EXPERIMENTAL

In this chapter, the experimental procedures for the preparation and/or modification of various supported Pd catalysts (viz. Pd/C, Pd/Al_2O_3, Pd/Ga_2O_3, Pd/ZrO_2, Pd/CeO_2, Pd/Hβ, Pd/SiO_2 etc.)

characterization of the catalysts by different surface and bulk analytical tools, e.g.

- crystalline phase (by XRD),
- surface area (using a Surface Area Analyzer),
- elemental concentration, crystal size and morphology (by EDAX-SEM),
- surface composition (by XPS), and
- palladium particle size (by TEM)

the catalytic reactions (direct oxidation of H_2 by O_2 to H_2O_2, decomposition of H_2O_2, hydrogenation of H_2O_2 and hydrazine oxidation by O_2 to H_2O_2)
have been described.

CHAPTER-3 DIRECT OXIDATION OF H_2 TO H_2O_2 OVER SUPPORTED Pd/CATALYSTS: INFLUENCE OF SUPPORT, METAL ADDITIVES AND OXIDATION/REDUCTION OF THE CATALYST

This chapter deals with a detailed study of the influence of support (viz. carbon, Al_2O_3, Ga_2O_3, CeO_2, ZrO_2, ThO_2, CeO_2-ZrO_2, BPO_4, H-β), oxidation state of Pd (Pd^0 or Pd^{+2}) and metal additives (Au, Ag, Pt, Ru, and Rh) present in the supported Pd catalysts on the H_2 conversion and selectivity of H_2O_2 in the H_2-to-H_2O_2 oxidation process and also on the H_2O_2 decomposition activity of the Pd catalysts. The influence of the concentration of metal additives on the activity and selectivity in the oxidation of H_2-to-H_2O_2 and also on the H_2O_2 decomposition for the Pd/ZrO_2 catalyst has also been investigated in more details.

CHAPTER-4 DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION /HYDROGENATION OF H_2O_2 OVER Pd/CARBON CATALYST :INFLUENCE OF CATALYST PRETREATMENT, LIQUID REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

This chapter deals with the detailed experimental investigation of the liquid phase direct oxidation of hydrogen to hydrogen peroxide over Pd/C using a mixed feed of hydrogen–oxygen (4.6 mol% H_2 in O_2). The influence of catalyst pretreatment, reaction medium, halide (F^-, Cl^-, Br^-, I^-) promoters and their concentrations in the reaction medium on the H_2 conversion and H_2O_2 selectivity in the direct oxidation process has been studied. The influence of the above factors on the H_2O_2 decomposition and H_2O_2 hydrogenation reactions, which are consecutive reactions, responsible for reducing the H_2O_2 selectivity on the direct oxidation process were also investigated. Both the catalytic activity and selectivity in the H_2-to-H_2O_2 oxidation and the activity in both the H_2O_2 decomposition and hydrogenation reactions are strongly influenced by the above factors.

CHAPTER-5 DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION / HYDROGENATION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/ALUMINA CATALYST: INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

This chapter deals with the liquid phase direct oxidation of H_2 to H_2O_2 over Pd/alumina catalysts. Influence of the reaction medium, oxidation state of Pd, presence of halide ions (F^-, Cl^-, $Br^-$and I^-) at different concentrations in the reaction medium on the activity and selectivity of Pd/alumina in the direct oxidation of H_2 to H_2O_2 and also on the H_2O_2 decomposition and hydrogenation reactions has been thoroughly investigated. Optimum reaction conditions have been obtained for getting high conversion and H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation over the Pd/alumina catalyst with or without the halide promoter.

CHAPTER-6 INFLUENCE OF HALIDE PROMOTER PRESENT IN REACTION MEDIUM ON THE H_2 TO H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION OVER OXIDIZED AND REDUCED Pd/Ga_2O_3, Pd/ZrO_2 AND Pd/CeO_2 CATALYSTS

The activity/selectivity in the H_2-to-H_2O_2 oxidation (at 25 ºC) and H_2O_2 decomposition (at 25 ºC) of Pd/Ga_2O_3, Pd/ZrO_2 and Pd/CeO_2 catalysts in the acidic reaction medium (0.03 M H_3PO_4 in water) containing different halides (F^-, Cl^-, Br^- and I^-) has been investigated. Influence of Br^- concentration in the medium on the performance of the Pd catalysts in both the reactions has also been studied. The activity/selectivity of all the catalysts in both the reactions is strongly influenced by the presence of halide promoter in the reaction medium and also by the halide concentration.

CHAPTER-7 INFLUENCE OF HALIDE PROMOTER IN SUPPORTED Pd CATALYSTS ON THEIR ACTIVITY / SELECTIVITY IN THE DIRECT OXIDATION OF H_2 TO H_2O_2 AND H_2O_2 DECOMPOSITION / HYDROGENATION OF H_2O_2

This chapter deals with the influence of various halide promoters added to the different supported Pd catalysts (Pd/C, Pd/Al_2O_3, Pd/Ga_2O_3, Pd/CeO_2, Pd/ZrO_2, Pd/ThO_2, Pd/H-β) on their activity/selectivity in the direct oxidation of H_2 to H_2O_2. Effect of the different halides (F^-, Cl^-, Br-, I^-), their concentrations and also the pretreatment to halide containing catalysts on their activity and selectivity in the direct oxidation of H_2-to-H_2O_2 has been thoroughly investigated. The influence of the above factors on the decomposition and/or hydrogenation of H_2O_2 over the catalysts under the conditions similar or close to that used in the direct oxidation of H_2 to H_2O_2 has also been studied.

CHAPTER-8 H_2O_2 FORMATION IN THE INTERACTION OF O_2 WITH HYDRAZINE–REDUCED BORON CONTAINING SUPPORTED Pd CATALYSTS AND IN THE OXIDATION BY O_2 OF HYDRAZINE OVER SUPPORTED Pd CATALYSTS: INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTERS IN THE MEDIUM

First part of this chapter deals with the investigation of H_2O_2 formation in the interaction of O_2 with a hydrazine–reduced boron containing supported Pd catalysts (viz. Pd/Al_2O_3-B_2O_3, Pd/Ga_2O_3-B_2O_3, Pd/CeO_2-B_2O_3, Pd/ZrO_2-B_2O_3 and Pd/boron phosphate) in an aqueous reaction medium with or without containing a mineral acid (H_3PO_4 or H_2SO_4) or a halide promoter. The second part of this chapter deals with the formation of H_2O_2 by a totally new route, which involves a liquid phase oxidation by O_2 of hydrazine or hydrazine sulphate over supported Pd catalysts (viz. Pd/C, Pd/Al_2O_3 and Pd/Ga_2O_3). In both the cases, the influence of reaction medium, halide promoter and its concentration and the support in the catalysts on the formation of H_2O_2 has been investigated.

CHAPTER-1

INTRODUCTION-OBJECTIVES AND SCOPE

Chapter-1

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1.1 ASPECTS ABOUT HYDROGEN PEROXIDE

Hydrogen peroxide (H_2O_2) is naturally produced by both animal and plant cells. It is associated with the mitochondial respiratory chain, as well as various hydroxylation and oxygenation reactions. H_2O_2 is one of the products of the activity of almost all oxidases [1] and it is known to be the cause of various kinds of DNA damage in mammalian [2-3] and plant cells [4]. H_2O_2 is formed in small amounts in living organism as a by-product of autoxidation reactions or during the one-electron reduction of dioxygen. The superoxide and hydroperoxo radicals created in the latter process undergo comproportionation either spontaneously or enzyme catalyzed (superoxide dismutase) to give H_2O_2 and dioxygen. H_2O_2 is present in small but significant concentrations in the atmosphere [5-6] and marine environment [7]. It is created in the atmosphere when ultraviolet light strikes oxygen in the presence of moisture i.e. a natural purification system in our environment. H_2O_2 apparently looks like water (H_2O), but the presence of extra oxygen atom makes it one of the powerful oxidizing agents.

1.2 GENERAL INTRODUCTION

Hydrogen peroxide is a versatile and environ-friendly oxidizing agent that has many practical applications both inside and outside the home. Among the many chemical oxidants available to the chemists, H_2O_2 is the ‘greenest’ since the by-product is water. Its global production is growing rapidly, and further expansion has been predicted [8]. As a replacement of chlorine containing (including hypochlorite and chlorine dioxide) compounds, it is an environmentally friendly oxidant that plays an important role in “green chemistry” [9-10]. It is widely used as a bleaching agent in textile and pulp/paper industries, for wastewater treatment and water disinfection [11-15], etching and purification of electronic materials, metallurgic processes and, also for catalytic oxidation processes in the synthesis of fine and bulk chemicals [14-34]. The cosmetic and pharmaceutical industry also uses the disinfecting properties of H_2O_2. In the manufacture of fine chemicals, H_2O_2 is just one of a large number of liquid-phase oxygen donors [35]. Especially, since the advent of Enichem’s Ti-modified silicate (TS-1), there are now a number of catalysts that are very effective for activating H_2O_2 into selective intermediates. For example, TS-1 can catalyze the direct ammoxidation of cyclohexanone to its oxime in the presence of ammonia and H_2O_2 [36].

Thenard discovered H_2O_2 in 1818 [37], 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) and chemical (viz. isopropanol oxidation, autoxidation of organic compounds) 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 [38] and also by the palladium complexes [39-42] have been reported. Inspite of the favourable thermodynamics of the reaction ($\Delta G = -134$ kJ/mol), the catalysts were quite inefficient for obtaining higher turnover numbers (TON, moles of H_2O_2 per mole of palladium) in the reaction, because of the rapid oxidation of the phosphane ligands. The reported TON of the employed catalyst (palladium trihphenyl phosphine complex) was only 5. A further improvement of the catalyst lifetime with a TON up to 87 was achieved by using more stable triphenylarsine as the palladium ligands [40]. 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 [42]. However, the process is still not suitable for practical application. Synthesis of H_2O_2 employing fuel cell system has been reported earlier [43-44]. More recently, direct and continuous production of H_2O_2 with 93% selectivity employing fuel cell has been reported [45]. However, most of the H_2O_2 is produced mainly by the autoxidation of alkyl anthraquinone, which involves indirect oxidation of hydrogen [46]. This process suffers from several limitations such as the cost of quinone components (required in stoichiometric amounts per cycle) and the requirement for periodic replacement of anthraquinone due to non-selective hydrogenation. The cost of H_2O_2 is therefore, high enough to use it for the production of bulk organic chemicals and, also for the wastewater treatments [14]. The process is only cost effective on a large-scale ($4\text{-}6 \times 10^4$ tpa, where tpa is tonnes per annum) production, although it is often required in smaller scale. If H_2O_2 could be manufactured more cheaply, then it would become the preferred choice of oxygen donor for mild oxidations in the synthesis of fine and/or bulk chemicals by virtue of its high-active oxygen content and the formation of an environmentally benign co-product, water.

The liquid phase 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 it has not been commercialized mainly because of the explosive nature of the H_2/O_2 gas mixture and also for the poor H_2O_2 selectivity in the process. Hence, it is practically very important to develop a highly active and selective catalyst and non–(or less hazardous) catalytic process for the direct oxidation of H_2 toH_2O_2 by thoroughly investigating the factors affecting the H_2 conversion activity and H_2O_2 selectivity of supported Pd catalyst in the H_2–to–H_2O_2 oxidation and/or to develop new route for the H_2O_2 production.

1.3 PROPERTIES OF HYDROGEN PEROXIDE

1.3.1 Physical Properties

Hydrogen peroxide is a clear, colourless and nonflammable liquid having water like appearance, but has characteristics pungent odor. It is miscible with water in all proportions and soluble in variety of organic solvents such as in alcohols, acids, ethers and aromatics etc. H_2O_2 is more hydrogen bonded than water, having higher boiling point than water. Like water, H_2O_2 is a very weak electrolyte with the electrical conductivity of its solutions being similar to that of water. H_2O_2 is also an excellent ionizing solvent. H_2O_2 and water do not form an azeotopic mixture and it can be separated completely by distillation. Table 1.1 summarizes the various physical properties of H_2O_2 and their values. Table 1.2 summarizes some physical properties of different aqueous H_2O_2 and their values.

Table 1. 1 ***Physical Properties of Hydrogen Peroxide***

Sr. No.	Property	Unit	Value
1.	Molecular weight	kg/kmol	34.016
2.	Melting point	º C	– 0.41
3.	Boiling point (at 101.3 kPa)	º C	150.2
4.	Heat of vaporization at 25 ºC	kJ/g	1.517

Table1.1 (continued)

Sr. No.	Property	Unit	Value
5.	Heat of fusion	J/g	367.64
6.	Relative density	-	…
	a) 0 ºC	g/ml	1.470
	b) 20 ºC	g/ml	1.450
	c) 25 ºC	g/ml	1.443
7.	Heat of dissociation	kJ/mol	34.3
8.	Dissociation constant at 20 ºC	-	1.78×10^{-12}
9.	Surface tension at 20 ºC	dyn/cm	80.4
10.	Specific conductance at 25 ºC	$(\Omega.\ cm)^{-1}$	4×10^{-7}

Table 1. 2 ***Physical Properties of Aqueous Hydrogen Peroxide***

Sr. No.	Property	H_2O_2 (wt %)			
		30	50	70	90
1.	Boiling point, º C (at 101.3 kPa)	106.2	113.8	125.5	141.3
2.	Freezing point, º C	–25.7	–52.2	– 40.3	– 11.5
3.	Density at 25 ºC, g/ml	1.1081	1.1914	1.2839	1.3867
4.	ΔH_{vap} at 25 ºC, kJ/g	1.192	2.017	1.832	1.627

1.3.2 Chemical Properties

H_2O_2 is weakly acidic, having a pKa = 11.75. In aqueous solution at 20 ºC it has dissociation constant 1.78×10^{-12}. As a weak acid H_2O_2 forms salts with various metals. H_2O_2 contains oxygen in a state of oxidation midway between molecular oxygen and water.

Therefore, it can behave both as an oxidizing and a reducing agent. Table 1.3 summarizes the various reactions of H_2O_2 classified in terms of their mechanism involved in the reaction.

Table 1. 3 ***Various types of reactions associated with Hydrogen Peroxide***

Reaction	Mechanism
a) Decomposition	$H_2O_2 \rightarrow 2OH^{\cdot}$ (1.1) $H_2O_2 + {}^{\cdot}OH \rightarrow {}^{\cdot}OOH + H_2O$ ${}^{\cdot}OOH + OH \rightarrow H_2O + O_2$ or (1.2) $2H_2O_2 \rightarrow 2\ H_2O + O_2$ (1.3)
b) Molecular additions	$H_2O_2 + Y \rightarrow Y^{\cdot} H_2O_2$ (1.4)
c) Substitutions	$H_2O_2 + RX \rightarrow ROOH + HX$ (1.5) $H_2O_2 + 2RX \rightarrow ROOR + 2HX$ (1.6)
d) Oxidations	$H_2O_2 + W \rightarrow WO + H_2O$ (1.7)
e) Free radical formations	H_2O_2 can form free radicals by homolytic cleavage (of either O–H or O – O bond) $HOOH \rightarrow H^{\cdot} + {}^{\cdot}OOH$, $\Delta H = 380$ kJ/mol (1.8) $HOOH \rightarrow 2\ OH$, $\Delta H = 210$ kJ/mol (1.9)
f) Reductions	$H_2O_2 + Z \rightarrow ZH_2 + O_2$ (1.10)

1.3.2.1 Decomposition

H_2O_2 is an intermediate product in the oxidation of H_2. It is thermodynamically less stable than both H_2O and O_2. The rate at which it decomposes (disproportionates) depends on the temperature and concentration. The stability of pure H_2O_2 solution increases with increasing its concentration. The decomposition rate of ultrapure H_2O_2 increases to about 2.2-2.3 fold for each 10 ºC rise in temperature from ambient to about 100 ºC [15]. H_2O_2 is very sensitive towards decomposition in presence of foreign substances. Many impurities catalyze the decomposition, which may become violent, especially with concentrated solutions. Catalysts include metal ions Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, metal surfaces such as Pt, Pd or Ag, MnO_2, charcoal or alkali even the small amount leached from glass catalyze H_2O_2 decomposition. The H_2O_2 decomposition reaction ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) is highly exothermic ($\Delta H = -105.8$ kJ/mol) and spontaneous ($\Delta G = -237.2$ kJ/mol) and takes place in the presence of small amount of catalyst even in the aqueous solution.

H_2O_2 decomposes more quickly in alkaline solution than in neutral or acidic medium. The maximum stability of H_2O_2 is between pH 3.5-4.5. Homogeneous Fe (II) catalyzed (Fenton's reagent) H_2O_2 decomposition in aqueous medium is widely employed in advance oxidation processes, involving the generation of highly reactive and non-selective hydroxyl radical (·OH) for destruction of organic pollutants in wastewater.

1.3.2.2 Oxidation and Reduction

Hydrogen peroxide can behave both as an oxidizing and a reducing agent.

a) System with redox potential $E_o < -1.80$ V at pH = 0 can not be oxidized by H_2O_2

For pH = 0, $HOOH + 2\ H^+ + 2e^- \rightarrow 2\ HOH$, E_o, V* = + 1.80

For pH = 14, $HOOH + 2\ e^- \rightarrow 2OH^-$, E_o, V* = + 0.87

b) System with redox potential $E_o > -0.66$ V at pH = 0 can not be reduced by H_2O_2

For pH = 0, $HOOH \rightarrow 2\ H^+ + O_2 + 2\ e^-$, E_o, V = – 0.066

For pH = 0, $HOOH + 2\ OH \rightarrow 2\ HOH + O_2 + 2\ e^-$, E_o, V = + 0.88

In most of its reactions, H_2O_2 acts as a strong oxidizing agent. In acidic solutions these reactions are often slow, but in basic solution they are usually fast. H_2O_2 oxidizes Fe^{2+} to Fe^{3+}, $[Fe^{II}(CN)_6]^{4-}$ (ferrocyanide) to $[Fe^{III}(CN)_6]^{3-}$ (ferricyanide). NH_2OH to HNO_3 and SO_3^{2-} to SO_4^{2-}.

With stronger oxidizing agents, H_2O_2 is oxidized (i.e. H_2O_2 is forced to act as a reducing agent) and, in such cases O_2 is always evolved.

$$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 5\ O_2 + 8\ H_2O$$

$$KIO_4 + H_2O_2 \rightarrow KIO_3 + O_2 + H_2O$$

$$2\ Ce(SO_4)_2 + H_2O_2 \rightarrow Ce_2(SO_4)_3 + 2\ H_2SO_4 + O_2$$

The ability of H_2O_2 to reduce chlorine and hypochlorite leads to the use of H_2O_2 as a pollution abatement treatment for industrial waste streams.

1.3.2.3 Substitution

A variety of peroxygen compounds are formed through substitution reactions of H_2O_2 with organic reagents. These compounds are commercially useful as catalysts for polymerizations and also as oxidizing agents for a number of specialized reactions. The reactant and principal product of such reactions include alkylating agents, i.e, alkylhydroperoxides; carboxylic and peroxy acids; acid anhydride or chlorides, i.e, diacyl peroxides; and ketones and ketone peroxides.

1.3.2.4 Molecular Addition

Oxyacid salts, metal peroxides, nitrogen compounds, etc. form crystalline peroxyhydrates in the presence of H_2O_2. Sodium peroxoborate, $Na_2[B_2(O_2)_2(OH)_4]^{\cdot}$ $6H_2O$, which is obtained from H_2O_2 and sodium borate, is used as a brightener in washing powders.

1.4 APPLICATIONS OF HYDROGEN PEROXIDE

Hydrogen peroxide is used in many applications throughout a wide variety of industries. The principal use areas are based on its oxidizing properties and some are derived from substitution, decomposition and the formation of perhydrates.

1.4.1 Bleaching Agent/Cleaning Agent

Environmental concerns have compelled the pulp and paper industries to turn to alkaline solutions of H_2O_2 as a replacement for chlorine and in some cases, for hypochlorite and chlorine dioxide in bleaching applications. It is widely used for bleaching and desizing on natural cellulosic fibers (cotton, flax, linen, jute etc.), protein fibers (wool, silk etc.) and synthetic blends. It is also used to bleach solid surfaces, such as wood or linoleum, and to remove the colour of oils and waxes. A massive amount of H_2O_2 is converted to sodium perborate, sodium percarbonate. The perborate and percarbonate, which are less harsh than chlorine-based cleaning agents, are used mainly in products for washing clothes and fabrics. The most important advantage of using H_2O_2 as a bleaching agent is its non-polluting oxidizing character.

1.4.2 Chemical Synthesis

Hydrogen peroxide and its in-situ derivatives are powerful oxidizing agents that are environmentally attractive, yet capable of oxidizing a wide range of organic compounds. It is widely used in epoxidation and hydroxylation reactions and it is an excellent choice in oxidative cleavage reactions and for oxidizing ketones, aldehydes, alcohols, organic nitrogen and sulfur compounds. The chemical process that currently consume H_2O_2 is the manufacture of epoxy ester (plasticisers) from oils viz. soybean oil, linseed oil etc. The epoxidising agent is a peracid (e.g. peracetic acid), which is formed *in situ* using H_2O_2 as the O-containing feedstock. The hydroxylation of olefins is an important use for H_2O_2, especially in the synthesis of glycerol from propylene. Also large volume of H_2O_2 is consumed for the manufacture of catechol/hydroquinone by the hydroxylation of phenol. Currently large amount of H_2O_2 is consumed for the manufacture of high value bulk chemicals such as propylene oxide from propylene, adipic acid from cyclohexene. Large amount of H_2O_2 is used for the ammoxidation of cyclohexanone to its oxime (cyclohexanone oxime) for the synthesis of caprolactum intermediate for manufacturing Nylon-6.

Hydrogen peroxide and its devatives are also used to prepare long chain amine oxide for detergent use, thiourea dioxide for oxidizing sulfur and vat dyes in textiles processing, di-tert-butyl-peroxy-cycohexanes for use in rubber vulcanization, magnesium silicate sols for fibers coating and forming, hydroxyimidazoles for use as antimycotics and herbicides, and 5-hydroxy-hydantion for use in penicillin and cephalosporin synthesis. H_2O_2 can also be used in a variety of solvent systems since it is soluble in water, many organic solvents or the substrate itself.

1.4.3 Environmental Applications

Hydrogen peroxide is an ecologically desirable pollution-control agent for a variety of water, soil and toxic air emissions, because it yields only water or oxygen on decomposition. In spite of its relatively high unit price (8 times than that of chlorine), H_2O_2 is widely used to detoxify and deodorize domestic and industrial effluent. H_2O_2 can treat or control aldehydes, phenols and other aromatic compounds and reduced sulfur compounds, chlorine, cyanides, NO_X, SO_X, BOD, COD and several other pollutants in various sources of ground and surface water. The treatment of drinking water with H_2O_2 and ozone combinations is increasingly used for enhanced taste and odor removal and organic oxidation. H_2O_2 is also employed for the replacement of objectionable taste and odor compounds, such as geosmin and 2-methyl-isoborneol (MIB) in surface water. Most recently, there has been interest in using H_2O_2 as an *in situ* oxygen source for maintaining aerobic bacteria needed for the bioremediation of organics.

1.4.4 Mining/Extraction of Metals

Various techniques for extracting and purifying metals depend on the use of H_2O_2. Solution mining of uranium is a well-established example, in which H_2O_2 is used to oxidize uranium ore to a form a salt that is soluble in a leaching solution.

1.4.5 Other Uses

There are numerous small speciality uses for H_2O_2. H_2O_2 together with sulfuric acid is used for etching printed circuit boards. Electronic grade (i.e. ultra pure) H_2O_2 is used as an oxidizing agent in the manufacture of semiconductors. 6% H_2O_2 is used by beauticians for coloring hair. The oxygen generated by the catalytic decomposition of H_2O_2 can be used an as in situ blowing agent for preparing certain foam rubbers and plastics. Small amount of H_2O_2 is used in cosmetic preparation, which employ its bleaching and oxidizing properties. H_2O_2 can also be used for controlling microorganisms growth (responsible for cancer) in the human body by injecting externally into the blood stream for certain medical treatment (oxytherapy). Table 1.4 summarizes the various applications of H_2O_2 as per grade.

Table 1.4 ***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 treatment/disinfection, 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 asceptic packaging system.
7.	90%	Used by the military as a source of oxygen. Also used as a propulsion source in rocket fuel.

1.5 MANUFACTURING METHODS OF H_2O_2

Hydrogen peroxide is produced from a variety of sources. Its industrial production has passed through three phases, starting with wet chemical process (hydrolysis of barium peroxide or sodium peroxide with an acid), followed by electrochemical process (electrolysis of H_2SO_4 or $(NH_4)_2SO_4$) and then by organic autoxidation process. Industrially most of the H_2O_2 is produced by the sequential/cyclic oxidation-reduction of alkyl anthraquinone involving indirect oxidation of H_2. Table 1.5 summarizes the various methods (feed stocks and catalysts) for the production of H_2O_2.

Table 1.5 ***Various processes feed stock and reactions involved in the synthesis of*** H_2O_2

Sr. No.	Processes/Feed stocks	Process with main reaction
I	II	III
1)	**Wet Process** Barium peroxide reacts with sulfuric acid or hydrochloride gives hydrogen peroxide and barium chloride.	i) $BaO_2 + 2\ HCl \rightarrow BaCl_2 + H_2O_2$ ii) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$
2)	**Electrolytic Methods** **a)** Electrolysis of H_2SO_4 or $(NH_4)_2SO_4$ at a high current density to form peroxosulphates, which are then hydrolyzed to produce H_2O_2. **b)** Cathodic reduction of dioxygen in alkaline electrolyte directly produces low strength H_2O_2 solution, this process is known as Huron-Dow Process.	i) $2\ SO_4^{2-} \xrightarrow{\text{electrolysis}} S_2O_8^{2-} + 2\ e$ ii) $H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$ iii) $H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$ Cathode reaction $O_2 + H_2O + 2e^- \rightarrow OH^- + HOO^-$ Anode reaction $2\ OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$

Table 1.5 (continued)

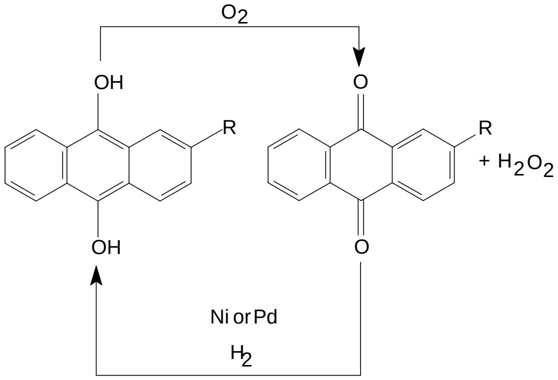
I	II	III
3)	**Organic auto-oxidation processes**	
	a) Anthraquinone auto-oxidation process (BASF process) 2-alkyl anthraquinone reacts with H_2 at a moderate temperature using Pt, Pd or Raney nickel catalyst to form corresponding anthraquinol. The anthraquinol is then oxidized by air or oxygen to produce H_2O_2 and corresponding quinone.	
	b) Alcohol autoxidation (Shell process) The noncatalytic partial oxidation of primary e.g. propyl alcohol and secondary viz. isopropyl alcohol, methyl benzyl alcohol alcohols using air or oxygen in liquid phase produce hydrogen peroxide and the corresponding aldehydes or ketones. The alcohol autoxidation is carried out in the range of 70-160 ºC and 10-20 atm.	i) $CH_3CH_2CH_2OH + O_2 \rightarrow CH_3CH_2CHO + H_2O_2$ ii) $(CH_3)_2CHOH + O_2 \rightarrow (CH_3)_2C = O$ iii) $C_6H_5CH(OH)CH_3 + O_2 \rightarrow C_6H_5COCH_3 + H_2O_2$ iv) $C_6H_5COCH_3 + H_2 \rightarrow C_6H_5CH(OH)CH_3$ The net reaction $H_2 + O_2 \rightarrow H_2O_2$

Table 1.5 (continued)

I	II	III
4)	**Biphasic Synthesis of H_2O_2 from CO, H_2O and O_2** CO, H_2O and O_2 in presence of palladium complexes viz. triphenylphosphane or triphenylarsine in trichlorobenzene/2-methyl-2-butanol/water mixture with a 5/25/40 (v/v/v) ratio at 70 ºC and P_{CO} = 600 kPa; P_{O2} = 6500 kPa produce H_2O_2.	$H_2O + CO + O_2 \longrightarrow H_2O_2 + CO_2$ ($\Delta G_0 = -134$ kJ/mol)
5)	**Production of H_2O_2 from H_2 and O_2:** **a)** 95% H_2 and 5 % O_2 in presence of water vapors at 150-160 ºC and 100 kPa gives H_2O_2 (10 %) aqueous solution minimum energy needed to produce 1 kg of H_2O_2 is 40 kw.h.	$H_2 + O_2 \xrightarrow[\text{150 -160 }^0\text{C, 100 kPa}]{\text{water vapour}} H_2O_2$
	b) Addition of H_2, O_2 and N_2 to acetone in presence of hydrochloric acid, sulfuric acid, and Pd-silica gel catalyst produces H_2O_2 of 50 % relative to H_2.	$H_2 + O_2 \xrightarrow[\text{HCl, } H_2SO_4]{\text{Pd-silica gel}} H_2O_2$
	c) H_2 and O_2 reacts over a Pd catalyst in a biphasic liquid system gives H_2O_2.	$H_2 + O_2 \xrightarrow[\text{catalyst}]{\text{Biphasic liquid}} H_2O_2$

1.5.1 INDIRECT OXIDATION OF H_2 TO H_2O_2 (AUTOXIDATION PROCESS)

Currently, most of the H_2O_2 is industrially manufactured by the sequential oxidation and reduction of alkyl anthraquinone. The process is known as the Riedl-Pfleiderer process, was developed in Germany by BASF during second world war (1935-1945). In this process, 2-Ethyl anthraquinol is oxidized by air or oxygen to the corresponding quinone and H_2O_2.The anthraquinone is reduced back to anthraquinol with hydrogen at a moderate temperature using Pt, Pd or Raney nickel as catalyst. The cycle is then repeated. The reaction is carried out in a mixture of organic solvents (ester/hydrocarbon or octanol/methyl-naphthalene) possessing the essential characteristics viz. should dissolve both quinol and quinone, resistance to oxidation and also should be immiscible with water. The H_2O_2 is extracted with water as a 1% solution. This is then concentrated by distillation under reduced pressure.

Although the process is used on a multi-million tonne scale production of H_2O_2, there are several drawbacks of the anthraquinone process, such as,

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 matters,
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 a costly excersize for this large-scale industrial process.

1.5.2 DIRECT OXIDATION OF H_2 BY O_2 TO H_2O_2 (A DREAM PROCESS)

The most obvious challenge to the anthraquinone process is the direct catalytic oxidation of H_2 by O_2 in aqueous medium for the production of H_2O_2.This process was first patented by Henkel et al in 1914 [49]. 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 Pd catalyzed direct oxidation of H_2 to H_2O_2 is covered in several patents [50–52, 54 –111], which have been summarized in Table 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 [50-52]. 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 [53].

However, 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. Gold catalyst has also been reported for the synthesis of H_2O_2 by the direct oxidation of H_2, but higher selectivity in the process was obtained only after the addition of Pd to the gold catalyst [48].

Early work on the direct formation of H_2O_2 has been noted by Pospelova et al [110-112] who published a series of three papers in 1961, where they discussed the fundamentals of the process viz. the palladium active state responsible for H_2O_2 formation from H_2 and O_2 gas mixture in the liquid medium, the role of acid reducing the decomposition of H_2O_2 etc. They noted that H_2O_2 yield reaches to a maximum value with short contact time and when the catalyst was poisoned 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 reach. The maximum H_2O_2 yield was obtained at H_2/O_2 ratio between 0.8 and 1.2.

Fu et al [113] reported 8.7% H_2O_2 selectivity (at 41% H_2 conversion) as the maximum selectivity in the reaction over Pd supported on hydrophobic fluorinated carbon catalyst (at 25 ºC and 0.65 Mpa pressure). They concluded that the decisive factor in determining H_2O_2 is the hydrophobicity of the catalyst; the Pd metal size or area is found to be less important.

Sellers and co-workers [114] concluded based on their theoretical work that the formation of H_2O_2 by direct oxidation of H_2 by O_2 is more favourable 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 shown promoter plays an important role for the production of H_2O_2.

Thompson and co workers [115] 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 is obtained. In another work, Thompson and co-workers [117] 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 is split 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.

Holderich et al carried out the synthesis of H_2O_2 from H_2 and O_2 over Pd-Pt/Ti-silicate catalyst [116]. They employed *in situ* generated H_2O_2 from H_2 and O_2 for the epoxidation of propylene to propylene oxide. They found the catalyst obtainted by the autoreduction of $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$, which were used as a precursor of Pd and Pt respectively, during the thermal decomposition under pure N_2 atmosphere, was more active than the catalyst reduced under an atmosphere of either H_2 or a mixture of 5% H_2 + 95% N_2 for the propylene epoxidation by the *in situ* generated H_2O_2 from H_2 and O_2.

Park et al have 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 [118].

Choudhary et al have reported non-hazardous direct oxidation of H_2 to H_2O_2 using novel composite Pd-membrane catalyst [119]. Almost 100% H_2 conversion with high H_2O_2 selectivity was obtained with the membrane catalyst.

Beckman et al 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 [120].

Choudhary and co-workers have 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 [121] and also the oxidized and reduced Pd-containing zeolite catalysts [122] 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 on the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. They observed 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 [123].

Lunsford et al [124,125] have 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 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 from H_2 and O_2 on the Pd.

Hutchings et al [126] have 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, but good H_2O_2 selectivity in the reaction was obtained only after the addition of Pd to the gold catalysts. In another work [127], 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 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.

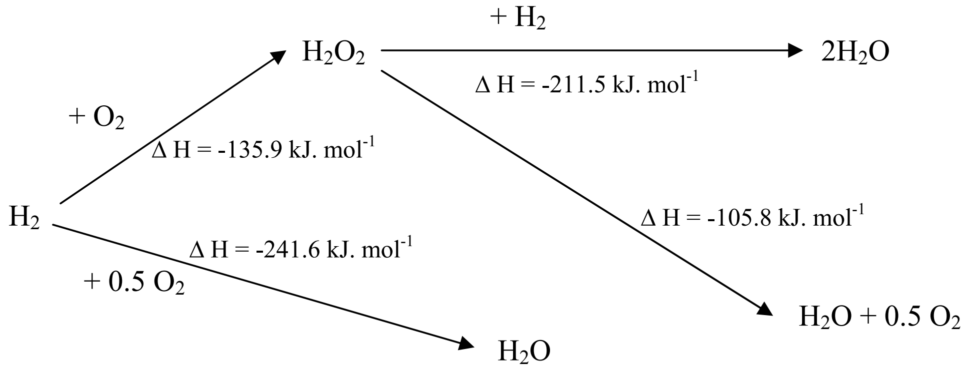
Haruta and co-workers have reported the direct synthesis of H_2O_2 from H_2 and O_2 over highly dispersed Au catalysts [128]. They have identified that the gold nanoparticles are only active for the production of H_2O_2 from H_2 and O_2.

Burch et al [129] reported that the use of low metal loading, an organic co-solvent and reduced Pd as the catalytic metal all lead to good activity and selectivity of the direct oxidation of H_2 to H_2O_2.

Yamanaka et al reported earlier the production of H_2O_2 using fuel cell system [43]. 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 [45]. 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. 7 wt% H_2O_2 was produced continuously at a rate of 8.3 $L.h^{-1}.m^{-2}$. They have concluded to produce a concentrated H_2O_2 solution concentration of O_2 at the cathode should be increased.

Recently, Lunsford [130] provided a brief review on the H_2-to-H_2O_2 oxidation. Very recently, Fierro and co-workers [131] have 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.

Very recently, Lunsford and co-workers [132] have 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. The 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 for 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. Hydronium ions, rather than adsorbed H_2 may react with a peroxo species to form H_2O_2 and H_3O^+ is reformed during the reduction of $PdCl_4^{2-}$ by H_2.



Scheme 1 Reactions involved in the direct synthesis of H_2O_2

The identification of a direct route for the synthesis of H_2O_2 from the reaction of O_2 and H_2 would be highly beneficial. For example, this presents the possibility of small-scale distributed synthesis. At, present no commercial process exits but there has been significant interest in this reaction in industrial laboratories. However, there are two major drawbacks to the operation of direct hydrogen peroxide synthesis. First, H_2/O_2 mixtures are explosive over a wide range of concentrations [47]. When the concentration of H_2 in air and oxygen is in the range 4 to 75 mol% and 4 to 94 mol% respectively, at 1.0 atm pressure, the resulting gas mixture is flammable/explosive, if ignited. The flammability/explosive range is further widen with increasing the pressure. Hence, the ratio of hydrogen to oxygen needs to be carefully controlled or a diluent such as nitrogen, carbon dioxide or argon should be added. In practice, this affects the rate of the direct synthesis reaction as it limits the concentration of the reagents. The other major problem is to obtain high selectivity for H_2O_2 rather than water. Because of the above serious problems, the direct oxidation of H_2 to H_2O_2 is often considered as a ‘Dream Reaction’.

Instead of the substantial efforts by the multi-national companies for development of H_2-to-H_2O_2 oxidation process for the production of H_2O_2, the direct oxidation process has yet not been commercialized mainly because of the hazardous nature of the H_2/O_2 gas mixtures and poor H_2O_2 selectivity in the reaction. If the process is developed and commercialized successfully, it would be a major breakthrough in the oxidation process technology.

Hence, it is practically very important to develop highly active and selective supported Pd-based catalysts and also to investigate the various catalyst/process parameters that influence the yield and/or selectivity of the liquid phase direct oxidation of H_2 to H_2O_2.

1.6 H_2O_2 DECOMPOSITION/HYDROGENATION OVER SUPPORTED METAL CATALYSTS

Hydrogen peroxide is one of the most commonly employed molecules for the investigation of catalysis. The thermodynamic instability of H_2O_2 with respect to disproportionation to H_2O and O_2, coupled with sluggish rate in the absence of catalyst make it an ideal system for investigating catalysis. 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 trace of cations e.g. elements of univalance or more such as Fe, Cu, Ni, Pb and Mn, active surface especially rough surfaces, pH, and, also by radiation especially the rays of short wavelength.

Both homogeneous and heterogeneous catalyzed decomposition of H_2O_2 have been widely investigated. Homogeneous Fe (II) catalyzed H_2O_2 decomposition is widely employed in advance oxidation processes which involve the generation of the highly reactive and non-selective hydroxyl radical (.OH) for the destruction of organic pollutants in wastewater. It has been shown that, the presence of chlorine, sulfate and nitrate ions influence the rate of H_2O_2 decomposition of the Fe (II)/H_2O_2 (Fenton’s reagent) and Fe (III)/H_2O_2 (Fenton’s like reagent) systems [134]. A novel heterogeneous Fenton catalyst for the destruction of pollutants in wastewater by the decomposition of H_2O_2 has been reported [135]. The catalyst was obtained by modifying a polyacrylonitrile fibre surface by treatment with a mixture of hydrazine and hydroxylamine. The surface modification was employed to introduce chelating functional groups containing transition metal cations onto the fibre surface. The H_2O_2 decomposition over a supported γ-FeOOH in a continuous fluidized-bed reactor has been studied [136]. It has been found that, at low H_2O_2 concentration, the H_2O_2 decomposition rate becomes proportional to both H_2O_2 and catalyst concentration. At high H_2O_2 concentration, however, the rate decreased with the increasing H_2O_2 concentration. The heterogeneous H_2O_2 decomposition activity over Fe^{+3} containing zeolite (Fe/ZSM-5) catalyst has been compared with the homogeneous Fe^{+3} catalyzed H_2O_2 decomposition activity under the identical experimental conditions [137]. It has been found that the heterogeneous Fe^{+3} catalysts have a higher activity and a reduced dependence on the pH of the solution as compared to the homogeneous Fe^{+3} catalysts. The catalytic H_2O_2 decomposition employing heteropoly complexes containing Fe (III) ions for the benzene oxidation has been reported [138]. Oxidation of unsaturated hydrocarbons by employing H_2O_2 decomposition catalyzed by Cr-containing heteropolytungstates has been reported [139]. Cu (I) and Cu (II) catalyzed H_2O_2 decomposition has been reported [140-142]. It has been shown that, the catalytic decomposition of H_2O_2 by Fe^{+3} ions in solution can be first or second order with respect to the peroxide concentration [143-144], whereas the supported metal catalysts decompose H_2O_2 by first order kinetics [145-146]. A number of studies on the H_2O_2 decomposition by encapsulated transition metal complexes in zeolite-Y have been reported [147-148]. The H_2O_2 decomposition over pure and ZnO-doped cobaltic oxide [149] and on the MgO and V_2O_5 doped Co_3O_4 [150] has also been reported. The influence of lithium on the H_2O_2 decomposition activity of manganese-alumina catalysts has been reported [151]. The catalytic H_2O_2 decomposition by Cu (II), Co (II) and Fe (III) amine complexes on the surface of silica-alumina has been reported [152]. The heterogeneous H_2O_2 decomposition over substituted magnetites [153] and perovskites type materials [154-157] have been investigated. A number of studies on the decomposition of H_2O_2 catalyzed by polymer supported transition metal complexes have been reported [158-166]. Modified activated carbon catalyzed heterogeneous decomposition of H_2O_2 has been reported. It has been found that the decomposition of H_2O_2 is suppressed significantly by the change of surface properties including the decreased pH_{pzc} modified with oxidizing agent, the reduced active sites occupied by the adsorption of 4–chlorophenol [167]. The apparent reaction rate of H_2O_2 decomposition is dominated by the intrinsic reaction rates on the surface of the activated carbon rather than the mass transfer rate of H_2O_2 to the solid surface. A number of carbon and modified carbon catalyzed H_2O_2 decomposition has been studied earlier [168-171]. Smith et al has explained the well documented decrease in catalytic activity with decreasing pH by proposing that H^+ ions are in competition with H_2O_2 molecules for the same adsorption sites on the carbon surfaces [172].

Heterogeneous Pd catalyzed H_2O_2 decomposition have been studied in the context of Pd catalyzed direct oxidation of H_2 to H_2O_2. Pospelova et al [112] noted the inhibition of the decomposition of H_2O_2 by hydrogen ions is mainly due to HO_2^-, formed as a results of the dissociation, $H_2O_2 \Leftrightarrow HO_2^- + H^+$. They 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 [113] reported that Pd deposited on the hydrophilic supports is very efficient for H_2O_2 decomposition. They observed 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 the some rise in the rate of H_2O_2 decomposition.

A number of studies on the heterogeneous H_2O_2 decomposition over supported Pd catalysts have been reported [121-123, 131] by Choudhary and co-workers. They observed that when acidic medium (0.02 M H_2SO_4) was used in place of pure water as the reaction medium catalytic H_2O_2 decomposition activity of the supported Pd catalysts was reduced appreciably, showing the important role of H^+ on 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 [131]. They have shown that 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 [121-123]. H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation over supported Pd catalysts was found to increase drastically with decreasing the H_2O_2 decomposition activity of the catalysts.

A little or no information is available on the hydrogenation of H_2O_2 over Pd catalyst [132].

It is practically very important to investigate the various parameters (viz. the presence of different halide anions and their concentrations in the catalyst and/or in the liquid reaction medium, the concentration of acid in the reaction medium, the Pd oxidation state, the effect of various supports of the supported Pd catalysts, the presence of different metal promoters in the supported Pd catalysts e.g. Au, Ag, Pt etc.) influencing the decomposition of H_2O_2, which results in a reduction of H_2O_2 yield and/or selectivity in the direct oxidation of H_2 to H_2O_2.

Table 1.6 ***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.	**50**
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.	**51**
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.	**52**
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.	**53**

Table 1.7 ***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.	**54**
GB 1056126	G. W. Hopper (1967)	Aqueous acidic + organic	Pd/Silica gel	50% H_2O_2 yield relative to H_2 was obtained.	**55**
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.	**56**
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.	**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 4,279,883	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.	**59**
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.	**60**
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.	**61**

Table 1.7 (continued)

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.	**62**
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.	**63**
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.	**64**
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).	**65**
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.	**66**
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.	**67**
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.	**68**
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.	**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**

Table 1.7 (continued)

I	II	III	IV	V	VI
EP 0 498 166 A1	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.	**71**
US 4,996,039	Pralus et al (1991)	Aqueous	Metal catalyst comprising platinum or palladium.	5.1 mg H_2O_2 was produced from the gaseous mixture of ($H_2 + O_2 + N_2$) containing 4.5 vol% H_2 in the gas mixture in 0.01 N HCl over 5% Pd/ carbon catalyst after 20 min.	**72**
US 5,082,647	Chuang et al (1992)	Acidic aqueous	VIII group metal on hydrophobic support (viz. styrene divinyl copolymer, polyethylene, polypropylene or ethylene-propylene copolymers etc)	0.23 wt% H_2O_2 was obtained after 5h.	**73**
US 5,135,731	L.W.Gosseer and M. A. Paoli (1992)	Aqueous acidic containing halide and a multifunctional phosphonate or 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.	**74**
US 5,132,099	Hiramatsu et al (1992)	Aqueous	Platinum group metal catalyst supported on a halogenated resin	The presence of halogen compound in the reaction medium was avoided by incorporating halogen into the catalyst support for Pd. The use of Pd/ halogenated material (halogenated resin) minimizes the corrosion of the reaction vessel and the catalyst dissolution in the reaction medium due to the presence of halogen in the reaction medium.	**75**
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.	**76**

Table 1.7 (continued)

I	II	III	IV	V	VI
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.	**77**
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 (molybdenum oxide supported on zirconia or tungsten oxide supported on zirconia.	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.	**78**
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.	**79**
EP 6 621 235 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.	**80**
US 5,447,706	Van Weynbergh et al (1995)	Aqueous	Palladium and Pd associated with at least one another noble metal on supported alkaline-earth metal sulfates or phosphates.	4.5 wt% H_2O_2 at 85% H_2O_2 selectivity was obtained over 2% Pd/BaSO4 catalysts at 25ºC after 8h.	**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; particle size, 0.2-1 mm; specific surface area, 605 m.sup.2 /g; true specific gravity, 1.01;water content, 56.3 wt. %) catalyst	**82**

Table 1.7 (continued)

I	II	III	IV	V	VI
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.	**83**
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.	**84**
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.	**85**
US 5,641,467	Huckins et al (1997)	Acidic aqueous	Group VIII metal supported catalysts	The safe operation of the H_2O_2 synthesis was performed by injecting dispersed minute bubbles of H_2 and O_2 into a rapidly flowing liquid medium, which was surrounded by the sufficient volume of the liquid medium for preventing an explosive reaction between the H_2 and O_2.	**86**
US 5,846,898	Chuang et al (1998)	Acidic aqueous	Group VIII metal supported on a partially hydrophobic, partially hydrophilic support, such as Pd on fluorinated carbon	A higher H_2O_2 selectivity was obtained by addition of sodium and chloride ions into the reaction medium and in the case of a fluorinated carbon support, adding a source of fluoride ions.	**87**
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.	**88**
US 5,972,305	Park et al (1999)	Aqueous	Pd or Pt supported zeolite catalysts containing organic compounds encapsulated onto the zeolite pores.	Direct synthesis of H_2O_2 in aqueous solution was carried out in the presence of a compound (viz. alkyl anthraquinone or anthraquinone encapsulated onto the zeolite pores) that can transfer H_2.	**89**

Table 1.7 (continued)

I	II	III	IV	V	VI
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.	**90**
US 5,961,948	Wanngard et al (1999)	Aqueous	VIII metals and gold supported on porous silica, alumina, non-fluorinated carbon etc.	73% H_2O_2 selectivity was obtained at 97 bar pressure using 3 vol% H_2 in the gas mixture in H_2SO_4 medium containing NaBr.	**91**
US 5,976,486	Thompson et al (1999)	Mixture of lower alkyl alcohol, a lower ketone, water and a mineral acid	The catalyst was composed of inert particles of between 1 and 100 microns, which was coated with three to ten layers of a zirconium or hafnium 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.	**92**
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.	**93**
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.	**94**
US 6,210,651	Nystrom et al (2001)	Acidic aqueous	Group VIII metal supported catalysts	The catalyst employed in the H_2 to H_2O_2 oxidation 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.	**95**

Table 1.7 (continued)

I	II	III	IV	V	VI
US 6,210,651	Nystrom et al (2001)	Acidic aqueous	Group VIII metal supported catalysts	The catalyst employed in the H_2 to H_2O_2 oxidation 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.	**95**
US 6,284,213	Paparatto et al (2001)	Water + alcohol.	Supported VIII group metal (e.g. Pd, Pt, Rh, Ru and Ir) on acid activated carbon functionalized with sulfonic groups.	6.22 wt% H_2O_2 was obtained at 88% H_2 conversion and 86% H_2O_2 selectivity after 60 h.	**96**
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.	**97**
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.	**98**
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.	**99**
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.	**100**
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.	**101**

Table 1.7 (continued)

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.	**102**
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.	**103**

Table 1.8 ***Summary of work on the synthesis of H_2O_2 from separated H_2 and O_2 feed (membrane process)***

I	II	III	IV	V	VI
US 4,393,038	Sun et al (1983)	Gold plated Pd membrane	Aqueous acidic medium containing phosphate stabilizer	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.	**104**
US 5,104,635	T. Kanada et al (1990)	Pt metal containing microporous membrane formed of a hydrophobic polymer.	Aqueous	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.	**105**
US 5,512,263	McIntyre et al (1996)	Composite membrane with multiphase conductivity path one – cation conductive phase (e.g. polymer of perfluorosulfonic acid) second- electron conductive phase (metal or metal screens).	Gas phase	0.05 % H_2O_2 was obtained after 4.25 h.	**106**
US 5,800,796	Webb et al (1998)	The composite membrane comprising the substrate of both oxidizing and reducing agent	Aqueous	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.	**107**
US 6,432,376	Choudhary et al (2002)	Hydrophobic composite Pd-membrane catalyst	Aqueous and or acidic aqueous	The potentially explosive reaction between H_2 and O_2 gas mixtures was eliminated by employing a membrane catalyst	**108**
US 6,448,199	Choudhary et al (2002)	Hydrophobic composite Pd-membrane catalyst	Aqueous and or acidic aqueous	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.	**109**

Table 1.9 ***Summary of work on the direct synthesis of H_2O_2 from H_2 and O_2***

Catalyst	Reaction medium/ **promoter**	**Reaction condition**	**Result / Remarks, if any**	**Investigator (s) (Year)**	**Ref**
I	**II**	**III**	**IV**	**V**	**VI**
Supported Pd catalysts (viz. Pd/SiO_2, Pd/WO_3, Pd/Al_2O_3, Pd/Charcoal etc	Aqueous acidic viz HCl, H_2SO_4, HNO_3 etc	Catalytic reaction was carried out in a reaction vessel clamped in a shaker which was operated at 300-400 vibration per minute in the temperature range of 3 to 35 ºC	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)	**110**
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)	**111**
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)	**112**
Pd supported on hydrophobic carbon, and supported on a mixture of hydrophobic and hydrophilic material	H_2SO_4	4.4 vol% H_2 in H_2-O_2 feed mixture was employed in the Parr reactor, which was operated at 25 ºC and 1.34 – 2.3 Mpa pressure	The maximum H_2O_2 selectivity obtained was 8.7% (at 41% H_2 conversion) even in the presence of a H_2O_2 stabilizer. The H_2 conversion is increased with increase in the F content in the carbon support, indicating a reduced mass transfer resistance for H_2 and O_2 to reach the catalyst sites on hydrophobic supports.	Fu et al (1992)	**113**
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)	**114**

Table 1.9 (continued)

I	II	III	IV	V	VI
Pd-Pt supported on porous zirconium phosphate viologen phosphonate	0.1 N HCl	Atmospheric pressure and room temperature	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)	**115**
Pd-Pt/TS-1	Methanol + water	Temperature = 10 ºC Pressure = [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)	**116**
Palladium supported on hafnium phosphate viologen phosphonate	Methanol + H_2SO_4	Room temperature and atmospheric pressure	Hydrogen is split into protons and electrons by the noble metal; the electrons are transferred to the viologen group whereas the reduced viologen reacts with O_2 producing H_2O_2.	Krishnan et al (2000)	**117**
Organic compound adsorbed zeolite beta-supported Pd catalysts	0.01 N HCl	Equimolar H_2 and O_2 (40:40 ml.min-1) diluted with 50% helium was reacted in glass reactor at room temperature and atmospheric pressure	Quinone adsorbed beta zeolite catalyst was used for the synthesis of H_2O_2.	S.-E. Park et al (2000)	**118**
Pd membrane catalyst	0.02 M H_2SO_4	The oxidation of H_2 in the membrane loop reactor was carried out batch wise with respect to H_2 and liquid medium and continuous with respect to O_2 (50 $cm^3.min^{-1}$)	100% H_2 conversion was achieved with the membrane catalyst; the direct contact between H_2 and O_2 in the liquid phase (for making the H_2-to-H_2O_2 oxidation process less and/or hazardous) was avoided using a Pd membrane catalyst.	Choudhary et al (2001)	**119**
Supported bimetallic Pd-Au catalysts	CH_3OH and super critical CO_2	Catalyst testing was carried out in a Parr stainless still autoclave with 0.5 g catalyst, 5%H_2/CO_2, 25% H_2/CO_2, at 9.2 Mpa pressure and at 35ºC	CO_2 was used as the reaction medium to overcome the transport limitations of the reactants in the process.	Hanchu et al (2001)	**120**

Table 1.9 (continued)

I	II	III	IV	V	VI
Pd-containing fluorinated or sulfated Al_2O_3, Ga_2O_3, ZrO_2, ThO_2, and Y_2O_3	Pure water and 0.02 M H_2SO_4	1.7 vol% H_2 in O_2, pressure = atmospheric, temperature = 22 ºC.	The yield and selectivity of H_2O_2 strongly depend on the acidity of the aqueous medium. The reduced Pd catalysts show much higher H_2O_2 decomposition activity and lower selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation.	Choudhary et al (2002)	**121**
Pd containing zeolite Pd containing zeolite catalysts	Acidic aqueous	1.7 vol% H_2 in O_2, pressure = atmospheric, temperature = 22ºC.	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)	**122**
Pd/Al_2O_3, Pd/ Ga_2O_3, Pd/ CeO_2, Pd/carbon, Pd/ ThO_2	0.02 M H_2SO_4	1.7 vol% H_2 in O_2, pressure = atmospheric, temperature = 22 ºC.	Oxidative pretreatment to the Pd catalyst increases the H_2O_2 selectivity of the catalyst in the H_2-to-H_2O_2 oxidation due to the bulk and/or subsurface oxidation of metallic Pd to PdO in the catalyst.	Choudhary et al (2002)	**123**
Colloidal Palladium (introduced either via $PdCl_2$ or via Pd/SiO_2)	Aqueous acidic (acidified with HCl)	Temperature = 25 ºC, pressure = 760 Torr and $O_2/H_2 = 2$.	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)	**124**
Colloidal Palladium (introduced either via $PdCl_2$ or via Pd/SiO_2)	Aqueous acidic (acidified with HCl)	Temperature = 25 ºC, pressure = 760 Torr and $O_2/H_2 = 2$.	The rate of H_2O_2 formation in the reaction between H_2 and O_2 is proportional to the amount of colloidal Pd rather than the total amount of Pd in the system.	Lunsford et al (2003)	**125**
Supported bimetallic Pd-Au catalysts	CH_3OH and supercritical CO_2	Temperature = 2 ºC, pressure 3.7 Mpa and O_2/H_2 mol ratio = 0.9-1.3.	Supported gold catalyst produce very little or no H_2O_2. The addition of Pd to the gold catalyst drastically improves the performance of the catalyst in the H_2-to-H_2O_2 oxidation.	Hutchings et al (2002)	**126**

Table 1.9 (continued)

Pd/sulfonated carbon and bimetallic Pd-Au catalysts	Methanol + water/HBr	5% H_2 in O_2 + CO_2 mixture at a total pressure 3.7 Mpa at 1-2 ºC	A higher H_2O_2 higher selectivity in the H_2-to-H_2O_2 oxidation is obtained at low temperature and short reaction time. The addition of Pd to the Au catalyst leads to the increase in the H_2O_2 yield/selectivity.	Landon et al (2003)	**127**
Supported nano gold catalysts	Water (P^H of which adjusted by adding HCl or NaOH)	The reaction was carried out at a maximum working pressure 2.0 Mpa with Oxygen and hydrogen molar ratio; 3:7, SV = 8000 mL/g-cat.h^{-1})	The size of Au particles on the support is the determining factor for the production of H_2O_2.	Okumura et al (2003)	**128**
Pd/TiO_2, Pd/WO_3, Pd/Al_2O_3, Pd/F/Al_2O_3	1.6 M H_3PO_4 / NaBr	2.3% H_2 in 75%O_2 + 22.7 N_2, reaction was performed in the Parr autoclave at 3.40 Mpa at room temperature	The low metal loading, an organic co-solvent and reduced palladium are the important factors that lead to the good activity and selectivity in the H_2-to-H_2O_2.	Burch et al (2003)	**129**
Pd loaded sulfonic acid polystyrene resin	Methanol: water (96:4) + 12 ppm HBr	Temperature = 313 K, gas composition (H_2:O_2:N_2 = 2:48:50), pressure = 10 MPa	5.8 wt% H_2O_2 was obtained after 2 h reaction at a high H_2 conversion (> 90%) and H_2O_2 selectivity (77%). 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. Higher surface density of the sulfonic acid group at the surface of the resin results more stabilization of Pd^{II} ions.	Fierro et al (2004)	**131**
Colloidal palladium (added to the system Pd supported on microspheoidal silica)	0.1 N HCl + 0.01 M Br$^-$	Temperature = 10 ºC, pressure = 1 atm, O_2/H_2 ratio = 4	2 wt% H_2O_2 was obtained with selectivity in excess of 90%, based on H_2 reacted. Water is formed both by a parallel reaction between H_2 and O_2 and a secondary reduction of H_2O_2 by H_2. The parallel reaction is inhibited by the presence of bromine.	Lunsford et al (2004)	**132**

1.7 OBJECTIVES AND SCOPE

The present work for the Ph. D thesis was undertaken as a part of the comprehensive R & D programme in our laboratory for developing a highly active and selective catalysts and non–(or less hazardous) catalytic process for the direct oxidation of H_2 to H_2O_2 by thoroughly investing the factors affecting the H_2 conversion activity and H_2O_2 selectivity of supported Pd catalyst in the H_2-to-H_2O_2 oxidation and also to explore new reactions for the H_2O_2 formation production with the following objectives.

1) To investigate thoroughly the factors strongly affecting the H_2 conversion activity and H_2O_2 selectivity of supported Pd catalyst for the slurry phase reaction, such as
   - catalyst support (both transition and non-transition metal oxides, mixed metal oxides),
   - catalyst promoters (e.g. Au, Ag, Pt, Ru, Rh etc) their nature and concentration,
   - presence of halide (F^-, Cl^-, Br^- or I^-) promoter in the catalyst and/or in the liquid reaction medium (aqueous and/or aqueous acidic).
2) To study the influence of above factors also on the decomposition of H_2O_2 and hydrogenation of H_2O_2 over different supported Pd catalysts under the conditions similar or close to that used in the H_2-to-H_2O_2 oxidation.
3) To explore other approaches for the non-hazardous preparation of H_2O_2 (e.g. possibility of oxidation of hydrazine or hydrazine salt by O_2 to H_2O_2).

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CHAPTER-2

EXPERIMENTAL

Chapter-2

EXPERIMENTAL

2.1 GASES AND CHEMICALS

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
Pd (5%)/Alumina	– Lancaster, UK
Palladium chloride	– 99.9% Lancaster, UK
Palladium acetate	– 99.9% Lancaster, UK
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
Thorium nitrate	– Loba Chemie Lab. Pvt. Ltd., Mumbai
Titanium dioxide	– 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
Hydrobromic acid	– s. d. FINE CHEMICALS, Mumbai
Hydroiodic acid	– s. d. FINE CHEMICALS, 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
Boric acid	– (99.5%) QUALIGENS FINE CHEMICALS, Galxo India Ltd
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 chloride	– QUALIGENS FINE CHEMICALS, Galxo (India) Ltd
Potassium bromide	– s. d. FINE CHEMICALS, Mumbai
Sodium bromide	– Sisco Research Laboratory Pvt. Ltd, Mumbai
Potassium iodate	– s. d. FINE CHEMICALS, Mumbai
Potassium fluoride	– s. d. FINE CHEMICALS, Mumbai
Potassium iodide	– E. Merck (India) Ltd, Mumbai
Hydrogen peroxide (30 w/v %)	– 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

2.2 CATALYST PREPARATION

2.2.1 Supported Oxidized and Reduced Pd Catalysts

The Al_2O_3 (prepared from bohemite by its calcination at 500 ºC for 2h) ZrO_2 (prepared from zirconyl nitrate by its hydrolysis to zirconium hydroxide by ammonium hydroxide and calcining at 500 ºC for 2h), Ga_2O_3, CeO_2, ThO_2 (prepared from thorium nitrate by its hydrolysis to thorium hydroxide by ammonium hydroxide and calcining at 500 ºC for 2h), SiO_2 (prepared from B-type silica gel, by calcining at 500 ºC for 3h), CeO_2-ZrO_2 (prepared by mixing CeO_2 and ZrO_2 with Ce/Zr mole ratio of 1.0, in the presence of deionised water just sufficient to form a thick paste, drying the wet mixture in an air oven at 100 ºC for 2h and then calcining it in air at 600 ºC for 3h), H-β (Si/Al = 27 and crystal size = 1.0 μm) and BPO_4 (prepared from a mixture of boric acid and orthophosphoric acid with B/P mole ratio of 1.0, drying the mixture in air oven at 100 ºC for 2h and then calcining it in air at 600 ºC for 3h) 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 500 ºC for 3h.

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 in an air oven.

2.2.2 Modification of Supported Pd Catalysts by Their Halogenation

The halogenated (viz. fluorinated, chlorinated or brominated) Pd/ZrO_2, Pd/Ga_2O_3, Pd/CeO_2, Pd/SiO_2 and Pd/H-β catalysts were prepared by impregnating the respective supported Pd catalyst (in its reduced form) with an ammonium halide (ammonium fluoride, chloride or bromide) from its aqueous solution by the incipient wetness technique, drying at 100 ºC for 2h and then calcining under different gaseous atmospheres (viz. flowing N_2, flowing air or static air) at 400 ºC for 1h. The halogen incorporated supported Pd catalyst calcined at 400 ºC in an inert gaseous atmosphere (N_2) was found to retain the metallic Pd phase. However, for the halogenated Pd catalyst calcined in air (static or flowing) the metallic Pd in the catalyst was oxidized to PdO.

2.2.3 Supported Bimetallic Catalysts

The ZrO_2 supported bimetallic catalysts (e.g. Au-Pd/ZrO_2, Pt-Pd/ZrO_2, Ru-Pd/ZrO_2 and Rh-Pd/ZrO_2) with different noble metal loadings (Pd loading of 2.5 wt%) were prepared by simultaneously impregnating fine particles of ZrO_2 with the corresponding noble metal chloride $PdCl_2$ from their aqueous acidic solution by the incipient wetness technique, drying at 100 ºC for 2h and then calcining in static air at 500 ºC for 3h.

The Ga_2O_3 supported Pd-Au catalysts with different Au loadings were prepared by impregnating fine particles of the oxidized Pd (2.5%)/Ga_2O_3 catalyst with the gold chloride ($HAuCl_4.4H_2O$) from its aqueous solution by the incipient wetness technique, drying at 100 ºC for 2h and then calcining in static air at 500 ºC for 3h.

2.2.4 Halogenated γ-Al_2O_3 Supported Oxidized and Reduced Pd Catalysts

The halogenated (e.g. fluorinated, chlorinated or brominated) γ-Al_2O_3 support was prepared by impregnating fine particles of γ-Al_2O_3 with the respective ammonium halide (5wt % halogen on the support) from its aqueous solution by the incipient wetness technique. After the impregnation, the wet catalyst mass was dried at 100 ºC for 4h and calcined in static air at 500 ºC for 3h. The halogenated γ-Al_2O_3 supported oxidized Pd (2.5 wt %) catalysts were prepared by impregnating the palladium acetate from its acetonitrile solution on the respective halogenated γ-Al_2O_3 by the incipient wetness technique, drying at 100 ºC for 2 h and then calcining in static air at 500 ºC for 3h. The halogenated γ-Al_2O_3 supported reduced Pd catalysts were prepared from the by reducing the respective oxidized Pd catalysts with an ammoniacal hydrazine solution at room temperature (27 ºC) for 2h followed by washing, filtration and drying at 100 ºC in an air oven.

2.2.5 Modification of Commercial Reduced Pd (5%)/Al_2O_3 Catalyst by Its Halogenation

The different halogens (F, Cl, Br or I) incorporated Pd/Al_2O_3 (Lancaster) catalysts with different halogen loadings were prepared by the similar method as described in **Section 2.2.2.** The brominated Pd/Al_2O_3 catalyst was also prepared by impregnating the other bromide precursors (viz. NaBr, KBr and HBr) from their aqueous solution, drying and then calcining in a flow of N_2 at 400 ºC for 1h.

2.2.6 Modification of Commercial Pd (5%)/C Catalyst by Its Halogenation

Fluorinated, chlorinated, brominated and iodinated Pd/C (Lancaster, UK) catalysts were prepared by impregnating the catalyst with the respective ammonium halide from its aqueous solution, drying and calcining in flowing N_2 at 400 ºC for 1h, similar to that described earlier (Section 2.2.4).

2.2.7 Modification of Commercial Pd (5%)/C by Oxidative Pretreatment

The Pd (5%)/C catalyst was modified by its oxidative pretreatments using $HClO_4$, H_2O_2 and air as the oxidizing agent, follows: The $HClO_4$ pretreatment was carried out by treating the catalyst with 1.0 M $HClO_4$ at 100 ºC on water bath for 2h, thoroughly washing the catalyst with deionised water and then drying in air oven at 100 ºC for 1h. The H_2O_2 pretreatment was carried out by treating the catalyst with 30 w/v % H_2O_2 for 2h at 30 ºC then filtering, washing and drying at 100 ºC for 1h. The catalyst was pretreated with air by calcining it in an air oven at 300 ºC for 2h.

2.3 CATALYST CHARACTERIZATION

2.3.1 X-Ray Diffraction (XRD)

The Pd^o and/or PdO phases in the supported Pd catalysts were determined by X-Ray powder diffraction method using a Holland Phillips, PW/1730 X-Ray generator with Cu K_α radiation (λ = 1.5406 Å; 40 kV, 25 Ma). The samples were prepared as thin layer on a glass slide. The average Pd particle size in the supported Pd catalysts was calculated from the Pd^o peak of the XRD spectra, using the Scherrer's formula as follows:

$$D = \frac{0.9\lambda}{\beta \times \pi/180 \times \cos\theta}$$

Where, λ = wavelength of the X-ray used (for Cu K_α radiation, λ = 1.5406 Å), β = Full width at half maximum, θ = Bragg's diffraction angle of Pd^o peak and D = particle size in Å. The corrected β value was determined by the following relation: $\beta = \sqrt{\ } [\beta^2_{(experimental)} - \beta^2_{(instrumental\ )}]$

2.3.2 Surface Area

The surface area of the catalysts was measured by the single point BET method by measuring the adsorption of nitrogen at liquid N_2 temperature and at the N_2 concentration of 30 mol % (balance helium), using a Monosorb Surface Area Analyzer (Quantachrome Crop., USA) based on dynamic adsorption/desoption technique.

Before carrying out surface area measurement experiments, the catalyst (0.1-1.0 g) was pretreated in situ in the sample cell at 300 ºC for 1h in flow of (30 $cm^3.min^{-1}$) of a mixture of helium and nitrogen to remove the traces of moisture and the analyzer was calibrated by injecting a known amount of air.

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

Surface area ($m^2.g^{-1}$) = (desorption counts × 2.84) / (Wt. of catalyst × counts of 1 ml of air).

(2.84 m^2.area = 1 cm^3 N_2 or air. Counts are expressed in terms of surface area, m^2)

2.3.3 X-Ray Photoelectron Spectroscopy (XPS)

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 as internal standard). The electron binding energies (with accuracy of 0.2 eV) were determined from the observed kinetic energies using the relation

Binding energy (B.E.) = hν - kinetic energy (K. E.).

The X-ray radiation (hν) used in the XPS was Mg Kα (1253.6 ev).

The atom ratio of two elements (say, A and B) on the catalyst surface was determined from the XPS peaks as follows:

A/B atom ratio = [peak area of A/photo ionization cross section of A]/[peak area of B/photo ionization cross section of B].

2.3.4 Energy Dispersive X ray Analysis (EDX)

The presence of halogens in the used catalysts was detected by EDX analysis of the used catalysts, using a Leico Cambridge model 440 instrument.

2.3.5 Transmisson Electron Microscopy (TEM)

The Pd particle size in few of the supported Pd catalysts was determined by using TEM. TEM measurements were performed on a JEOL model 1200 EX instrument at an accelerating voltage at 120 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.

2.4 CHEMICAL ANALYSIS

2.4.1 Quantitative Analysis of H_2O_2 by Iodometric Titration Method

Principle of Iodometric Titration: H_2O_2 oxidizes iodide to iodine in the presence of acid. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator [1].

$$H_2O_2 + 2\ KI + H_2SO_4 \rightarrow I_2 + K_2SO4 + 2\ H_2O$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$$

The concentration of H_2O_2 (expressed in terms of wt %) is estimated using the following formula:

Weight % H_2O_2 = [(A - B) × (Normality of $Na_2S_2O_3$) × 1.7] / Sample weight in grams

Where; A = volume of $Na_2S_2O_3$ solution (ml) for sample; B = volume of $Na_2S_2O_3$ solution (ml) for blank and 1.7 = titration factor.

Procedure: 1 ml of 30 w/v % H_2O_2 solution is added to the acidified KI solution in a conical flask (typically 1 gm KI is dissolved in 50 ml 2N H_2SO_4), and is kept for 30 min for the complete liberation of iodine. The liberated iodine is titrated with a standardized $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ solution is added dropwise in the reaction mixture and the flask is gently swirled (to minimize iodine loss), when the solution becomes faint yellow or straw in colour 2 ml starch indicator is added in the reaction mixture and the titration is continued until the blue color just disappears. A blank iodometric titration (without H_2O_2) is carried out to obtain B value.

2.4.2 Detection of Palladium Leaching

Pd leaching (if any) from the Pd catalyst in the reaction medium was detected by adding an aqueous ethanolic dimethyl glyoxime (1%) solution to a 5 ml filtered reaction mixture. The observed yellow orange precipitate of palladium dimethylglyoximate indicates the presence of palladium (in trace amounts) in the reaction mixture.

2.4.3 Quantitative Determination of Hydrazine by KIO_3 Titration

Principle: Hydrazine reacts with potassium iodate [2] under the usual Andrew's conditions (in the presence of a high concentration of hydrochloric acid, iodate is reduced to iodine monochloride; $IO_3^- + 6\,H^+ + Cl^- + 4\,e = ICl + 3\,H_2O$)

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

Thus $KIO_3 \equiv N_2H_4$

Or, 1 ml 0.025 M $KIO_3 \equiv 0.008013$ g $N_2H_4 \equiv 0.003253$ g. $N_2H_4.H_2SO_4$

Procedure: Accurately weighted 0.8-0.1 g hydrazine sulfate is taken into a 250 ml stoppered conical flask. A mixture of 30 ml concentrated hydrochloric acid, 20 ml water and 5 ml chloroform are added to the conical flask. A standard 0.025 M KIO_3 solution is added slowly from a burette (with shaking the stoppered bottle between the additions) until the organic layer just decolorized.

2.5 CATALYTIC REACTIONS

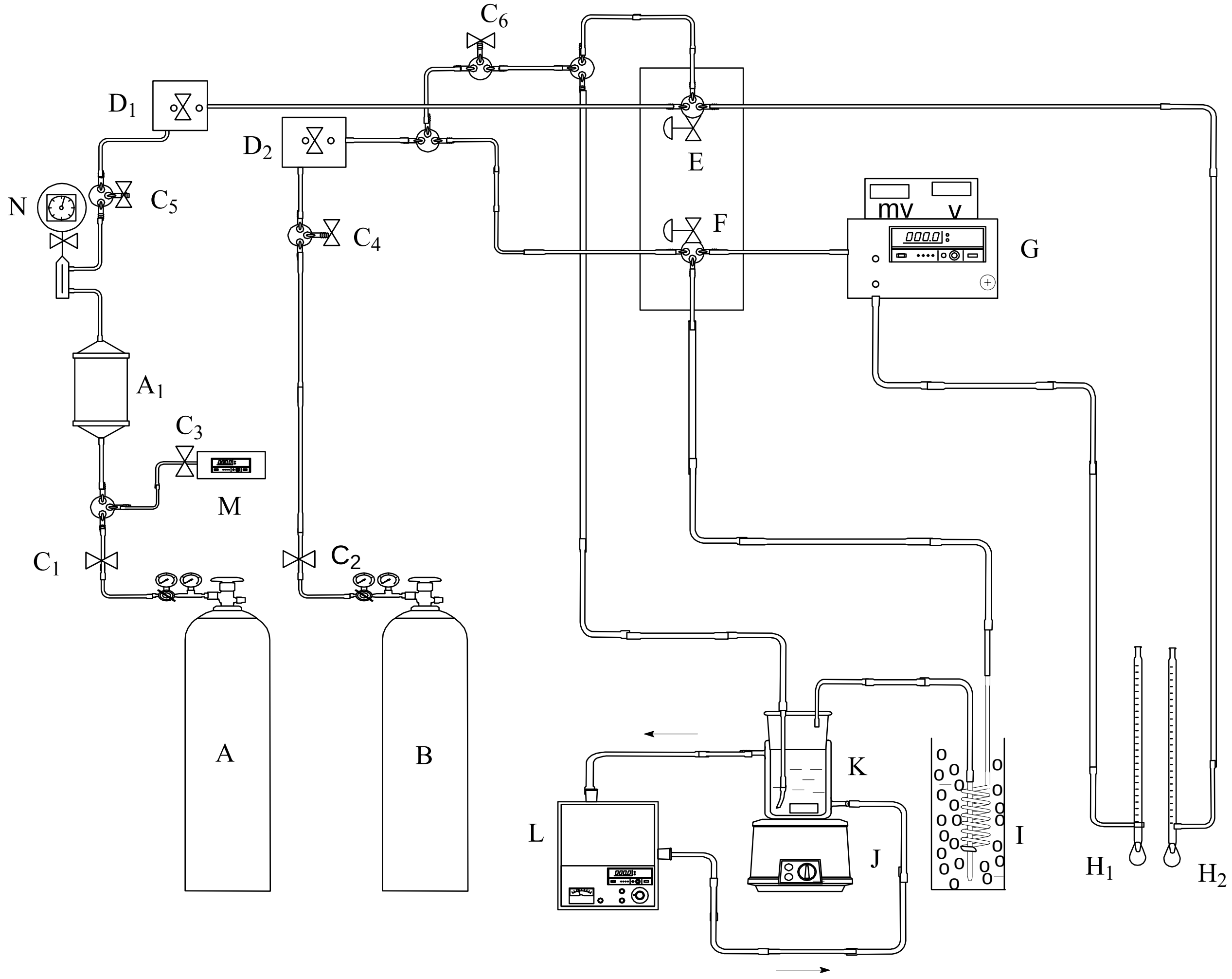
2.5.1 Direct Oxidation of H_2 to H_2O_2 over Supported Pd Catalysts

The Schematic diagram of the experimental set up used for the catalytic oxidation of H_2 to H_2O_2 is described in Figure 2.1. The direct oxidation of H_2 by O_2 to H_2O_2 over the supported Pd catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred glass reactor (capacity 250 cm^3) containing 0.5 g catalyst in a fine power form and an aqueous acidic solution (150 cm^3) as a reaction medium. A H_2/O_2 (4.6 mol % H_2) gas mixture was bubbled (using a fine glass trip) continuously through the reaction medium containing the catalyst under vigorous stirring at a constant temperature. The temperature of the reaction was controlled by passing continuously water through the reactor jacket from thermostatic bath. The concentration of unreacted hydrogen present in the effluent gases, after removing the water vapours from them by condensation at 0 ºC, was measured by an online hydrogen analyzer (Kathorometer, Nucon, New Delhi) based on a thermal conductivity detector. After the reaction, the solid catalyst from the reaction mixture was separated by filtration and the filtrate was analyzed for the H_2O_2 formed in the reaction by iodometric titration. The conversion of H_2, H_2O_2 yield and selectivity were obtained as follows:

H_2 conversion (%) = {[(moles of H_2 in the feed) - (moles of H_2 in the effluent gases)]÷ (moles of H_2 in the feed)} × 100

H_2O_2 yield (%) = [(moles of H_2O_2 formed) ÷(moles of H_2 in the feed)] × 100

H_2O_2 selectivity (%) = [(moles of H_2O_2 formed) ÷(moles of H_2 consumed)] × 100



A = Hydrogen gas main cylinder
A_1 =1000cc hydrogen gas cylinder
B = Oxygen gas cylinder
C_1, C_2, C_3, C_4, C_5, C_6 = Off-on valve
D_1, D_2 = Differential flow controller for hydrogen and oxygen
E = Three way key
F= Two way key
G = Hydrogen analyzer
H_1, H_2 = Soap bubble meter
I = Water vapour trapper
J = Magnetic stirrer
K = Jacketted glass reactor
L = Costant temperature water circulating bath
M = Pressure meter for hydrogen supply
N = Pressure gauge for 1000 cc hydrogen cylinder

Figure 2.1 Experimental set up for liquid phase direct oxidation of H_2 to H_2O_2

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 glass reactor (capacity: 250 cm^3) containing 0.2 g catalyst and 150 cm^3 of an aqueous reaction medium, with or without containing acid and/or halide anions, by injecting 1.0 ml of 30 w/v% H_2O_2 solution in the reactor under vigorous stirring and measuring 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 temperature and atmospheric pressure, as a function of time, using a constant pressure gas collector as shown in Figure 2.2.

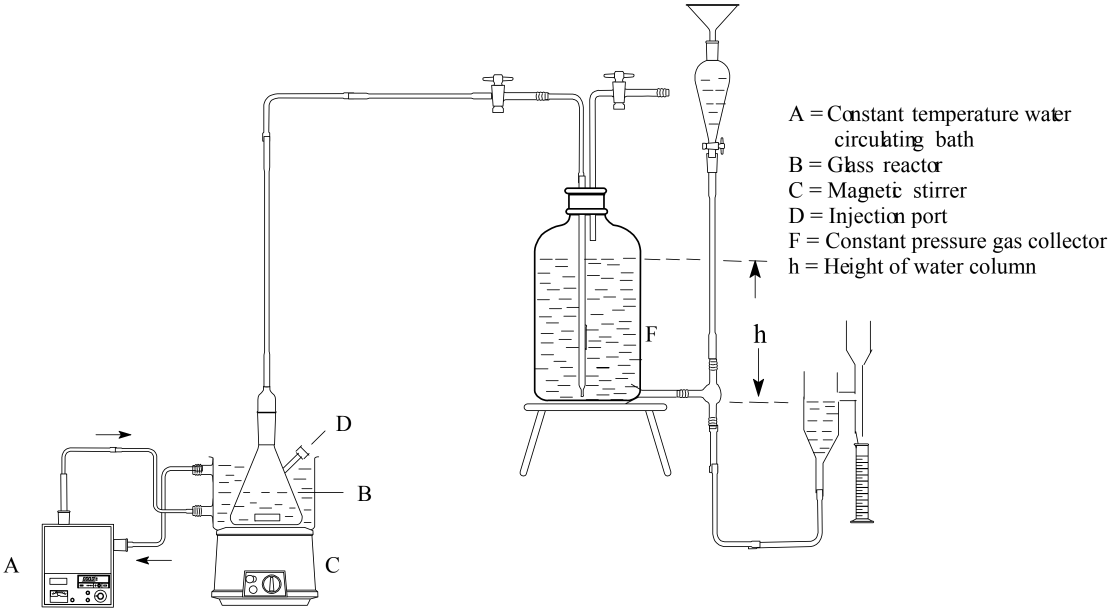


Figure 2.2 Experimental set up for catalytic decomposition of H_2O_2

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 Pd catalysts was evaluated in term of a pseudo first order rate constant (k_d) according to the first order rate expression: $\ln [V_T/(V_T - V_t)] = k_d\, t$ (where, V_T = volume of O_2 evolved in the complete H_2O_2 decomposition, V_t = volume of O_2 evolved in time 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- volume of H_2O_2 solution injected] × [{P – P_w - (h/13.6)}/760] × [273/Tw]

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 temperature of the gas collector, h is the height of the water column and T_w is the temperature of the gas collector (at K).

2.5.3 Hydrogenation of H_2O_2 over Supported Pd Catalysts

The schematic diagrams of the experimental set up used for studying the hydrogenation of H_2O_2 are described in Figures 2.3 and 2.4. The catalytic conversion of H_2O_2 under flowing H_2 was carried out in a magnetically stirred glass reactor (capacity: 250 cm^3) containing 0.1 g catalyst (in fine powder form) and 150 cm^3 of an aqueous acidic solution with or without containing halide anions, as follows: at first all the air in the reactor was thoroughly flushed by passing a pure hydrogen gas and then hydrogen gas was bubbled (at a definite flow) through the reaction medium and after that 3.0 ml of 30 w/v % H_2O_2 was injected (by a glass syringe) in the reactor under vigorous stirring and the gas consumed in the hydrogenation H_2O_2 ($H_2O_2 + H_2 \rightarrow 2H_2O$) or evolved in the H_2O_2 decomposition was measured as function of time using a constant pressure gas collector while making all the necessary corrections.

The catalytic conversion of H_2O_2 under static H_2 was carried out in a glass reactor (capacity: 250 cm^3) containing 0.1 g catalyst (in fine powder form) and 150 cm^3 of an aqueous acidic solution with or without containing halide anions, as follows: at first all the air in the reactor was thoroughly flushed by a pure H_2. After that the reactor was connected (using a two way stopcock as shown in Figure 2.4) 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 w/v% 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 volumetrically from the burette readings, and at constant pressure. The progress of the H_2O_2 conversion reaction was also followed (both in the flowing and volumetric system) by measuring the unconverted H_2O_2 in the reaction medium by taking out the reaction mixture, as a function of time, and analyzing the H_2O_2 by the iodometric titration.

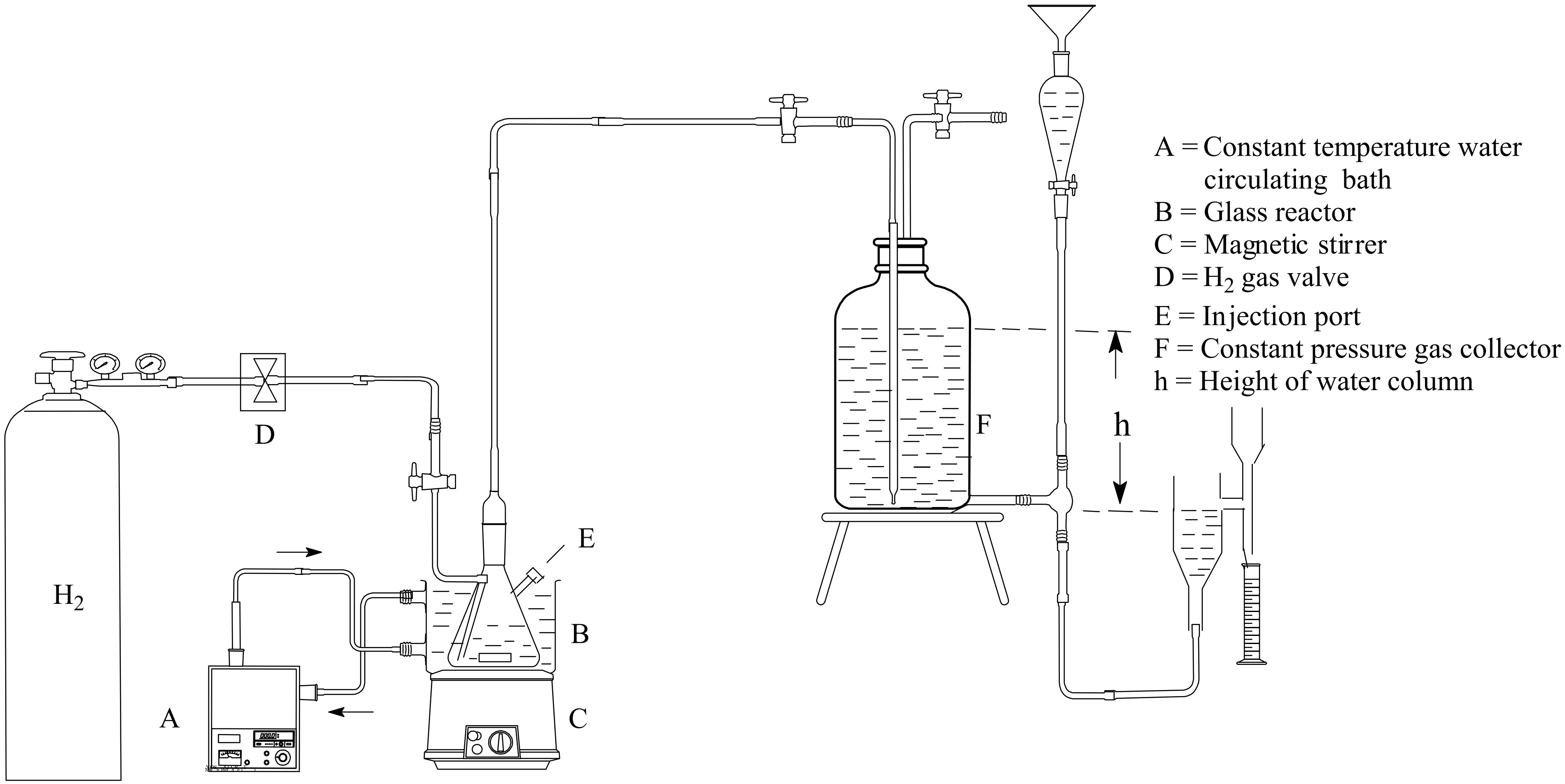
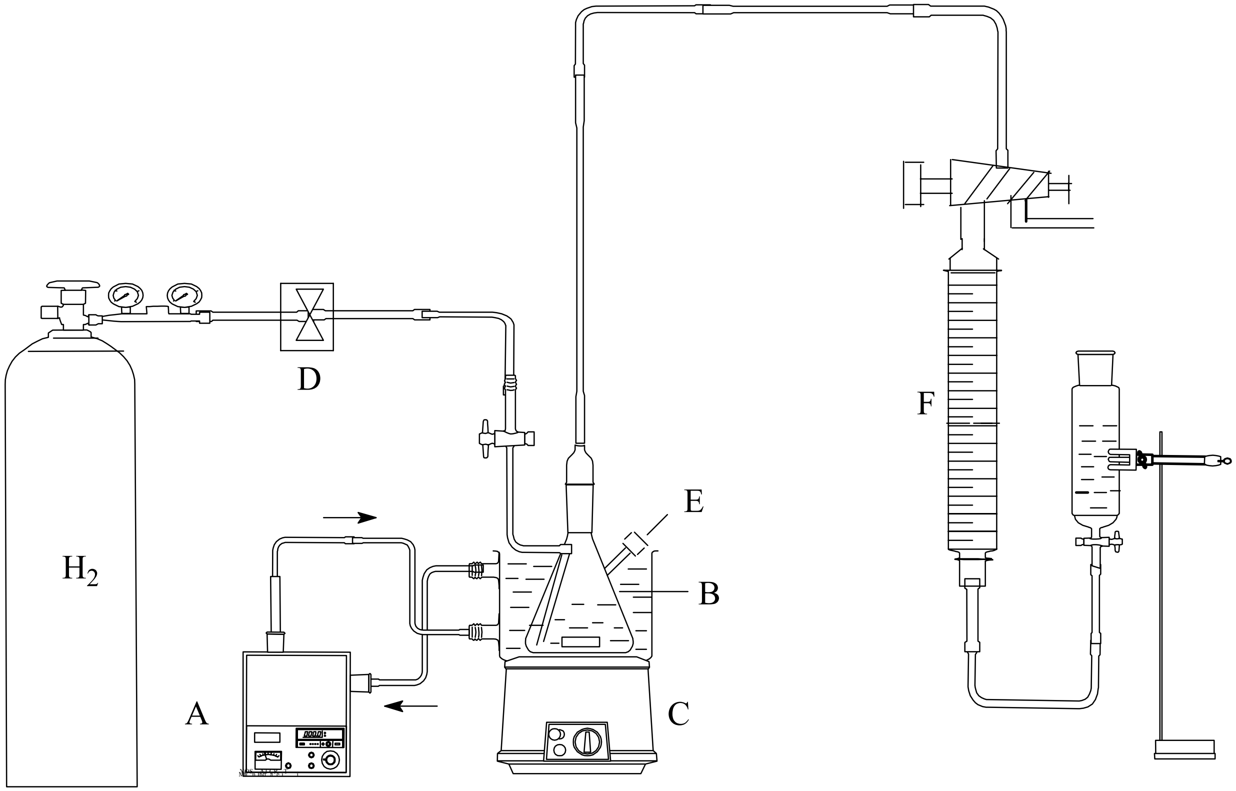


Figure 2.3 Experimental set up for catalytic conversion of H_2O_2 under flowing H_2



A = Constant temperature water circulating bath
B = Glass reactor
C = Magnetic stirrer
D = H_2 gas valve
E = Injection port
F = Gas burette

Figure 2.4 Typical experimental set up for catalytic conversion of H_2O_2 under static H_2

2.5.4 Oxidation of Hydrazine and Hydrazine sulfate by Molecular O_2 over Supported Pd Catalysts

The catalytic oxidation (by O_2) of 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 (or 0.2) 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. A pure O_2 (99.9%) was continuously bubbled through the reaction mixture under vigorous stirring at atmospheric pressure (95 kPa) and constant temperature. The temperature of the reaction was controlled by passing continuously thermostatic water maintained at a desired temperature through the reactor jacket. The H_2O_2 formed 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 as follows:

Conversion of hydrazine hydrate or hydrazine salt (%) = [(moles of the hydrazine hydrate or hydrazine salt in the reaction mixture)$_{t = t}$ / (moles of the hydrazine hydrate or hydrazine salt in the reaction mixture)$_{t = 0}$] × 100 (t = reaction time).

Yield of H_2O_2 = [(Moles of H_2O_2 formed per mole of hydrazine hydrate or hydrazine salt present in the reaction medium) ÷ 2] × 100. The factor 2 was taken since hydrazine (source of hydrogen for the production of H_2O_2) contains four hydrogen atoms.

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CHAPTER-3

DIRECT OXIDATION OF H_2 TO H_2O_2 OVER SUPPORTED Pd CATALYSTS: INFLUENCE OF SUPPORT, METAL ADDITIVES AND OXIDATION/REDUCTION OF THE CATALYST

CHAPTER-3

DIRECT OXIDATION OF H_2 TO H_2O_2 OVER SUPPORTED Pd CATALYSTS: INFLUENCE OF SUPPORT, METAL ADDITIVES AND OXIDATION / REDUCTION OF THE CATALYST

3.1 GENERAL INTRODUCTION-BACKGROUND AND OBJECTIVES

Demand for hydrogen peroxide in the pulp/paper and water treatment industries as an environment friendly alternative to chlorine has been increasing day-by-day [1]. Also there is a trend to use H_2O_2 as a green oxidant in the large volume processes such as caprolactum synthesis and propylene epoxidation. At present, H_2O_2 is produced commercially mainly by the anthraquinone process, involving indirect oxidation of H_2. However, the current cost of H_2O_2 (obtained by the anthraquinone process) still does not allow for the economical production of bulk/inexpensive compounds in large quantities. Hence, there is an urgent need for developing a process for the production of low cost H_2O_2. The liquid phase direct oxidation of H_2 to H_2O_2 is an attractive alternative to the anthraquinone process and lot of efforts have been made since long to produce H_2O_2 by this route; the process is covered in several patents [2-23]. Also, recently, a large number of publications on the H_2-to-H_2O_2 oxidation have been appeared in the literature [24-35], indicating both the scientific and technological importance of the direct oxidation process. Among the noble metals, palladium is unique in catalyzing the formation of H_2O_2 in the reaction between H_2 and O_2. Although, one patent indicates that gold in the form of particles of 50 nm diameter on a hydrophobic support is active for catalyzing the formation of H_2O_2 in the reaction between H_2 and O_2 [36]. Supported nano gold particles have been found active for catalyzing the H_2O_2 formation in the reaction between H_2 and O_2 but the larger gold particles result the formation of water [32]. Use of Pt (which itself is an active catalyst for H_2O formation in the reaction between H_2 and O_2) as a promoter for Pd catalyst to enhance the yield of H_2O_2 in the H_2-to-H_2O_2 oxidation is reported in the earlier patent [8].

The present study was undertaken with the objective of investigating the performance of different supported Pd catalysts in the liquid phase oxidation of H_2 by O_2 to H_2O_2. Influence of the supports and the Pd oxidation state in the catalysts on their activity/selectivity in the H_2-to-H_2O_2 oxidation has been investigated. Influence of the different metal additives and their concentrations in the oxidized Pd/ZrO_2 (or Ga_2O_3)

catalyst on its performance in the H_2-to-H_2O_2 oxidation has been studied. Influence of the above factors on the H_2O_2 decomposition activity of the catalyst has also been studied.

3.2 RESULTS AND DISCUSSION

3.2.1 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 [35]. 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 only has a little or no influence on the reaction rate.

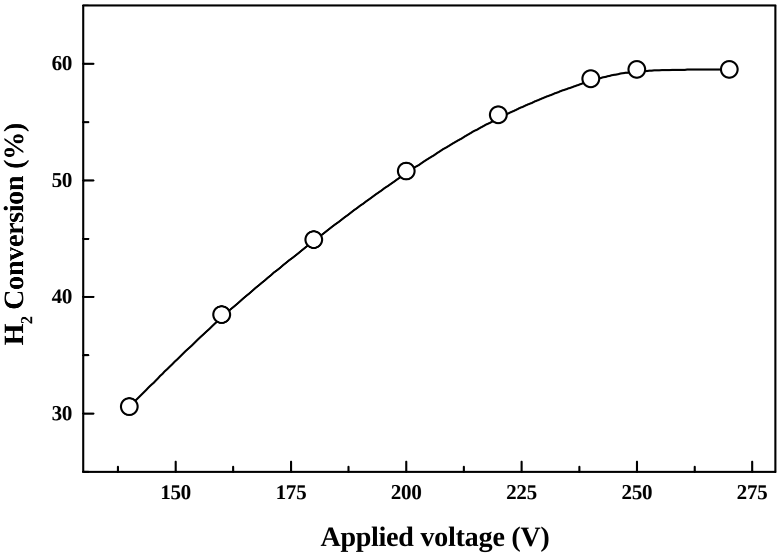

Figure 3.1 Effect of the stirring speed on the conversion of H_2 in the reaction between H_2 and O_2 over the reduced Pd/C catalyst in aqueous acidic (0.03 M H_3PO_4) reaction medium [reaction conditions: volume of the reaction medium = 150 cm^3, amount of catalyst = 0.5 g, H_2 concentration in O_2 = 4.6 mol %, reaction temperature = 25 ºC and reaction period = 3h].

The conversion of H_2 has been determined for different agitation rates with all other variables remaining constant (Figure 3.1). 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.

3.2.2 H_2-to-H_2O_2 Oxidation over Different Supported Pd Catalysts: Influence of the Pd Oxidation State in the Catalyst

Results showing the performance of different reduced and oxidized Pd catalysts in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Tables 3.1 and 3.2.

Table 3.1 Results of the direct oxidation of H_2 to H_2O_2 over different reduced Pd catalysts (Pd loading = 2.5 wt%) [reaction conditions: reaction medium = 0.03 M H_3PO_4, volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, reaction temperature = 25 ºC, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Catalyst	H_2 to H_2O_2 oxidation			H_2O_2 decomposition activity
	H_2 Conversion (%)	H_2O_2 Yield (%)	H_2O_2 Selectivity (%)	$k_d \times 10^4$ (min^{-1})
Pd/C [a]	58.5	0.0	0.0	133.0
Pd/Al_2O_3	50.7	0.6	1.2	48.6
Pd/Ga_2O_3	50.0	5.4	10.8	42.2
Pd/ZrO_2	43.7	3.9	11.2	38.0
Pd/CeO_2	51.8	6.9	13.6	40.3
Pd/CeO_2–ZrO_2	49.1	4.3	8.9	37.2
Pd/ThO_2	31.6	1.2	3.9	32.4
Pd/Hβ	64.5	0.0	0.0	135.8
Pd/BPO_4	57.4	1.2	2.2	49.7
Pd/SiO_2	50.3	0.0	0.0	542.0

[a] *Pd loading = 5 wt%.*

A comparison of results in Table 3.1 and 3.2 reveals that an oxidized Pd catalyst is much more selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation than the corresponding reduced Pd catalyst. The reduced Pd catalyst shows both the higher H_2

conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition activities than the corresponding oxidized Pd catalyst. The H_2 conversion and H_2O_2 decomposition activities differ from one catalyst to another, indicating strong influence of the support on the activity of the catalyst.

Table 3.2 Results of the direct oxidation of H_2 to H_2O_2 over different oxidized Pd catalysts (loading of Pd as (PdO) = 2.5 wt%) in aqueous acidic (0.03 M H_3PO_4) reaction medium. [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, H_2 concentration in O_2 = 4.6 mol %, reaction temperature = 25 ºC and reaction period = 3h].

Catalyst	H_2 to H_2O_2 oxidation			H_2O_2 decomposition activity [a]
	H_2 Conversion (%)	H_2O_2 Yield (%)	H_2O_2 Selectivity (%)	$k_d \times 10^4$ (min^{-1})
Pd/Al_2O_3	28.6	10.6	37.1	3.8
Pd/Ga_2O_3	27.8	8.9	32.5	3.5
Pd/ZrO_2	31.9	12.1	37.9	3.1
Pd/CeO_2	23.8	9.2	38.7	2.9
$Pd/CeO_2–ZrO_2$	24.8	6.7	27.0	4.2
Pd/ThO_2	22.1	5.2	23.5	4.9
Pd/Hβ	32.9	7.1	21.5	5.2
Pd/BPO_4	19.5	7.8	39.9	2.6
Pd/SiO_2	38.9	8.3	21.3	5.8

[a] *k_d = Pseudo first order H_2O_2 decomposition rate constant*

In the H_2-to-H_2O_2 oxidation over the Pd catalyst, the selective H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) and non-selective water ($H_2 + 0.5\ O_2 \rightarrow H_2O$) forming reactions occur simultaneously. The low stability of H_2O_2 molecule in the presence of Pd catalyst leads its further conversion to water ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$), which masks the selective H_2O_2 forming reaction. Hence, a lowering of the H_2O_2 conversion activity of the catalyst should increase the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. Indeed, a close relationship is observed between the selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition activity of the catalysts (Figure 3.2). The surface and bulk properties (viz. metal particle size and surface area) of the reduced Pd catalysts (Table 3.3) are found to be less important in determining the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation as most the reduced Pd catalysts are found to give more or less similar results (little or no H_2O_2 selectivity) in the H_2-to-H_2O_2 oxidation because of their very high H_2O_2 decomposition activity. A similar conclusion have been drawn earlier by Fu et al [37] that the effects of metal particle size and surface area are least important in determining the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation.

Table 3.3 Surface and bulk properties of the different reduced Pd catalysts

Catalyst	Form of palladium (Pd^o or PdO)[a]	Surface area ($m^2\ g^{-1}$)	Average Pd particle size (nm)
Pd (2.5%)/Al_2O_3	Pd^o	176.5	24.4 [b]
Pd (2.5%)/Ga_2O_3	Pd^o	35.8	22.6 [b]
Pd (2.5%)/CeO_2	Pd^o	18.5	45.6 [c]
Pd (2.5%)/ZrO_2	Pd^o	58.6	54.8 [C]
Pd (2.5%)/ThO_2	Pd^o	0.9	-
Pd (2.5%)/SiO_2	Pd^o	230.6	12.1[b]
Pd (2.5%)/ CeO_2-ZrO_2	Pd^o	7.6	-
Pd (2.5%)/BPO_4	Pd^o	24.8	-
Pd (2.5%)/Hβ	Pd^o	165.4	18.5 [b]

[a] Confirmed by XRD, [b] Determined by using Scherrer's formula. [c] Obtained from TEM.

The H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation depends mainly on the extent of non-selective/undesirable H_2-to-water oxidation and consecutive H_2O_2 decomposition/ hydrogenation reactions over the catalyst. Hence, inhibition either in the H_2-to-water oxidation or H_2O_2 decomposition/hydrogenation over the catalyst should increase the H_2O_2 selectivity in the process. The presence of PdO phase in the catalyst drastically reduces the

H_2O_2 decomposition activity of the catalyst and consequently H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation is increased.

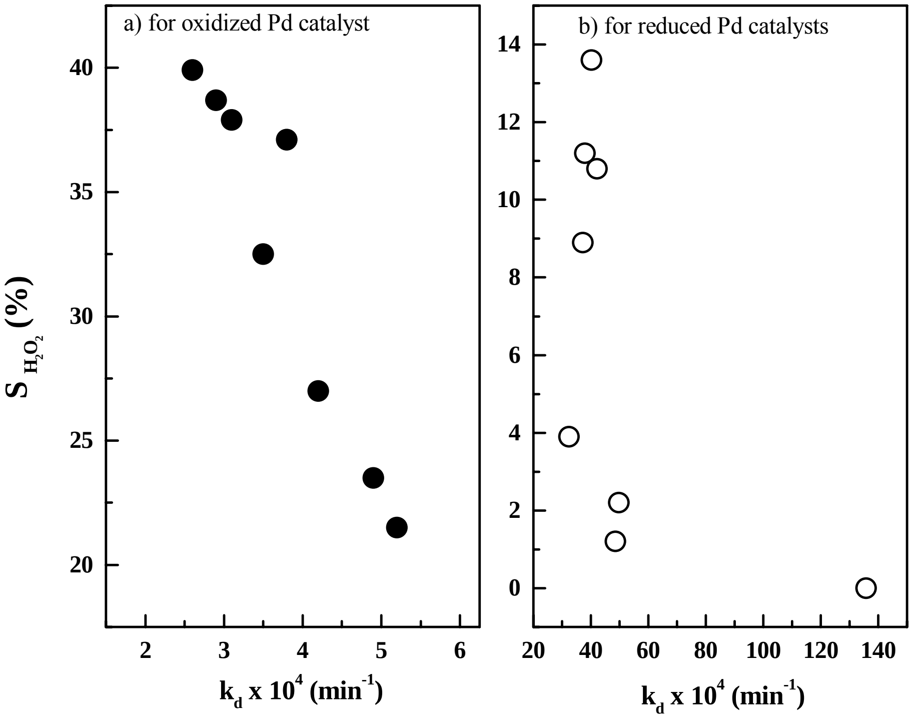

Figure 3.2 Variation of H_2O_2 selectivity ($S_{H_2O_2}$) in the H_2-to-H_2O_2 oxidation with the H_2O_2 decomposition activity for the different supported oxidized (a) and reduced (b) Pd catalysts (k_d = pseudo first order H_2O_2 decomposition rate constant).

3.2.3 Influence of Au Concentration in the Oxidized Pd/Ga_2O_3 Catalyst on Its Performance in H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions in Acidic (0.03 M H_3PO_4) Reaction Medium

Results showing the influence of gold (Au) concentration in the oxidized Pd/Ga_2O_3 catalyst on its performance in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.03 M H_3PO_4) medium are presented in Figure 3.3. Au was incorporated in the oxidized Pd/Ga_2O_3 catalyst from the aqueous solution of $HAuCl_4$ by incipient wetness technique, drying and calcining in static air at 500 ºC.

The H_2 conversion over the catalyst is increased with the increase in the gold loading in the catalyst. However, the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is increased and then passes through a maximum with the increase in the Au loading in the catalyst.

Thus, there is an optimum Au concentration for achieving highest H_2O_2 yield in the reaction. The observed lower H_2O_2 yield at the higher Au concentration in the catalyst is because of the higher H_2O_2 decomposition activity of the catalyst, as shown in Figure 3.4a. The observed increase in the H_2 conversion with increase in the Au loading is probably due to the increased dissociative chemisorption of H_2.

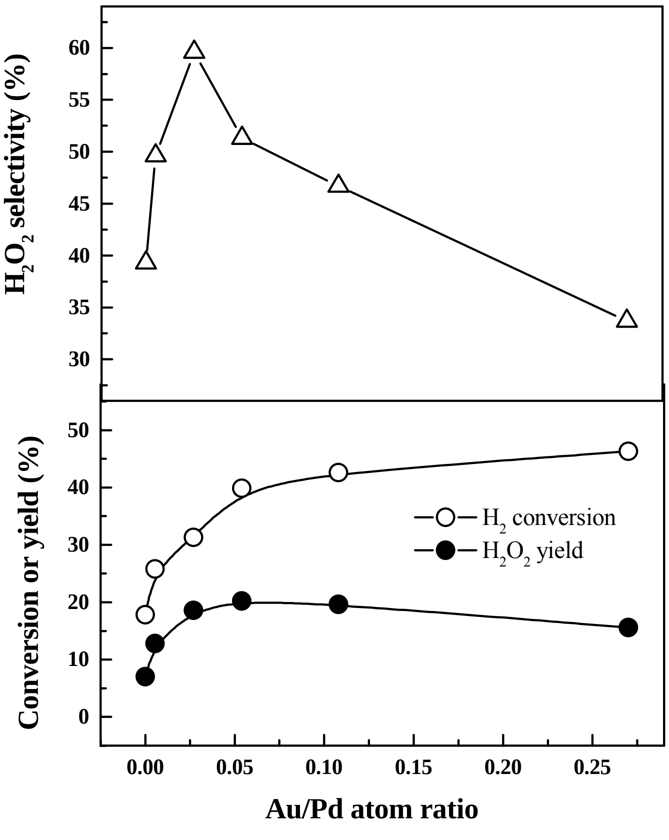

Figure 3.3 Influence of the concentration of gold loaded in the oxidized Pd/Ga_2O_3 catalyst on the H_2-to-H_2O_2 oxidation in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC).

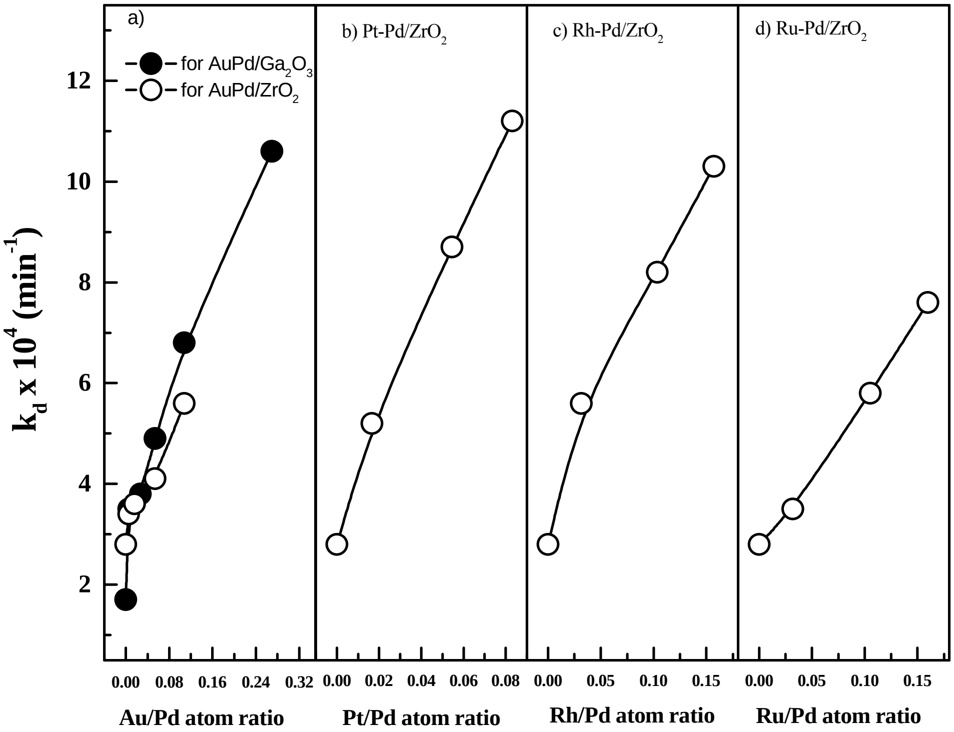

Figure 3.4 Effect of Au or noble metal additive on the H_2O_2 decomposition rate constant (k_d) for the oxidized Au-Pd/Ga$_2$O$_3$, Au-Pd/ZrO$_2$ and Pt-Pd/ZrO$_2$, Ru-Pd/ZrO$_2$ and Rh-Pd/ZrO$_2$ catalysts.

3.2.4 Direct Oxidation of H_2 to H_2O_2 over Pd/ZrO$_2$ Catalyst in Acidic (0.03 M H_3PO_4) Reaction Medium: Influence of Different Metal Additives

Results showing the influence of Au concentration in the oxidized Pd/ZrO$_2$ catalyst on its performance in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Figure 3.5. The results reveal that there is an optimum concentration of Au in the catalyst for achieving maximum yield of H_2O_2 in the H_2-to-H_2O_2 oxidation. Both the H_2 conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition activities of the catalyst are increased with increasing the Au concentration in the catalyst (Figure 3.4a).

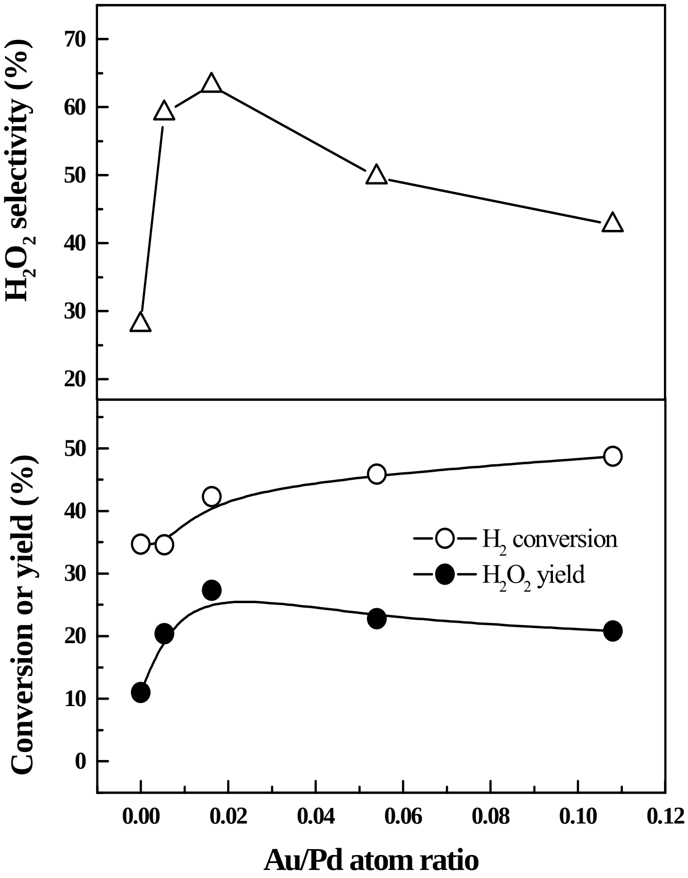

Figure 3.5 Influence of the concentration of Au in the oxidized Pd (2.5%)/ZrO_2 catalyst on the H_2-to-H_2O_2 oxidation in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC).

Results showing the influence of Pt concentration in the oxidized Pd-Pt/ZrO_2 catalyst on its performance in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.03 H_3PO_4) reaction medium are presented in Figure 3.6. The H_2O_2 selectivity and yield in the H_2-to-H_2O_2 oxidation are lower at the higher Pt concentration in the catalyst. However, the H_2 conversion activity of the catalyst is increased with the increase in the Pt concentration in the catalyst. The observed decrease in the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation with the increase in the Pt concentration in the catalyst is mainly attributed to the increased H_2O_2 decomposition activity of the catalyst (Figure 3.4b)

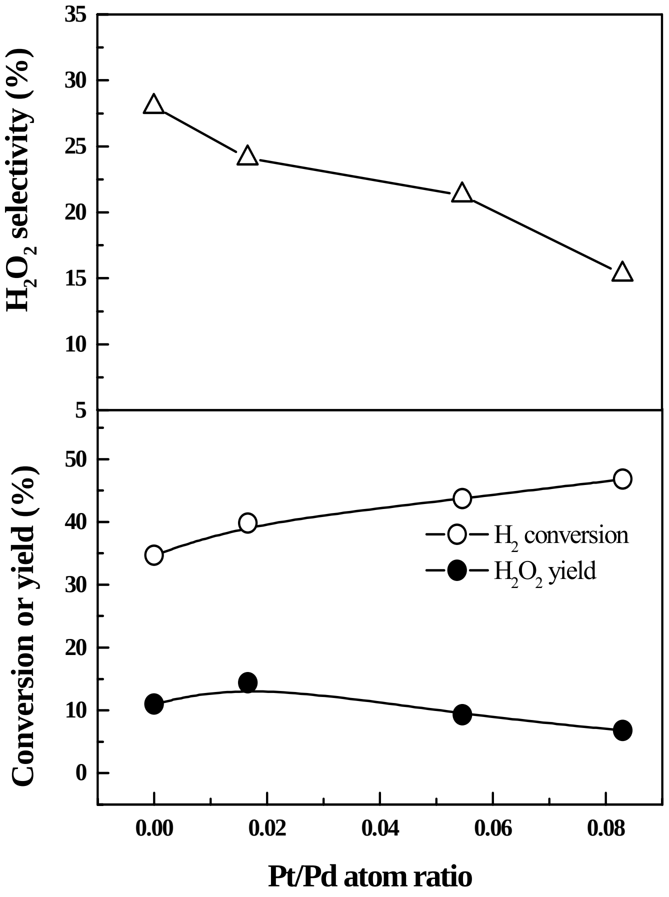

Figure 3.6 Influence of the concentration of Pt in the oxidized Pd (2.5%)/ZrO_2 catalyst on the H_2-to-H_2O_2 oxidation in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC).

Results in Figure 3.7 reveal that the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation over the catalyst is decreased with the increase in the concentration of Rh in the Pd/ZrO_2 catalyst. It may be noted that the presence of Rh in the catalyst does not enhance the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation; indicating Rh is not a promoter for the H_2O_2 forming reaction. The observed decrease in the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation with the increase in the Rh concentration is mainly attributed to the increased H_2O_2 decomposition activity of the catalyst (Figure 3.4c).

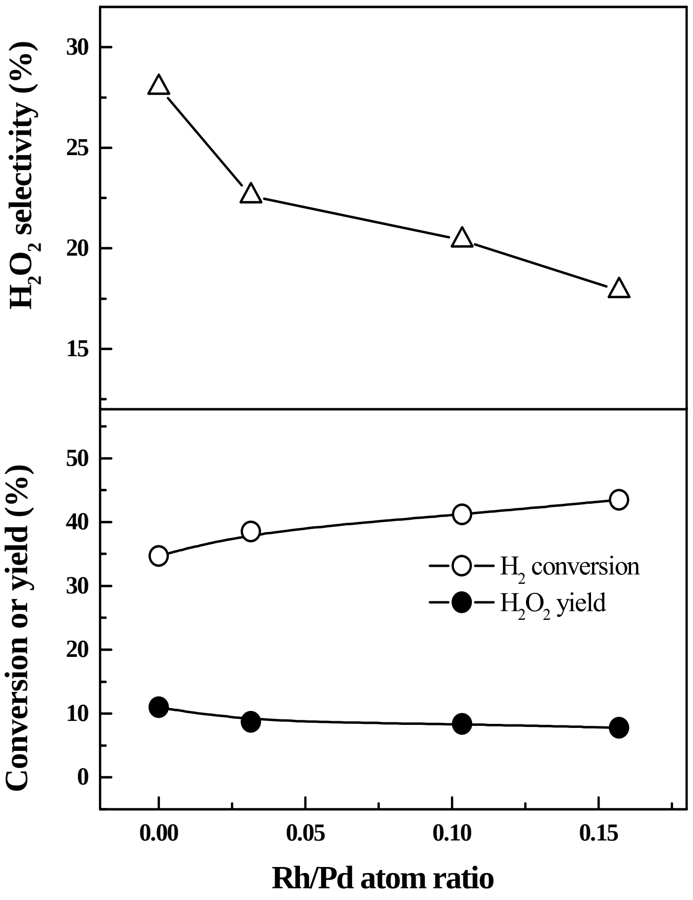

Figure 3.7 Influence of the concentration of Rh in the oxidized Pd (2.5%)/ZrO_2 catalyst on the H_2-to-H_2O_2 oxidation in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC)

Results in Figure 3.8 reveal that both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation are reduced with the increase in the Ru concentration in the oxidized Pd/ZrO_2 catalyst. Like Rh, Ru is also found not to enhance the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation.

The observed decrease in the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation in the presence of Ru, Rh or Pt may also be partly due to an enhancement in the direct non-selective parallel H_2-to-water oxidation reaction and/or H_2O_2 hydrogenation reaction. The H_2O_2 hydrogenation is addressed later.

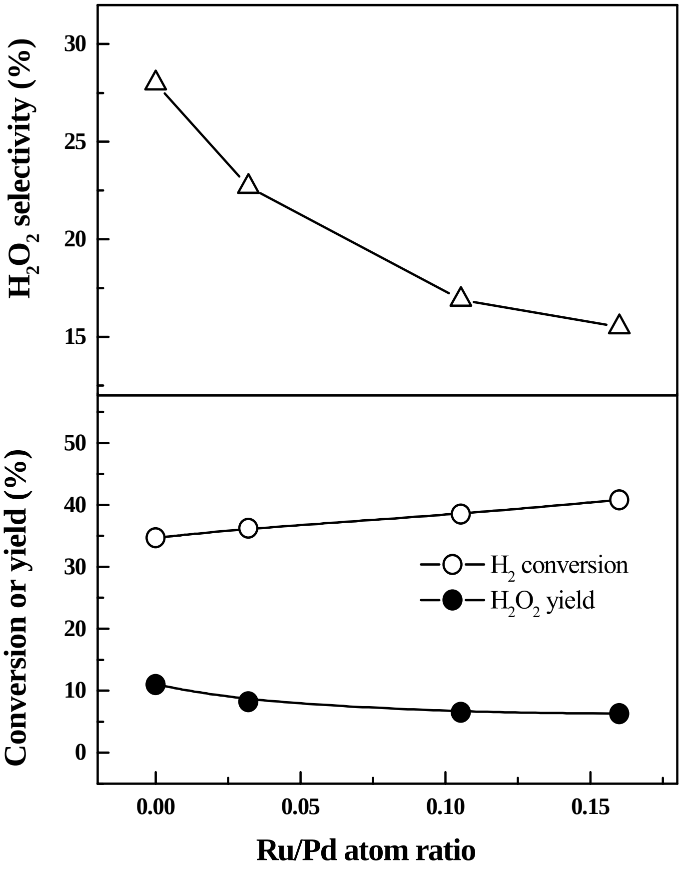

Figure 3.8 Influence of the concentration of Ru in the oxidized Pd (2.5%)/ZrO_2 catalyst on the H_2-to-H_2O_2 oxidation in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC)

3.3 CONCLUSIONS

From the above observations, following conclusions have been drawn:

1. The supported metallic Pd (i.e. Pd^o containing) catalysts are highly active but less selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation due to their very high activity for H_2O_2 decomposition. The corresponding oxidized Pd (i.e. PdO containing) catalysts are less active but much more selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The reduced Pd catalysts are much more active for H_2O_2 decomposition than the oxidized catalysts.
2. The Pd particle size (which depend upon the metal support interaction and therefore varies from support to support) and total surface area of the catalysts are less important parameters for determining the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation reaction.
3. The addition of Au or Pt to the Pd catalyst at optimum concentration is beneficial for the H_2-to-H_2O_2 oxidation for achieving higher H_2O_2 selectivity and/or yield.

However, high Au or Pt loadings leads to a large increase in the H_2O_2 decomposition activity of the catalyst, reducing both H_2O_2 yield and selectivity in the process. The addition of Rh or Ru to Pd catalysts causes a decrease in both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation and a large increase in the H_2O_2 decomposition activity of the catalyst.

4. For both the reduced and oxidized Pd catalysts, the H_2O_2 selectivity, in the H_2-to-H_2O_2 oxidation is drastically reduced with increasing their H_2O_2 decomposition activity.
5. The H_2O_2 decomposition and H_2-to-H_2O_2 oxidation reactions over the supported Pd catalyst are strongly influenced by the support used in the catalyst.

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CHAPTER-4

DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION/HYDROGENATION OF H_2O_2 OVER Pd/CARBON CATALYST: INFLUENCE OF CATALYST PRETREATMENT, LIQUID REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

CHAPTER-4

DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION /HYDROGENATION OF H_2O_2 OVER Pd/CARBON CATALYST: INFLUENCE OF CATALYST PRETREATMENT, LIQUID REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

4.1 GENERAL INTRODUCTION-BACKGROUND AND OBJECTIVES

Hydrogen peroxide (a versatile and clean oxidizing agent) is used extensively as a bleaching agent in the textile and pulp/paper industries, for wastewater treatments and water disinfection and also for the catalytic oxidation processes in the synthesis of fine and bulk chemicals [1-4]. Its demand particularly for the wastewater treatment and catalytic oxidation processes has been increasing day-by-day. At present, H_2O_2 is produced commercially mainly by the anthraquinone process. Although, H_2O_2 is produced on a multi-million tonne scale annually, the current cost of it still does not allow for the economical production of bulk chemicals and wastewater treatments. The liquid-phase direct oxidation of H_2 to H_2O_2 is an attractive alternative to the anthraquinone process and efforts have been made since long to produce H_2O_2 by the oxidation of H_2 by O_2 using Pd-based catalysts. This process is covered in several patents [5-18]. A number of patents have been issued in which carbon supported Pd catalyst has been employed for the synthesis of H_2O_2 from H_2 and O_2 [19-25]. Earlier, Fu et al [26] have carried out liquid-phase H_2 to H_2O_2 oxidation in an acidic medium over Pd/fluorinated carbon catalyst; the maximum H_2O_2 selectivity reported was 8.7% (at 41% H_2 conversion) even in the presence of a H_2O_2 stabilizer. Pd/sulfonated carbon catalyst has also been employed for the synthesis of H_2O_2 in the direct oxidation of H_2 [27].

In the present investigation, influence of the different reaction mediums, the different halides and their concentrations in the reaction medium, acid concentration in the reaction medium, oxidative pretreatments to the catalyst etc. on the performance of the Pd/C catalyst in the H_2-to-H_2O_2 oxidation has been studied. The influence of the above factors on the H_2O_2 decomposition and/or H_2O_2 hydrogenation (both these reactions are responsible for lowering the H_2O_2 selectivity in the process) activity of the catalyst has also been studied in details.

4.2 DIRECT OXIDATION OF H_2 TO H_2O_2 OVER Pd/C CATALYST

4.2.1 Influence of Reaction Medium

Results showing the influence of different reaction mediums on the activity/selectivity of the Pd/C catalyst in the H_2-to-H_2O_2 oxidation are presented in Table 4.1. The results lead to the following important observations:

- The catalyst shows no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation in the absence of acid in the aqueous medium but very high H_2O_2 decomposition activity.
- In the presence of hydrochloric acid in the aqueous medium the H_2O_2 decomposition activity of the catalyst is drastically reduced leading to the formation of H_2O_2 in good yield in the H_2-to-H_2O_2 oxidation.
- In the presence of oxyacids (viz. H_3PO_4, H_2SO_4, H_3BO_3, HNO_3) in the aqueous medium, the H_2O_2 decomposition over the catalyst is reduced markedly but there is no formation of H_2O_2 in the H_2-to-H_2O_2 oxidation.
- The H_2 conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition activities of the catalyst are drastically reduced in the presence of HBr and HI in the reaction medium.

In the direct oxidation of H_2 to H_2O_2 over the Pd catalyst, both the selective H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) and non-selective/undesired water ($H_2 + 0.5\ O_2 \rightarrow$ water) forming reactions occur simultaneously. The low stability of H_2O_2 molecules in the presence of Pd catalyst leads to their decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$), which masks the selective H_2-to-H_2O_2 oxidation. Hence, to obtain H_2O_2 in the H_2-to-H_2O_2 oxidation with high selectivity, both the non-selective H_2-to-water oxidation and decomposition of H_2O_2 over the catalyst should be minimized simultaneously. It may be noted that, in presence of the oxyacid in the aqueous medium, there is no formation of H_2O_2 in the H_2-to-H_2O_2 oxidation, even though the H_2O_2 decomposition activity of the catalyst is reduced markedly. This indicates that the presence of protons (i.e. H^+ ions) in the reaction medium reduces the H_2O_2 decomposition activity of the catalyst but has little or no influence on directing the H_2 oxidation reaction to H_2O_2. However, in presence of HCl in the aqueous medium, the H_2O_2 selectivity is increased markedly due to promoting action of the acid (protons, which reduce the H_2O_2 decomposition activity of the catalyst) and halide anions (which direct the H_2 oxidation reaction to H_2O_2 and also reduce the H_2O_2 decomposition rate) in the H_2-to-H_2O_2 oxidation over the catalyst. The results also indicate that just reduction in the H_2O_2 decomposition activity is not enough for achieving the selective oxidation of H_2 to H_2O_2.

Table 4.1 Results of the direct oxidation of H_2 to H_2O_2 over the reduced Pd (5%)/C catalyst in different reaction mediums [reaction conditions**:** volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, temperature = 27 ºC, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Reaction medium	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})[a]
Distilled water	48.5	0.00	0.00	758.1
0.1 N H_3PO_4	57.9	0.00	0.00	151.0
0.1 N H_2SO_4	54.8	0.00	0.00	133.0
0.1 N HNO_3	48.7	0.0	0.0	141.5
0.1 N H_3BO_3	59.4	0.3	0.5	164.8
0.1 N HCl	28.6	8.7	30.4	18.0
0.1 N HBr	0.4	0.0	-	6.1
0.1 N HI	0.0	0.0	-	2.3

[a] *Pseudo first order H_2O_2 decomposition rate constant.*

4.2.2 Influence of Presence of Different Potassium Halides in Reaction Medium

Results showing the influence of different alkali halides added to the aqueous acidic reaction medium (0.03 M H_3PO_4 and 0.05 M H_2SO_4) on the performance of the reduced Pd/C catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 4.2. From the results following important observations can be made:

- In the absence of any halide or presence of KF in the aqueous acidic reaction medium, there is no H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The H_2O_2 decomposition activity of the catalyst is increased in the presence KF in the reaction medium.

Table 4.2 Results of the direct oxidation of H_2 to H_2O_2 over Pd/C catalyst in two different aqueous acidic reaction mediums containing different halide anions [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, temperature = 27 ºC, pressure = 0.95 atm, H_2 concentration in O_2 = 4.6 mol%, reaction period = 3h and concentration of halides in the reaction medium = 2.7 $mmol.dm^{-3}$].

Alkali halide present in reaction medium	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC) $k_d \times 10^3$ (min^{-1})
	Conversion of H_2 (%)		H_2O_2 selectivity (%)	
	Total	To H_2O_2		
Reaction medium = 0.03 M H_3PO_4				
None	58.5	0.0	0.0	15.1
KF	58.3	0.6	1.0	18.2
KCl	54.2	15.8	29.2	1.9
KBr	36.2	11.5	31.8	0.71
KI	1.6	0.0	0.0	0.2
Reaction medium = 0.05 M H_2SO_4				
None	54.8	0.0	0.0	13.3
KF	59.2	0.54	0.9	14.3
KCl	52.3	13.5	25.8	0.98
KBr	34.9	9.8	28.1	0.34
KI	0.9	0.0	-	0.05

- The presence of KCl or KBr in the reaction medium increases drastically the selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation. The H_2O_2 decomposition activity of the catalyst is reduced drastically due to the presence of KCl or KBr in the reaction medium. Chloride is more effective than bromide (at the same halide concentration) in the H_2-to-H_2O_2 oxidation over the Pd/C catalyst.

- The addition of KI to the reaction medium causes a drastic reduction in both the H_2 conversion and H_2O_2 decomposition over the catalyst, indicating a strong poisoning of the catalyst due to the presence of KI in the reaction medium.

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 activity of the catalyst (except for F^-). The halide ions are adsorbed from the reaction medium on the catalyst (which was confirmed by detecting the halide in the used catalysts by EDX and XPS analysis). The strongly adsorbed halide anions block and/or modify certain active sites, responsible for the dissociation of dioxygen and/or decomposition of H_2O_2. To form H_2O_2, oxygen in molecular form is required; if oxygen-oxygen bond is broken, water is expected to be the only product in the H_2 oxidation. Hence, the inhibition to the cleavage of oxygen-oxygen bonds is expected to increase the selectivity for H_2O_2 in the process. Another aspect that may be important is that adsorption of electronegative species, such as chloride ions, may change the electron density on the metal and thus affect its activity. Making the surface more electron deficient would favour the adsorption of hydrogen relative to oxide ions, leading to an increase in the selective hydrogenation reaction of O_2 to H_2O_2. The electronegativity of the halogens however, does not have a linear effect on their promoting effect on the H_2O_2 selectivity since F^- is less effective promoter than Cl^- or Br^-.

4.2.3 Influence of Cl^--Containing Compounds Present in Reaction Medium

Results showing the influence of different chlorine-containing compounds added to the aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the Pd/C catalyst in the H_2-to-H_2O_2 oxidation are presented in Table 4.3. The results obtained with the different chlorine-containing compounds are comparable, emphasizing the importance of the chloride anions over the associated cations; the cations (except H^+ ions) play a little or no role for influencing the H_2O_2 selectivity in H_2-to-H_2O_2 oxidation and/or H_2O_2 decomposition reactions.

Table 4.3 Results of the direct oxidation of H_2 to H_2O_2 over the reduced Pd/C catalyst in aqueous acidic (0.03 M H_3PO_4) reaction medium containing different chlorine containing compounds [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, H_2 concentration in O_2 = 4.6 mol%, reaction temperature = 27 ºC, pressure = 0.95 atm, concentration of halide ions in the reaction medium = 2.7 $mmol.dm^{-3}$ and reaction period = 3h].

Chloride compound added to the reaction medium	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
HCl	54.9	15.4	28.1	10.2
NaCl	56.5	15.1	26.7	10.6
KCl	54.2	15.8	29.2	10.8
NH_4Cl	60.9	13.8	22.7	12.1

4.2.4 Influence of Concentration of Chloride Anions in Reaction Medium

Results showing the influence of Cl^- concentration in the acidic (0.03 M H_3PO_4 and 0.05 M H_2SO_4) reaction mediums on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition over the Pd/C catalyst are presented in Table 4.4. With increasing the Cl^- concentration, the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is increased and then passes through a maximum. Thus, an optimum concentration of Cl^- in the reaction medium is essential for obtaining maximum H_2O_2 yield in the process. Both the H_2 conversion and H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation are decreased at the higher Cl^- concentration in the reaction medium. However, the H_2O_2 decomposition activity of the catalyst is decreased continuously with increasing the Cl^- concentration in the reaction medium. It may be noted that in aqueous medium containing Cl^- ions but without acid, there is no formation of H_2O_2 in the H_2-to-H_2O_2 oxidation. This indicates the presence of protons (H^+ ions) in the reaction medium is must for obtaining H_2O_2; otherwise H_2O_2 formed should be destroyed by its decomposition over the catalyst.

The improved performance of the catalyst in the H_2 to H_2O_2 oxidation due to the presence of Cl^- in the reaction medium is attributed to the inhibition in the H_2O_2

decomposition activity of the catalyst. The direct water forming reaction may also be inhibited in the presence of Cl^- in the reaction medium. The modification of the active sites in the catalyst (due to the adsorption of Cl^- ions from the reaction medium) is mostly responsible for the observed beneficial effect on the H_2-to-H_2O_2 oxidation in presence of Cl^- ions in the reaction medium.

Table 4.4 Results of the direct oxidation of H_2 to H_2O_2 over Pd/C catalyst in an aqueous acidic (0.03 M H_3PO_4) reaction medium containing chloride anions at different concentrations [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, reaction temperature = 27 ºC, pressure = 0.95 atm, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Concentration of KCl in reaction medium ($mmol.dm^{-3}$)	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC) $k_d \times 10^4$ (min^{-1})
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	
Reaction medium = 0.03 M H_3PO_4				
0.9	56.7	12.6	22.2	22.5
2.7	54.2	15.8	29.2	18.7
5.4	55.7	17.5	31.4	8.5
8.1	53.5	16.7	31.2	6.5
24.3	47.4	10.7	22.6	4.1
2.7 [a]	48.9	0.0	0.0	475.0
Reaction medium = 0.05 M H_2SO_4				
0.9	56.7	9.2	16.3	17.7
2.7	52.3	13.5	25.8	9.8
4.0	49.8	17.8	35.7	8.3
8.1	47.4	10.9	23.0	7.3
24.3	36.7	7.4	20.2	4.2

[a] *Reaction medium = pure water*

4.2.5 Influence of Concentration of Bromide Anions in Acidic Reaction Medium

Results showing the influence of Br^- concentration in aqueous acidic (0.03 M H_3PO_4 and 0.05 M H_2SO_4) reaction mediums on the performance of the Pd/C catalyst in the H_2-to-H_2O_2 oxidation are presented in Table 4.5. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are reduced with the increase in the Br^- concentration in the reaction medium. However, the H_2O_2 yield in reaction is increased and then passes through the maximum with increasing the Br^- concentration in the reaction medium. At the high Br^- concentration both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are reduced markedly due to the blockage of the catalytic active sites.

Table 4.5 Results of the direct oxidation of H_2 to H_2O_2 over the reduced Pd/C catalyst showing effect of the concentration of KBr in two different acidic reaction mediums [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, H_2 concentration in O_2 = 4.6 mol %, temperature = 27 ºC, pressure = 0.95 atm, and reaction period = 3h].

Concentration of KBr in reaction medium ($mmol.dm^{-3}$)	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
Reaction medium = 0.03 M H_3PO_4				
0.9	45.9	2.0	12.8	16.5
2.7	36.2	11.5	31.8	7.1
4.7	32.5	9.7	29.8	4.9
9.4	30.8	7.8	25.3	3.2
Reaction medium = 0.05 M H_2SO_4				
0.2	49.3	8.1	16.4	12.5
0.9	38.7	11.9	30.7	6.8
2.7	34.9	9.8	28.1	3.4
5.4	28.5	7.9	27.7	2.7

4.2.6 Influence of Concentration of Iodide Anions in Acidic Reaction Medium

Results showing the influence of I^- concentration in aqueous acidic (0.03 M H_3PO_4 and 0.05 M H_2SO_4) reaction mediums on the performance of the Pd/C catalyst in the H_2-to-H_2O_2 oxidation are presented in Table 4.6. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are drastically reduced with the increase in the I^- concentration in the reaction medium. It may be noted that, the H_2 conversion activity of the catalyst is highly sensitive to the presence of iodide anions in the reaction medium. The poisoning of the catalyst by the I^- ions is much higher as compared to that by the Cl^- or Br^- ions (at the same halide concentration).

Table 4.6 Results of the direct oxidation of H_2 to H_2O_2 over the reduced Pd/C catalyst showing effect of the concentrations of KI in two different acidic reaction mediums [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, reaction temperature = 27 ºC, pressure = 0.95 atm, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Concentration of KI in reaction medium ($mmol.dm^{-3}$)	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
Reaction medium = 0.03 M H_3PO_4				
0.02	53.2	2.9	5.5	18.8
0.09	25.8	1.6	6.2	8.5
0.9	9.5	0.0	0.0	5.3
2.7	1.6	0.0	-	2.0
Reaction medium = 0.05 M H_2SO_4				
0.013	53.2	2.9	5.5	3.5
0.093	26.4	1.8	6.8	1.5
0.94	8.7	0.0	0.0	0.8
2.7	0.9	0.0	-	0.5

4.2.7 Influence of Concentration of Fluoride Anions in Acidic Reaction Medium

Results in Table 4.7 show that with the increase in the fluoride concentration in aqueous acidic (0.03 H H_3PO_4 or 0.05 M H_2SO_4) reaction medium, the H_2O_2 decomposition activity of the catalyst is increased; indicating that the presence F^- has a detrimental/undesired effect on the H_2-to-H_2O_2 oxidation. However, the H_2 conversion activity of the catalyst is almost not affected due to the presence of F^- anions at widely different concentrations.

Table 4.7 Results of the direct oxidation of H_2 to H_2O_2 over Pd/C catalyst showing effect of the concentrations of KF in two different acidic reaction mediums [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, reaction temperature = 27 ºC, pressure = 0.95 atm, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Concentration of KF in reaction medium ($mmol.dm^{-3}$)	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
Reaction medium = 0.03 M H_3PO_4				
0.3	57.6	0.6	1.04	153.0
0.9	56.4	0.9	1.6	168.7
2.7	58.3	0.6	1.0	181.8
8.2	54.9	0.0	0.0	237.5
Reaction medium = 0.05 M H_2SO_4				
0.9	57.2	0.6	1.0	136.5
2.7	59.2	0.54	0.9	142.5
8.2	53.6	0.0	0.0	179.1

4.2.8 Influence of the Acid Concentration in Reaction Medium Containing Chloride Anions

Results in Table 4.8 show that with the increase in the acid (H_3PO_4) concentration in the aqueous medium containing Cl^- anions (5.4 $mmol.dm^{-3}$), the H_2O_2 yield in the H_2-to-

H_2O_2 oxidation is increased. However, there is an optimum concentration of acid in the reaction medium for achieving the maximum H_2O_2 yield in the process. The H_2O_2 decomposition activity of the catalyst is decreased continuously with the increase in the acid concentration in the reaction medium. It may be noted that both the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation are decreased at the higher acid concentration in the reaction medium. This is may be due to the lower hydrogen solubility at the concentrated H_3PO_4 solution (the precise data, are however not available).

Table 4.8 Results of the direct oxidation of H_2 to H_2O_2 over the reduced Pd/C catalyst in aqueous acidic medium containing H_3PO_4 at different concentrations and KCl (5.4 mmol.dm^{-3}) [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, temperature = 27 ºC, pressure = 0.95 atm, H_2 concentration in O_2 = 4.6 mol % and reaction period = 3h].

Concentration of H_3PO_4 in reaction medium (mol.dm^{-3})	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 25 ºC)
	H_2 Conversion (%)	H_2O_2 Yield (%)	H_2O_2 Selectivity (%)	$k_d \times 10^4$ (min^{-1})
0.0	48.5	0.00	0.00	758.1
0.01	58.9	10.6	18.0	24.6
0.03	55.7	17.5	31.4	12.3
0.1	64.2	19.1	29.8	4.3
1.0	47.8	16.8	35.1	2.1
3.3	38.5	11.5	29.9	1.6

4.2.9 Influence of Catalyst Pretreatment

Results showing the influence of oxidative pretreatment to the Pd/C catalyst on its performance in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Table 4.9. The H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation is drastically increased whereas the H_2O_2 decomposition activity is drastically reduced due to the oxidative pretreatments to the catalyst. However, the H_2 conversion activity of the catalyst is reduced after its oxidative pretreatment. The improved H_2O_2 selectivity of the catalyst due to its oxidative pretreatment is attributed to the bulk and/or surface oxidation of Pd^o to PdO in the catalyst, causing a drastic reduction in the H_2O_2 decomposition activity of the catalyst. Perchloric acid is found to be the most effective oxidizing agent.

Table 4.9 Influence of the oxidative pretreatment to the Pd/C catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 27 ºC).

Oxidizing agent	XRD Phases (s) [a] (Pd^o or PdO)	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity (at 27 ºC) $k_d \times 10^4$ (min^{-1})
		H_2 Conversion (%)	H_2O_2 Yield (%)	H_2O_2 Selectivity (%)	
None	Pd^o	57.9	0.0	0.0	151.0
$HClO_4$	Pd^o, PdO	43.8	10.8	24.6	19.5
H_2O_2	Pd^o, PdO	47.5	8.7	18.3	25.4
Air	Pd^o, PdO	45.2	8.9	19.4	21.8

[a] *Confirmed by XRD.*

4.3 DECOMPOSITION OF H_2O_2 OVER Pd/C CATALYST: FACTORS AFFECTING THE H_2O_2 DECOMPOSITION

4.3.1 Effect of Acid Present in Reaction Medium

4.3.1.1 *Effect of the Nature of Acid*

Results showing the influence of different reaction mediums on the H_2O_2 decomposition over the reduced Pd/C catalyst are presented in Figure 4.1. The catalyst shows very high activity for H_2O_2 decomposition in the aqueous medium but its activity is reduced markedly in the presence of acid in the aqueous medium. The presence of halogen acids (viz. HCl, HBr, HI) causes a marked decrease in the H_2O_2 decomposition activity of the catalyst as compared to the presence of oxyacids (viz. H_3PO_4, H_2SO_4, HNO_3 etc.) in the aqueous medium.

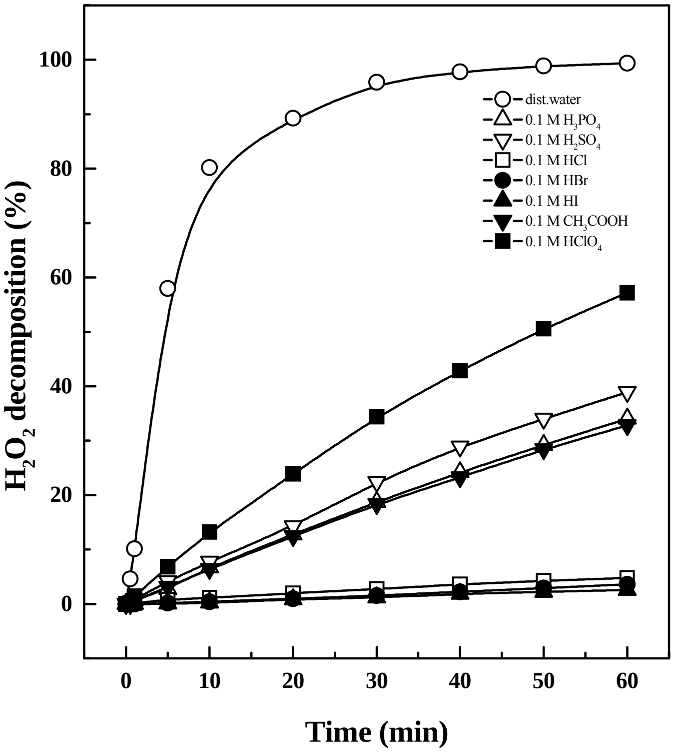


Figure 4.1 Effect of different reaction mediums on the decomposition of H_2O_2 over the reduced Pd/C catalyst at 25 ºC.

The associated anions of the acid employed in the reaction medium plays an important role in determining the H_2O_2 decomposition activity of the catalyst. The H_2O_2 decomposition activity of the catalyst in different reaction mediums is as follows: distilled water >>> $HClO_4$ > H_2SO_4 > H_3PO_4 > CH_3COOH > HCl > HBr > HI (Fig. 4.2). The low H_2O_2 decomposition activity of the catalyst (measured in terms of the first order H_2O_2 decomposition rate constant, k_D) in the halogen acid medium is due to the presence of halide ions, which are adsorbed on the catalyst (confirmed by XPS), blocking and/or modifying some catalytic active sites and thereby reducing the H_2O_2 decomposition activity of the catalyst.

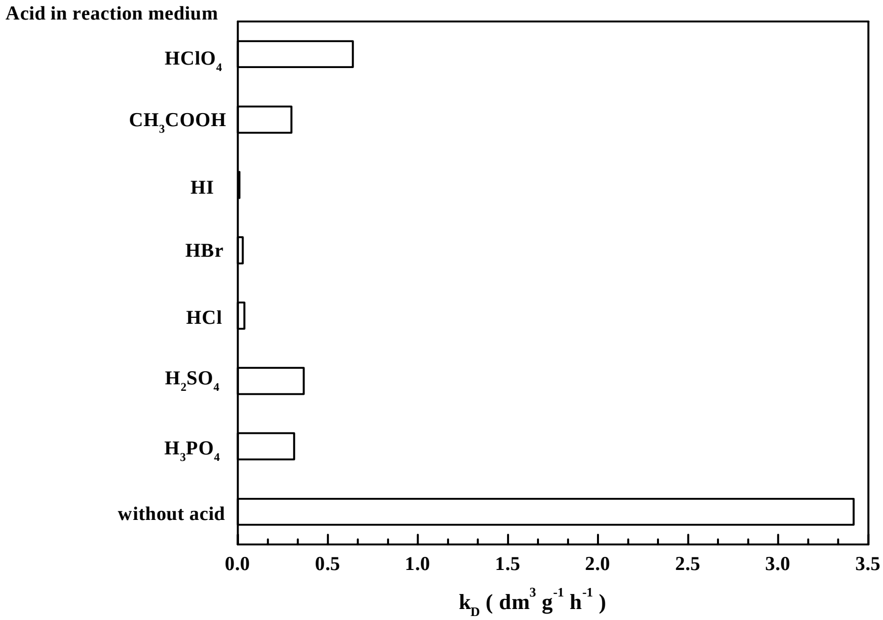


Figure 4.2 Influence of different reaction mediums on the H_2O_2 decomposition activity (at 25 ºC) of the reduced Pd/C catalyst.

4.3.1.2 Effect of Concentration of Acid in Reaction Medium

Results showing the influence of H_2SO_4 and H_3PO_4 acid concentration in the aqueous reaction medium on the H_2O_2 decomposition over the reduced Pd/C catalyst are presented in Figure 4.3. The variation in the H_2O_2 decomposition activity of the catalyst with the acid (H_3PO_4 and H_2SO_4) concentration in the aqueous reaction medium is presented in Figure 4.4. The H_2O_2 decomposition activity of the catalyst is reduced sharply with the increase in the acid concentration in aqueous medium (Figure 4.4). This is attributed to the shifting of the equilibrium towards the H_2O_2 side of the H_2O_2 ionization reaction: $H_2O_2 \leftrightarrows H^+ + HO_2^-$. It may be noted that in the acidic reaction medium, H^+ ions may be in competition with the H_2O_2 molecules for the same adsorption sites on the Pd surface in the catalyst and consequently, some of the active sites are blocked, reducing the H_2O_2 decomposition over the catalyst. It may be noted that the associated anions of the acid present in the reaction medium may also be playing an important role in determining the H_2O_2 decomposition activity of the catalyst.

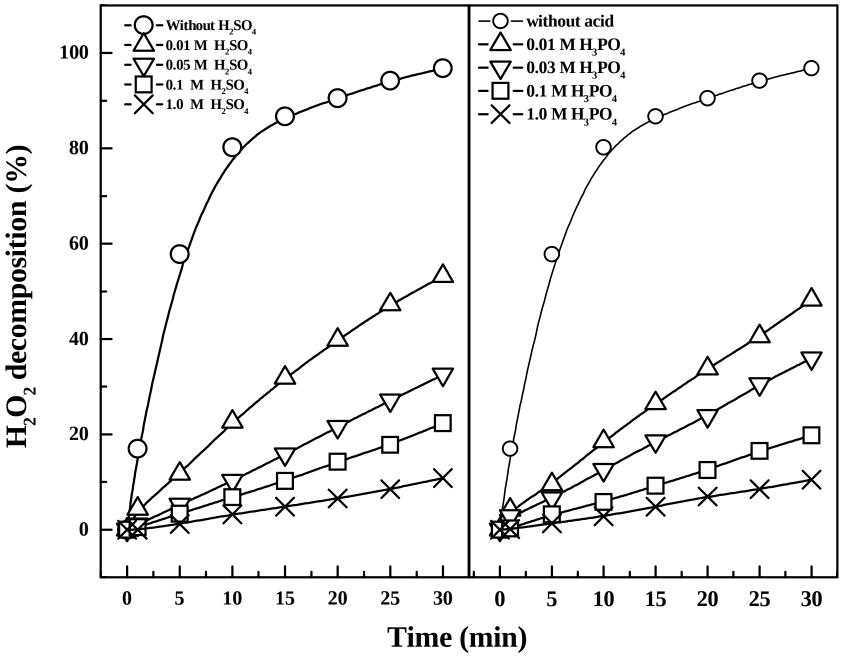


Figure 4.3 Effect of H_2SO_4 and H_3PO_4 acid concentration in aqueous medium on the H_2O_2 decomposition over the reduced Pd/C catalyst.

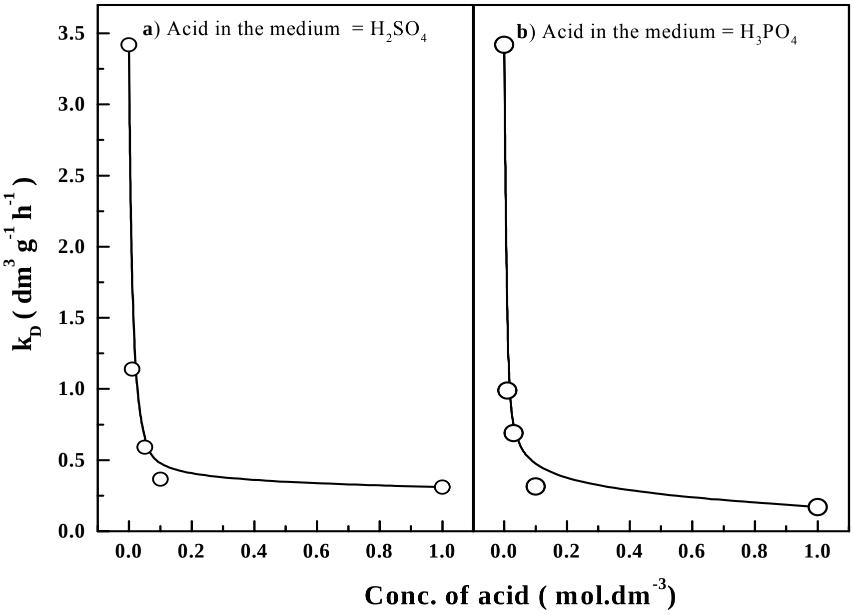


Figure 4.4 Effect of H_2SO_4 and H_3PO_4 acid concentration in aqueous medium on the H_2O_2 decomposition activity of the reduced Pd/C catalyst at 25 °C (k_D = first order H_2O_2 decomposition rate constant).

4.3.2 Effect of the Nature and Concentration of Halide Anions in Reaction Medium

a) Reaction Medium: Aqueous Non-Acidic

Results showing the influence of different halides and their concentrations in the aqueous medium on the H_2O_2 decomposition over the reduced Pd/C catalyst are presented in Figure 4.5. The H_2O_2 decomposition activity of the catalyst is reduced markedly in the presence of chloride or bromide anions in the reaction medium. The H_2O_2 decomposition activity is further reduced at the higher chloride or bromide concentration in the reaction medium. In the presence of fluoride ions, there is only a small change in the rate of H_2O_2 decomposition over the catalyst. However, because of the presence of iodide anions, the H_2O_2 decomposition rate is reduced appreciably.

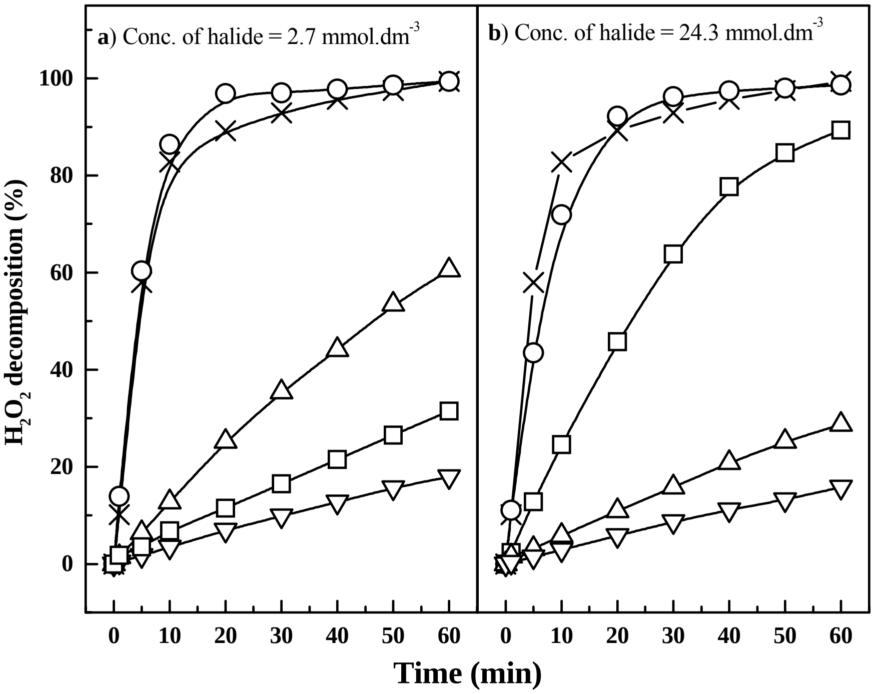


Figure 4.5 Effect of the different halides and their concentrations in aqueous (pure water) reaction medium on the decomposition of H_2O_2 (at 25 ºC) over the reduced Pd/C catalyst [halides in the reaction medium: without halide (×), KF (O), KCl (Δ), KBr (∇) and KI (□)].

Interestingly, the rate of H_2O_2 decomposition over the catalyst is increased at the higher iodide concentration in the aqueous reaction medium. This is attributed to the homogeneous iodide (present in large excess) catalyzed decomposition of H_2O_2.

b) Reaction Medium: Aqueous Acidic

Results showing the influence of different halide anions and their concentrations in the aqueous acidic reaction medium (0.1 M H_2SO_4 or H_3PO_4) on the decomposition of H_2O_2 over the reduced Pd/C catalyst are presented in Figures 4.6 and 4.7. The rate of H_2O_2 decomposition over the catalyst is drastically reduced in the presence of chloride, bromide or iodide anions in the acidic reaction medium. The rate of H_2O_2 decomposition is further reduced with increasing the halide (viz. Cl^-, Br^- or I^-) concentration in the acidic reaction medium.

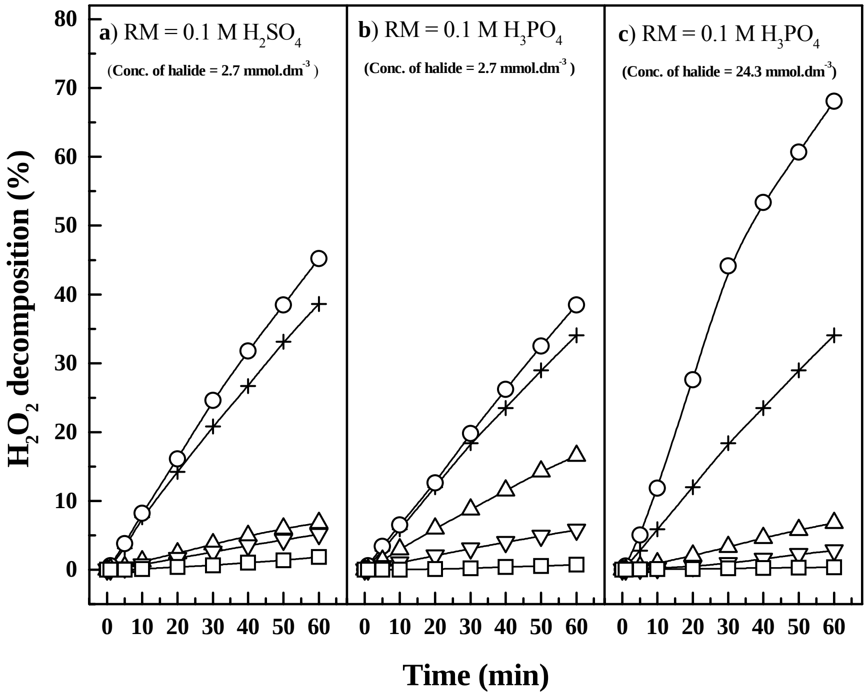


Figure 4.6 Effect of the different halides and their concentrations in aqueous acidic reaction medium (RM) on the decomposition of H_2O_2 (at 25 ºC) over the reduced Pd/C catalyst [halides in the reaction medium: without halide (×), KF (O), KCl (Δ), KBr (∇) and KI (□)].

However, the H_2O_2 decomposition activity of the catalyst is increased in the presence of fluoride anions in the reaction medium. The catalytic activity for H_2O_2 decomposition is further increased with increasing the fluoride concentration in the reaction medium. The presence of iodide anions in the reaction medium causes a drastic decrease in the H_2O_2 decomposition over the catalyst, indicating a strong poisoning of the catalyst due to the I^- ions. The observed increase in the H_2O_2 decomposition activity of the catalyst in presence of the fluoride ions may be attributed to the higher electronegativity and also the large positive standard electrode potential of fluorine, and consequently to the lower reducing strength (electron donating ability) of fluoride anions.

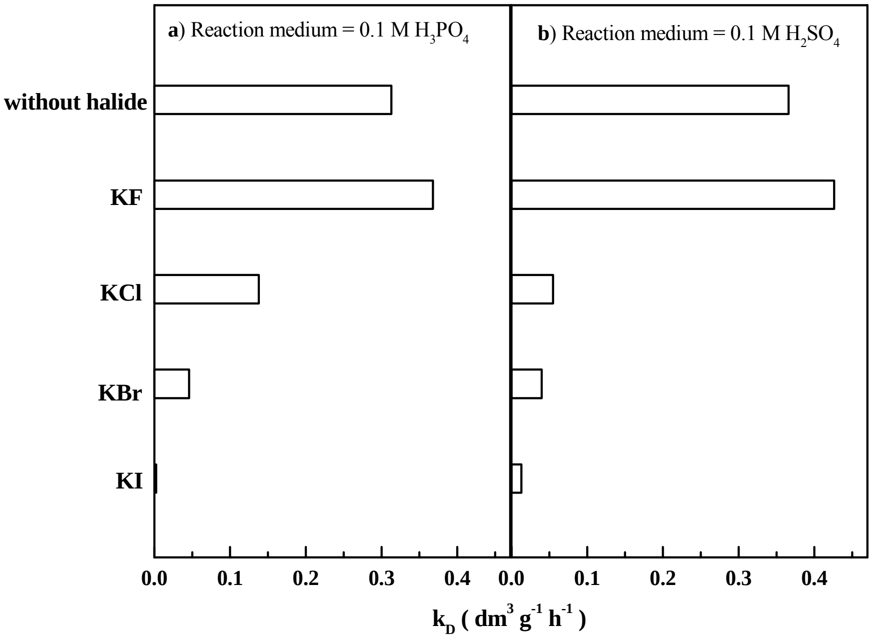


Figure 4.7 H_2O_2 decomposition activity (at 25 ºC) of the reduced Pd/C catalyst in different acidic reaction mediums with or without containing halides (concentration of halide in the reaction medium = 2.7 $mmol.dm^{-3}$).

4.3.3 Effect of Catalyst Pretreatment on H_2O_2 Decomposition

4.3.3.1 Catalyst Pretreatment by H_2 and O_2

Results showing the influence of H_2 and O_2 pretreatments to the Pd/C catalyst on its H_2O_2 decomposition activity in non-acidic aqueous and acidic aqueous (0.1 M H_3PO_4) reaction mediums are presented in Figure 4.8. The H_2 or O_2 gas pretreatment was carried out in the glass reactor containing the catalyst in pure water or aqueous 0.1 M H_3PO_4 medium, first by flushing the reactor with O_2-free N_2 (30 $cm^3.min^{-1}$) and then passing pure H_2 or O_2 through the reactor under vigorous stirring for 1h at room temperature. After that the gas atmosphere (H_2 or O_2) in the reactor was flushed with O_2-free N_2.

The H_2 pretreated catalyst showed a very high H_2O_2 decomposition activity, whereas the O_2 pretreatment results in a large decrease in its H_2O_2 decomposition activity. The observed much higher H_2O_2 decomposition activity of the H_2 pretreated catalyst is attributed to the surface/sub-surface reduction of Pd in the catalyst. However, the lower H_2O_2 decomposition activity of the O_2 pretreated catalyst is because of surface/sub-surface oxidation of Pd to PdO in the catalyst. For the H_2 or O_2 pretreated catalyst, its H_2O_2 decomposition activity in the presence of acid is much lower than that in the absence of the acid.

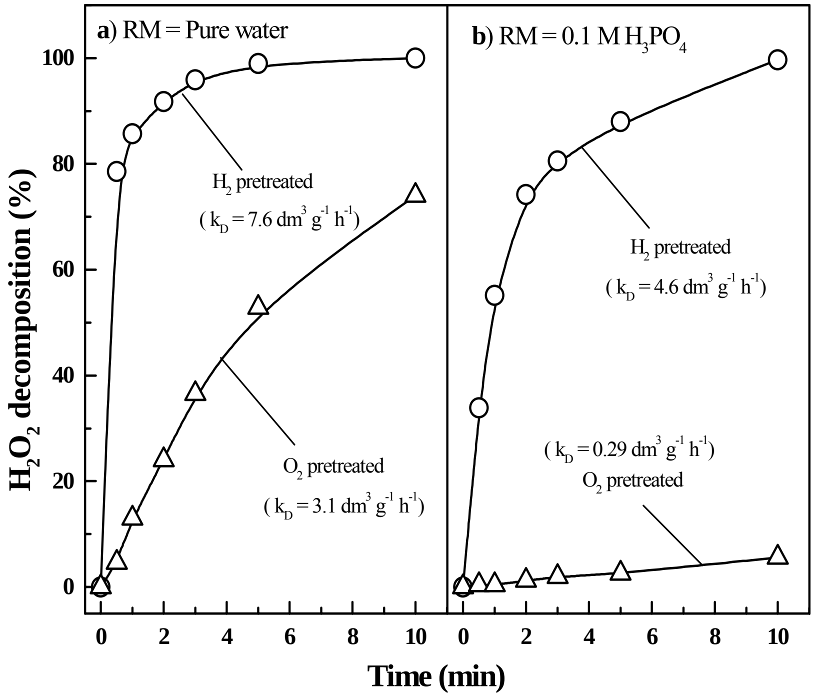


Figure 4.8 Influence of H_2 and O_2 pretreatments to the Pd/C catalyst on its H_2O_2 decomposition activity (at 25 ºC) in aqueous (pure water) and aqueous acidic (0.1 M H_3PO_4) reaction medium.

4.3.3.2 Effect of the Catalyst Insitu Pretreatment during H_2O_2 Decomposition

Results showing the successive insitu pretreatment of the catalyst during the decomposition of H_2O_2 over the catalyst in aqueous medium on its H_2O_2 decomposition activity are presented in Figure 4.9. The results show the H_2O_2 decomposition activity of the catalyst is reduced after its use in the H_2O_2 decomposition. The gradual decrease in the

H_2O_2 decomposition activity (Figure 4.9) of the catalyst with its successive use in the H_2O_2 decomposition is due to the subsurface oxidation of Pd by H_2O_2, which is a strong oxidizing agent. The resulting PdO phase which is less active for H_2O_2 decomposition leads to the observed decrease in the H_2O_2 decomposition activity of the catalyst.

The results reveal that in the H_2-to-H_2O_2 oxidation over reduced Pd catalyst, the activity and selectivity of the catalyst is expected to vary with the reaction time and also it would depend upon the number of uses of the catalyst.

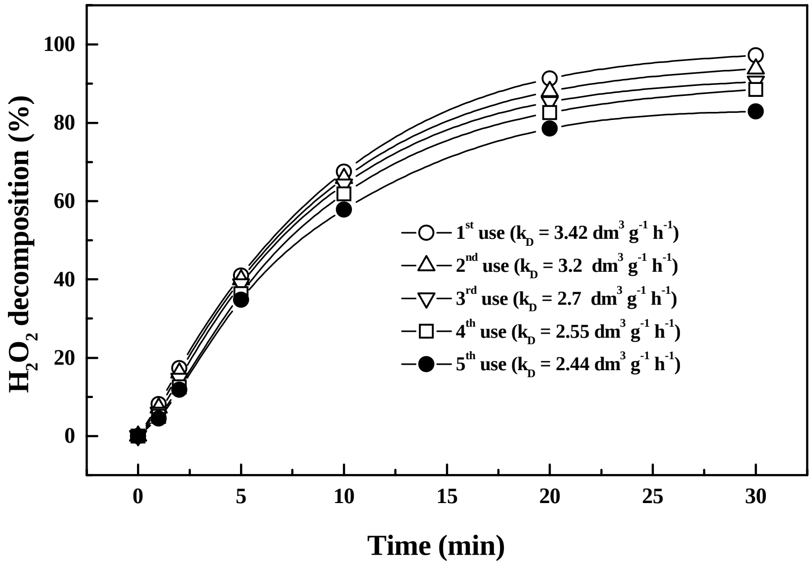


Figure 4.9 Effect of the catalyst oxidation by the successive pretreatment by H_2O_2 (in the reaction medium) on the decomposition of H_2O_2 (at 25 °C) over the Pd/C catalyst.

4.3.3.3 Catalyst Pretreatment by Perchloric Acid

A comparison of the H_2O_2 decomposition activity of with and without $HClO_4$ pretreated Pd/C catalysts in non-acidic aqueous and acidic aqueous (0.1 M H_3PO_4) reaction mediums (Figure 4.10) reveals that the H_2O_2 decomposition activity of the catalyst is reduced markedly after the $HClO_4$ pretreatment to the catalyst. This is attributed to the partial bulk and and/or sub-surface oxidation Pd^o to PdO (Figure 4.11). The resulting PdO phase, which is less active than metallic Pd for H_2O_2 decomposition, is responsible for the reduced H_2O_2 decomposition activity of the catalyst. It may be noted that the incorporation of ClO_4^- anions in the catalyst during its $HClO_4$ pretreatment is also expected to play an important role for reducing the H_2O_2 decomposition activity of the catalyst.

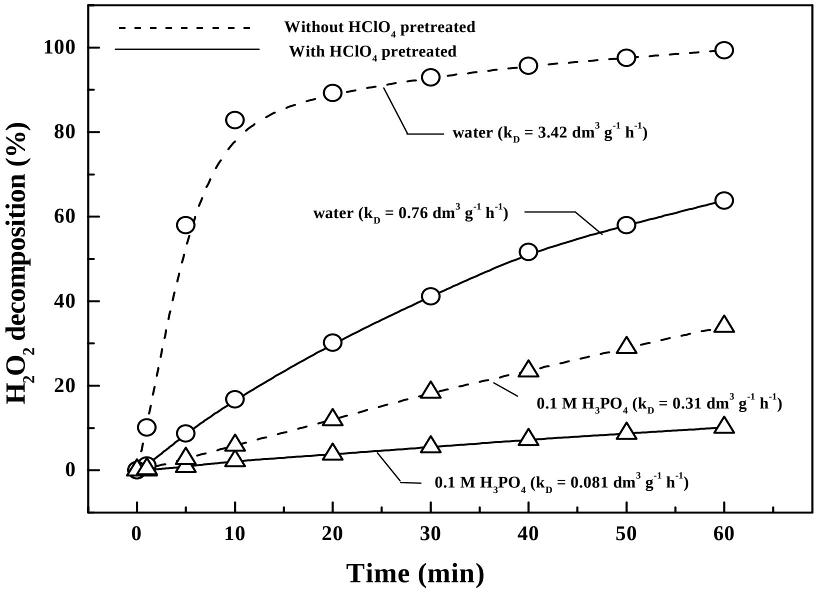


Figure 4.10 Comparison of the H_2O_2 decomposition activity of $HClO_4$ pretreated and without $HClO_4$ pretreated Pd/C catalysts in aqueous (pure water) and aqueous acidic (0.1 M H_3PO_4)) reaction medium.

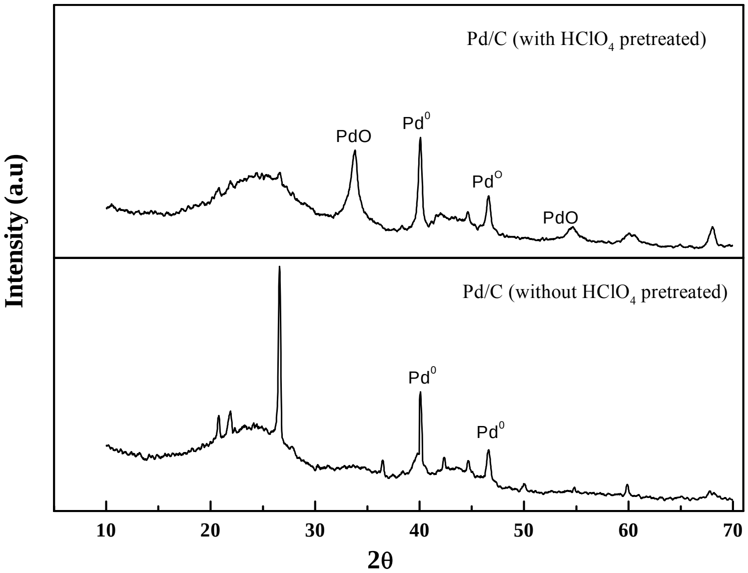


Figure 4.11 XRD spectra of the Pd/C catalysts, with and without the $HClO_4$ pretreatment.

4.3.4 Effect of Halide Incorporated in Catalyst

Results showing the influence of different halides incorporated in the Pd/C catalyst on its H_2O_2 decomposition activity in an aqueous acidic (0.05 M H_2SO_4) reaction medium are presented in Figure 4.12. The halides (F^-, Cl^-, Br^- and I^-) were incorporated into the Pd/C catalyst by impregnating the respective ammonium halide from its aqueous solution and the impregnated catalyst mass was dried on water bath and then calcined in a flow of N_2 at 400 ºC for 1h. XRD analysis of the halogenated catalyst showed that metallic Pd phase remains intact in the catalyst even after its halogenation. The H_2O_2 decomposition activity of the catalyst is increased markedly after its fluorination (Figure 4.13). The incorporation of the chloride or bromide in the catalyst causes a reduction in the H_2O_2 decomposition activity of the catalyst. The incorporation of iodide in the catalyst causes a very marked decrease in the H_2O_2 decomposition activity of the catalyst, indicating a strong poisoning of the catalyst due to the iodide ions. It may be noted that the above observations are quite similar to that observed for the different halides present in the reaction medium. Interestingly, at the lower Cl^- concentration in the catalyst, the H_2O_2 decomposition activity of the catalyst is increased but at the higher chloride concentration the activity is decreased markedly (Figure 4.14).

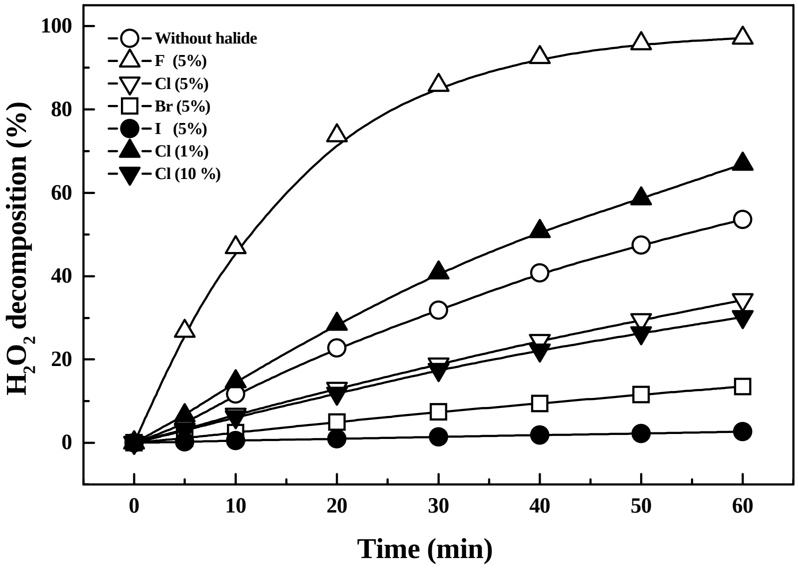


Figure 4.12 Influence of the different halogens incorporated in the Pd/C catalyst on its activity for H_2O_2 decomposition (at 25 ºC) in aqueous acidic (0.05 M H_2SO_4) reaction medium.

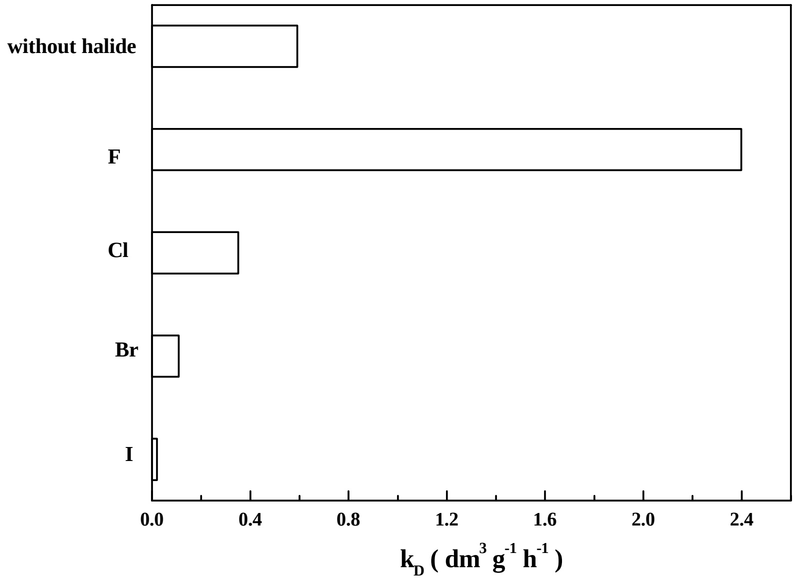


Figure 4.13 Influence of the different halogens (halogen loading = 5 wt%) incorporated into the Pd/C catalyst on its H_2O_2 decomposition activity (at 25 ºC) in aqueous acidic (0.05M H_2SO_4) reaction medium.

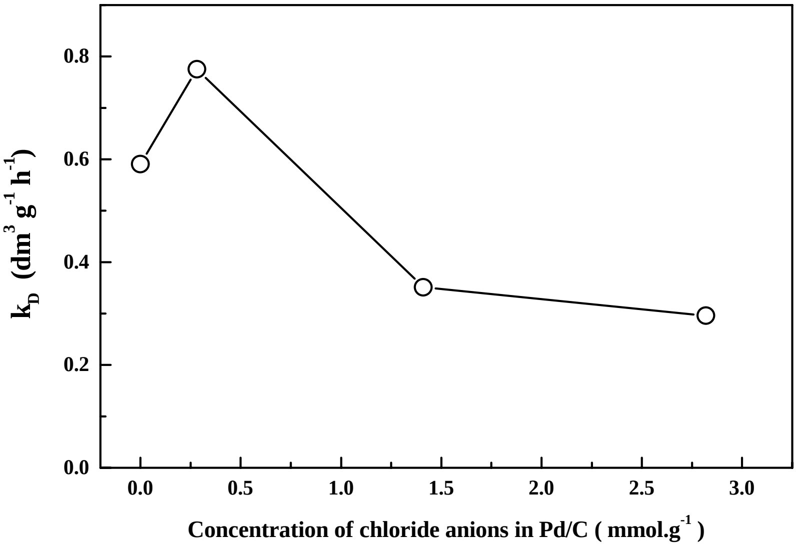


Figure 4.14 Effect of the chloride concentration incorporated in the Pd/C catalyst on its H_2O_2 decomposition activity (at 25 ºC) in aqueous acidic (0.05 M H_2SO_4) reaction medium.

4.4 CONVERSION OF H_2O_2 OVER Pd/C CATALYST IN PRESENCE OF H_2

In the direct oxidation of H_2 to H_2O_2, apart from the decomposition of H_2O_2 another consecutive reaction-the hydrogenation of H_2O_2 to water is also responsible for a low H_2O_2 selectivity in the process.

In the direct oxidation of H_2 to H_2O_2, the following reactions occur simultaneously.

$H_2 + O_2 \rightarrow H_2O_2$ $\Delta H^o_{298K} = -135.9$ kJ.mol^{-1}, $\Delta G^o_{298K} = -120.4$ kJ.mol^{-1} ------ (4.1)

$H_2 + 0.5\ O_2 \rightarrow H_2O$ $\Delta H^o_{298K} = -241.6$ kJ.mol^{-1}, $\Delta G^o_{298K} = -237.2$ kJ.mol^{-1} ------ (4.2)

$H_2O_2 \rightarrow H_2O + 0.5\ O_2$ $\Delta H^o_{298K} = -105.8$ kJ.mol^{-1}, $\Delta G^o_{298K} = -116.8$ kJ.mol^{-1} ----- (4.3)

$H_2O_2 + H_2 \rightarrow 2H_2O$ $\Delta H^o_{298K} = -211.5$ kJ.mol^{-1}, $\Delta G^o_{298K} = -354.0$ kJ.mol^{-1} ---- (4.4)

All these reactions are exothermic in nature and thermodynamically highly favourable, and also catalyzed by Pd. The hydrogenation of H_2O_2 is thermodynamically the most favored among the four reactions. From the stoichiometric viewpoint, the reaction (4.4) may be considered as the sum of reactions (4.2) and (4.3). It is therefore of both scientific and practical interest to know the factors that appreciably affect the H_2O_2 conversion activity of a Pd catalyst in the presence of H_2, which is the situation in the H_2-to-H_2O_2 oxidation.

4.4.1 H_2O_2 Conversion under Static H_2

4.4.1.1 Effect of Halides Present in Reaction Medium

A comparison of results in Table 4.10 reveals that the conversion of H_2O_2 in the presence of H_2 is much more as compared to that in the presence of air (or in the absence of H_2). The results also reveal that even in the presence of H_2, the H_2O_2 conversion is markedly decreased because of the presence of halide, particularly the chloride, bromide and iodide, in the reaction medium. The influence of the different halides on the H_2O_2 conversion is in the following order: $F^- > Cl^- > Br^- >>> I^-$. In the presence of KI, the conversion of H_2O_2 was negligibly small (< 1.0 % in 0.5 h). However, in the presence of other halides or in their absence, the H_2O_2 conversion was complete between 3 and 15 min (Figure 4.15), depending upon the halide.

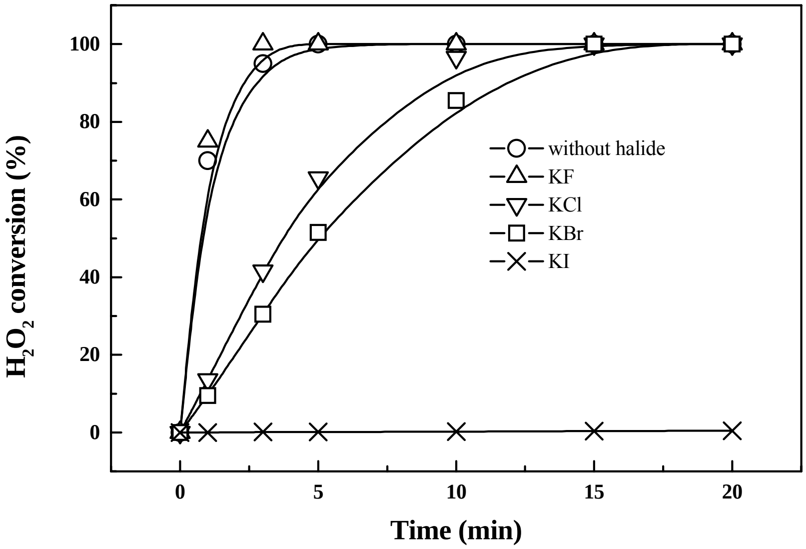
Table 4.10 Influence of the presence of different halides (2.7 mmol. dm^{-3}) on the conversion of H_2O_2 by its decomposition and/or hydrogenation in the reaction of H_2O_2 over the Pd/C catalyst in aqueous H_3PO_4 (0.03 M) medium under H_2 (static) and air (static) atmosphere (reaction period = 15 min).

Halide in the reaction medium	H_2O_2 conversion (%) (In presence of air)	H_2O_2 conversion (%) [a] (In presence of H_2)	
		By decomposition	By hydrogenation
None	17.5	≥ 70.0	≤ 30.0
KF	21.8	≥ 74.0	≤ 26.0
KCl	2.3	0.0	100.0
KBr	1.8	0.0	100.0

[a] *The H_2O_2 conversion by the individual H_2O_2 decomposition and hydrogenation reactions were evaluated from the amount of gas consumed in the hydrogenation or evolved in the decomposition (measured volumetrically) in the complete conversion of H_2O_2 to water and the stoichiometry of the reactions ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$ and $H_2O_2 + H_2 \rightarrow 2H_2O$). Details of the estimation of H_2O_2 conversion by decomposition and hydrogenation are provided in Appendix-4.1.*

The observed much higher H_2O_2 destruction activity of the catalyst in the presence of H_2 as compared to that for the H_2O_2 decomposition in the presence of air (Table 4.10) is because of the hydrogenation of H_2O_2 over the catalyst to a very large extent. The increased H_2O_2 destruction activity of the catalyst in the presence of H_2 is attributed to the reduction of surface and subsurface PdO to metallic Pd, leading to the activation of the catalyst for the H_2O_2 decomposition and/or hydrogenation. It may be noted that, in the absence of any halide or in the presence of F^-, the complete H_2O_2 destruction in the presence of H_2 occurs by the decomposition and/or hydrogenation reactions over the catalyst. In the absence of any halide anions or in the presence of F^- anions, the H_2O_2 destruction in the presence of H_2 is mainly due to the H_2O_2 decomposition and also the H_2O_2 decomposition rate is much higher than that observed in the absence of H_2. However, in the presence of the Cl^- or Br^-, only the H_2O_2 hydrogenation reaction is responsible for the H_2O_2 destruction in the presence of H_2. The modification of the catalyst by changing its electronic environment due to the adsorbed halide anions from the reaction medium (the adsorbed halide anions were detected by the XPS as shown in Figures 4.16, 4.17 and 4.18) is responsible for the observed effects on the H_2O_2 decomposition and hydrogenation reactions.

Figure 4.15 Influence of the presence of different halides (2.7 mmol.dm^{-3}) in the acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 conversion in the reaction of H_2O_2 over the Pd/C catalyst (at 27 ºC) in the presence of hydrogen.



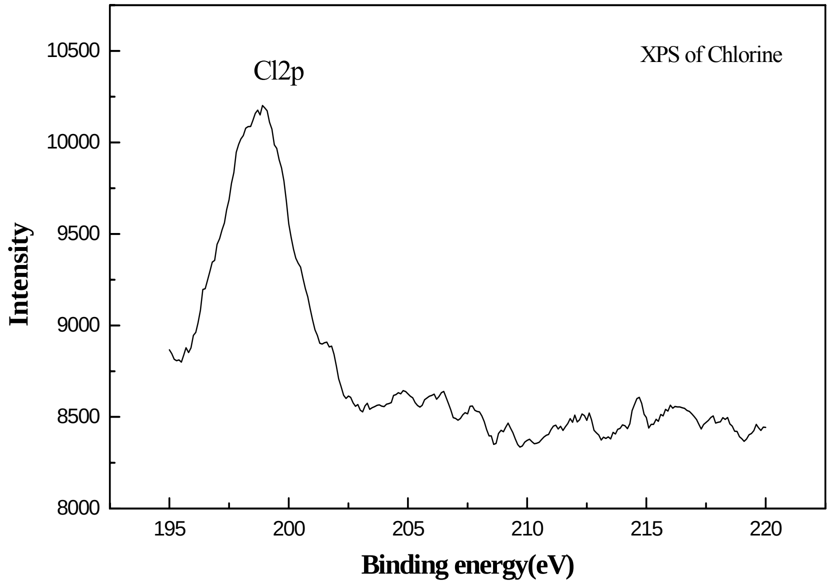


Figure 4.16 X-ray photoelectron spectra of Cl 2p from the used Pd/C catalyst.

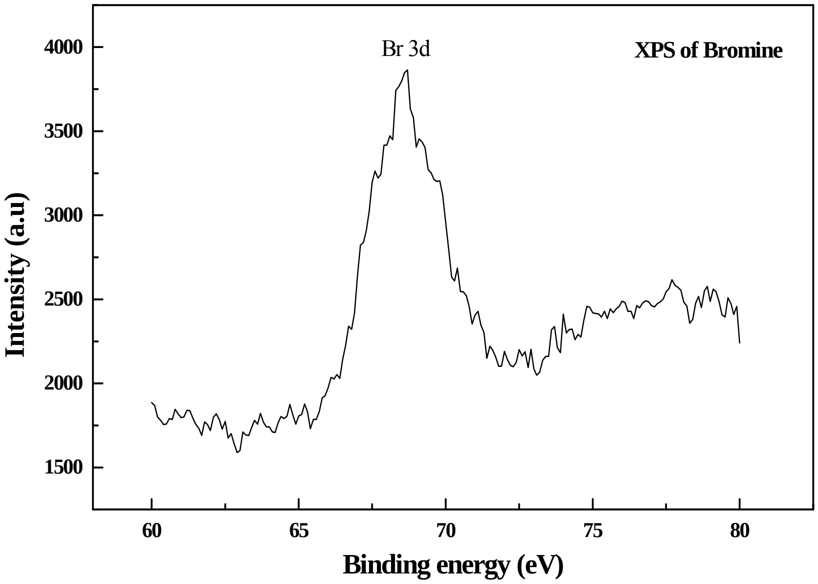


Figure 4.17 X-ray photoelectron spectra of Br 3d from the used Pd/C catalyst.

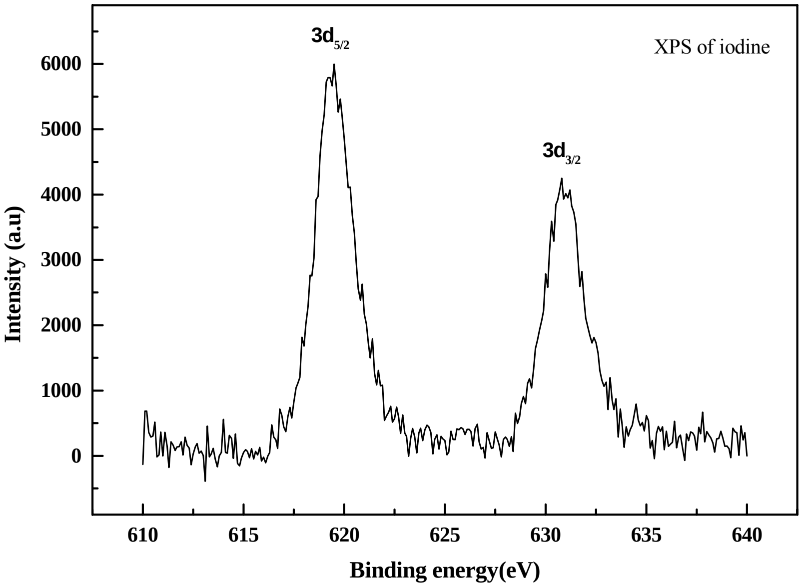


Figure 4.18 X-ray photoelectron spectra of I 3d from the used Pd/C catalyst.

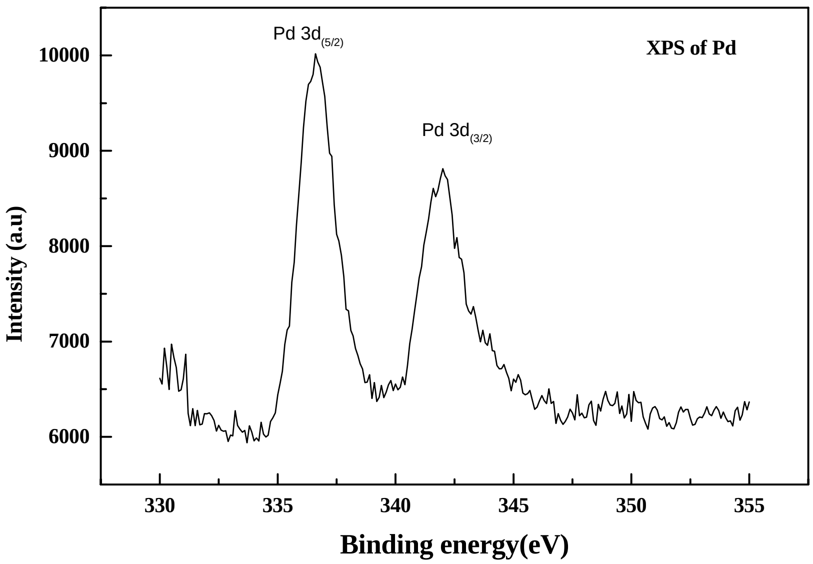


Figure 4.19 X-ray photoelectron spectra of Pd 3d from the Pd/C catalyst.

4.4.1.2 Effect of Br^- Concentration in Acidic (0.03 M H_3PO_4) Reaction Medium on H_2O_2 Hydrogenation over Pd/C Catalyst

Results in Figure 4.20 reveal that the time required for half the H_2O_2 destruction in the presence of H_2 over the Pd catalyst is sharply increased and then leveled off with increasing the bromide concentration in the reaction medium.

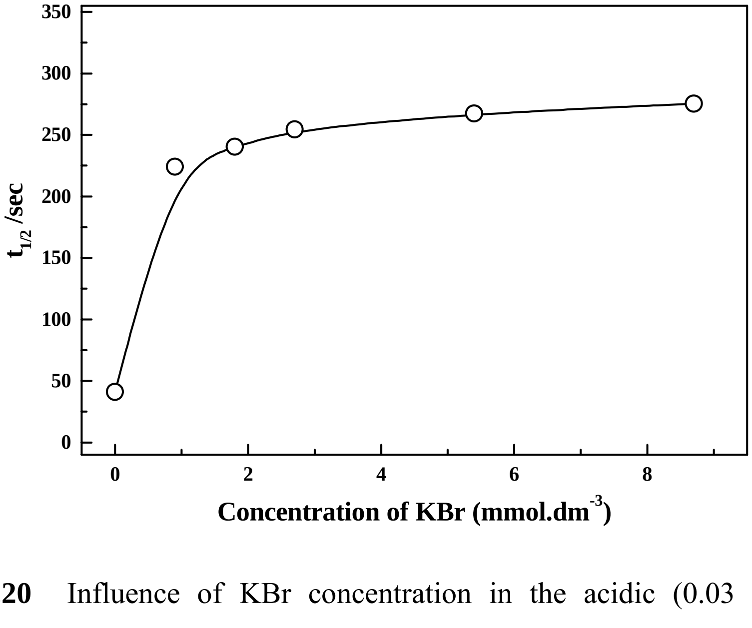


Figure 4.20 Influence of KBr concentration in the acidic (0.03 M H_3PO_4) reaction medium on the time required for half the H_2O_2 conversion [$t_{½}$] over the Pd/C catalyst (at 27 ºC) in the presence of H_2.

This reveals that the H_2O_2 hydrogenation rate is sharply decreased with increasing the bromide concentration. This is probably because of the blockage of the more catalytic reactive sites with increasing the KBr concentration in the reaction medium.

4.4.1.3 Effect of Cl^- Concentration in Acidic (0.03 M H_3PO_4) Reaction Medium on H_2O_2 Hydrogenation over Pd/C Catalyst

Results in Figure 4.21 reveal that, with increase in the chloride concentration in the acidic (0.03 M H_3PO_4) reaction medium, the rate of H_2O_2 hydrogenation over the catalyst is decreased.

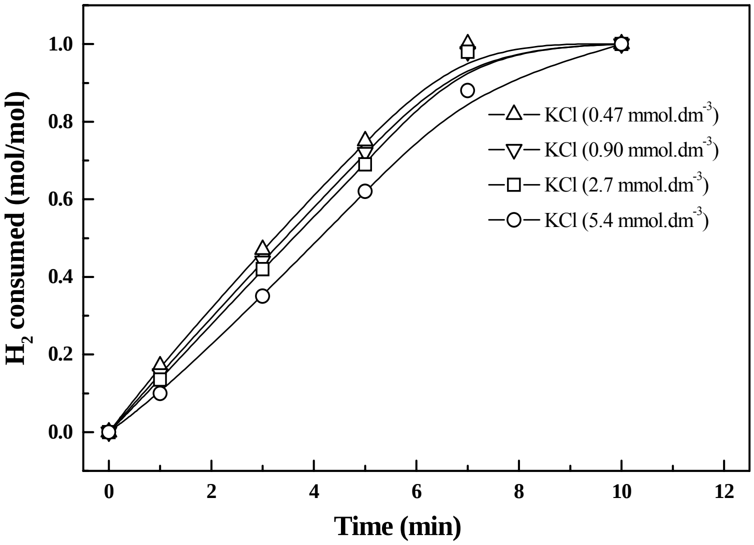


Figure 4.21 Effect of KCl concentration in aqueous acidic (0.03 M H_3PO_4) reaction medium on the hydrogenation of H_2O_2 over the reduced Pd/C catalyst (at 27 ºC).

4.4.2 H_2O_2 Hydrogenation under Flowing H_2: Factors Affecting the H_2O_2 Hydrogenation over Pd/C Catalyst

4.4.2.1 Effect of Stirring Speed

Results in Figure 4.22 reveal that the rate of H_2O_2 hydrogenation is increased with increasing the voltage applied to the magnetic stirrer upto 240 V. This indicates the rate of H_2O_2 hydrogenation is strongly influence by the gas-liquid mass transfer (i.e. the rate of transport of the gaseous reactant (H_2) into the bulk liquid reaction medium) at the lower stirring speeds. However, a further increase in the voltage to 260 V has no significant effect on the H_2 consumed in the reaction.

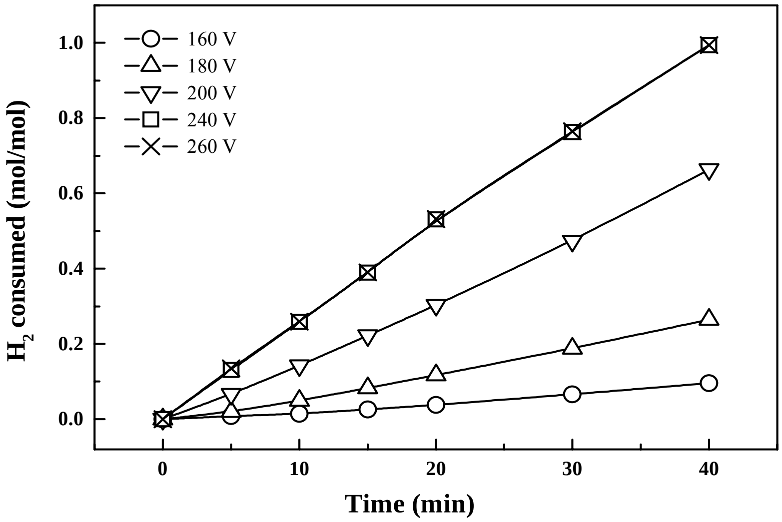


Figure 4.22 Effect of the stirring speed on rate of H_2O_2 hydrogenation (under flowing H_2) over the Pd/C catalyst in an aqueous acidic (0.03 M H_3PO_4) reaction medium containing KCl (5.4 mmol.dm^{-3}) [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.1 g, amount of H_2O_2 = 3 ml of 30 w/v %, H_2 flow = 30 ml. min^{-1} and temperature = 27 ºC].

4.4.2.2 Effect of Catalyst Loading

Results in Figure 4.23 reveal that with the increase in the catalyst loading in the reactor, the rate of H_2O_2 hydrogenation is increased markedly. This indicates the H_2O_2 hydrogenation rate is not controlled by the gas-liquid mass transfer at the reaction conditions employed; the rate of H_2 consumed varies almost linearly with the catalyst loading.

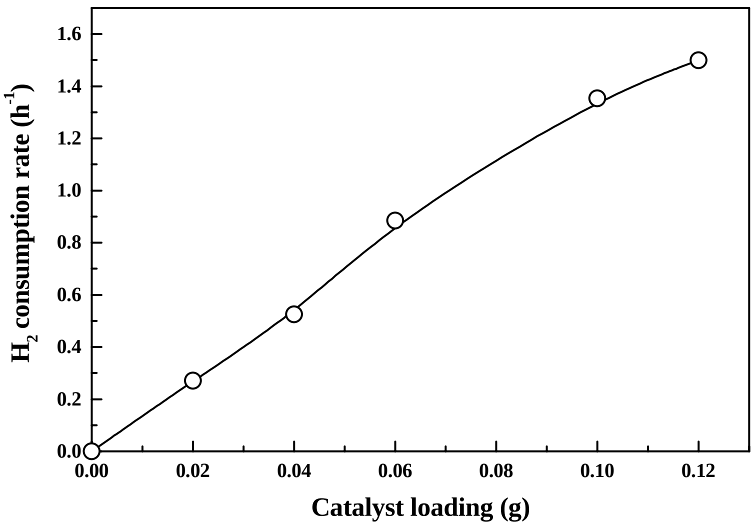


Figure 4.23 Effect of the catalyst loading in the reaction medium (0.05 M H_2SO_4) containing KBr (5.4 mmol.dm^{-3}) on the rate of H_2O_2 hydrogenation over the Pd/C catalyst under flowing H_2 [reaction conditions: volume of reaction medium = 150 cm^3, amount of H_2O_2 = 3 ml of 30 w/v %, H_2 flow = 30 ml. min^{-1}, temperature = 27 ºC and applied voltage = 260 V].

4.2.2.3 Effect of Different Acidic Reaction Medium Containing Cl$^-$ (5.4 mmol.dm^{-3})

Results showing the influence of different reaction mediums containing KCl (5.4 mmol.dm^{-3}) on the hydrogenation of H_2O_2 over the reduced Pd/C catalyst are presented in Figure 4.24. The H_2O_2 hydrogenation activity of the catalyst is extremely low in the HI medium. This observation is consistent with the earlier observed reduction in the H_2O_2 hydrogenation activity of the Pd/C catalyst due to the presence of iodide ions in the reaction medium.

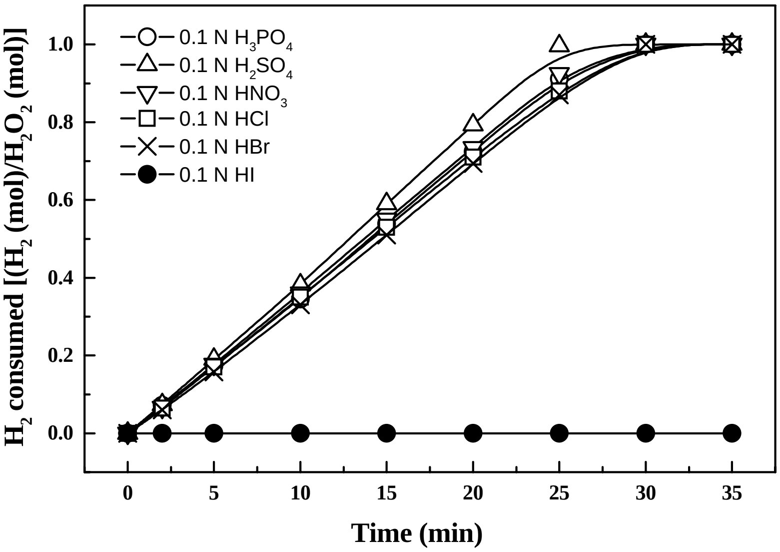


Figure 4.24 Effect of the different acidic reaction mediums containing KCl (5.4 mmol. dm^{-3}) on the conversion of H_2O_2 over the reduced Pd/C catalyst under flowing H_2 [reaction conditions: same as given in Figure 4.23].

4.2.2.4 Effect of Cl$^-$ Concentration in Reaction Medium

Results showing the influence of Cl$^-$ (introduced as KCl) concentration in the aqueous acidic (0.05 M H_2SO_4) reaction medium on the conversion of H_2O_2 under flowing H_2 over the Pd/C catalyst are presented in Figure 4.25. At the lower Cl$^-$ concentration in the reaction medium (0.18 mmol.dm^{-3}) the H_2O_2 is converted mostly by its decomposition rather than via its hydrogenation. However, at the higher chloride concentration in the reaction medium (≥ 2.7 mmol.dm^{-3}), the hydrogenation of H_2O_2 is mainly responsible for the conversion of H_2O_2 over the catalyst. At the intermediate Cl$^-$ concentration, both the H_2O_2 decomposition and hydrogenation reactions are responsible for the H_2O_2 conversion.

The high activity of the catalyst for H_2O_2 decomposition, at the lower Cl$^-$ concentration in presence H_2 may be due to the surface/subsurface reduction of PdO to metallic Pd.

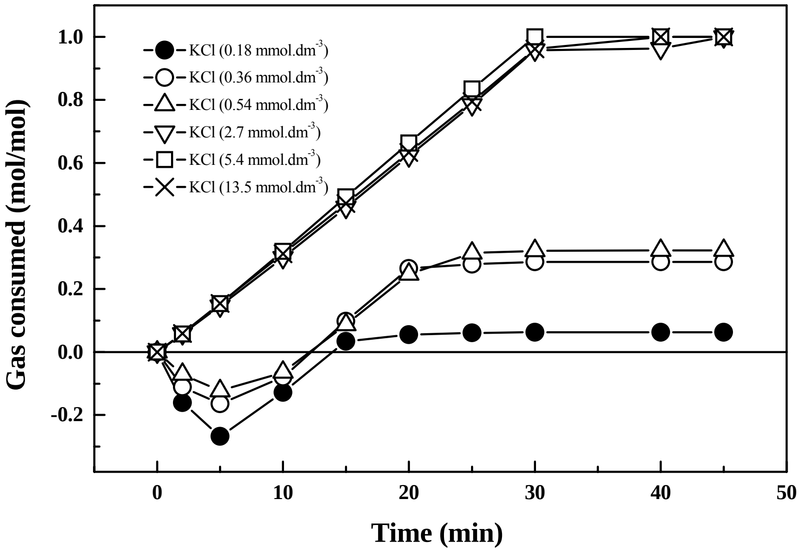


Figure 4.25 Effect of KCl concentration in aqueous acidic (0.05 M H_2SO_4) reaction medium on the hydrogenation of H_2O_2 over Pd/C catalyst under flowing H_2 [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.1 g, amount of H_2O_2 = 3 ml of 30 w/v%, H_2 flow = 30 ml.min^{-1} and temperature = 27 ºC].

4.2.2.5 Effect of Br$^-$ Concentration in Reaction Medium

Results in Fig. 4.26 reveal that, with increasing the Br$^-$ concentration in the reaction medium (0.05 M H_2SO_4), the rate of H_2O_2 hydrogenation over the catalyst is decreased. This is consistent with that observed in the presence of static H_2.

It is interesting to note that, at all the Br$^-$ concentration, the mole of H_2 consumed per mole of H_2O_2 converted (up to reaction period 40 min) is 1.0. This reveals that the H_2O_2 conversion in the presence of the Br$^-$ ions (at all the concentrations) is only due to the hydrogenation reaction.

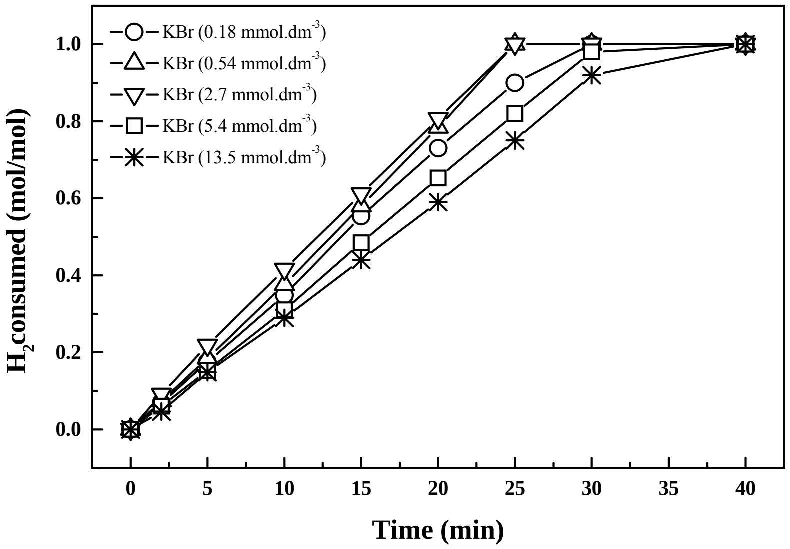


Figure 4.26 Effect of KBr concentration in aqueous acidic (0.05 M H_2SO_4) reaction medium on the H_2O_2 hydrogenation over Pd/C catalyst under flowing H_2 [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.1 g, amount of H_2O_2 = 3 ml of 30 w/v %, H_2 flow = 30 ml/min and temperature = 27 ºC].

4.5 CONCLUSIONS

From the present studies on the direct oxidation of H_2 to H_2O_2 and decomposition and hydrogenation of H_2O_2, over Pd/C catalyst the following important conclusions have been drawn:

1. The Presence of acid in the aqueous reaction medium drastically reduces the H_2O_2 decomposition activity of the catalyst. The presence of Halas acid (viz. HCl or HBr) in the reaction medium causes both the acidic type (reducing H_2O_2 decomposition) and halide type (selective formation of H_2O_2) promotions on the H_2-to-H_2O_2 oxidation leading to the net formation of H_2O_2 with appreciable yield in the H_2-to-H_2O_2 oxidation.
2. The oxidation of bulk and/or sub-surface oxidation of Pd^o to PdO cause a drastic decrease in the H_2O_2 decomposition activity of the catalyst. The H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation is also improved due to the oxidation of surface/sub-surface oxidation of metallic Pd in the catalyst.
3. The presence of Cl^- or Br^- ions in the acidic reaction medium causes a drastic increase in the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation.

4. The H_2O_2 decomposition activity of the catalyst is increased because of the presence of F^- ions in the reaction medium or in the catalyst.
5. The H_2O_2 decomposition activity of the catalyst is very drastically reduced due to the presence of I^- ions in the catalyst and/or in the reaction medium.
6. Except protons (H^+), other cations (associated with the halide anions) have a little or no influence on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the catalyst.
7. Depending upon the reaction conditions, the H_2O_2 decomposition reactions occurs simultaneously with the H_2O_2 hydrogenation reaction over the catalyst in the presence of H_2. The H_2O_2 decomposition activity of the catalyst is increased in the presence of H_2 because of the surface and sub-surface reduction of PdO to Pd^o. The H_2O_2 hydrogenation activity of the catalyst is decreased markedly with the Br^- or Cl^- concentration in the acidic reaction medium. However, in the presence of chloride anions ($\geq$ 2.7 $mmol.dm^{-3}$) and bromide anions in the reaction medium, the H_2O_2 hydrogenation predominates over the H_2O_2 decomposition.
8. The promoting effect of chloride or bromide anions on the H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation is mostly attributed to the drastic reduction in the H_2O_2 conversion activity of the catalyst.

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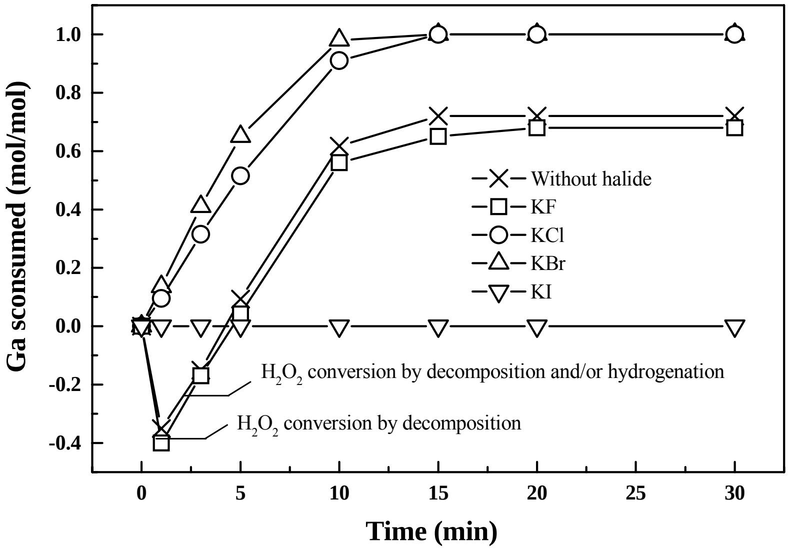
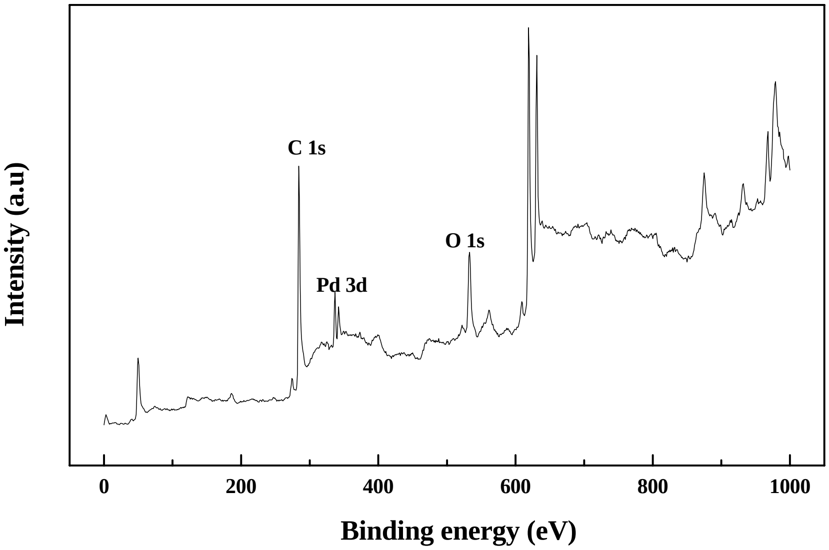
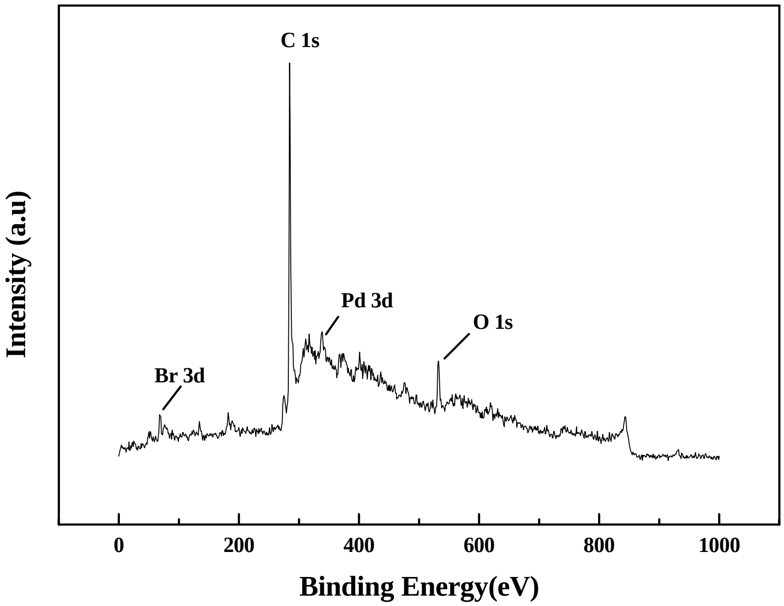
4.7 APPENDIX



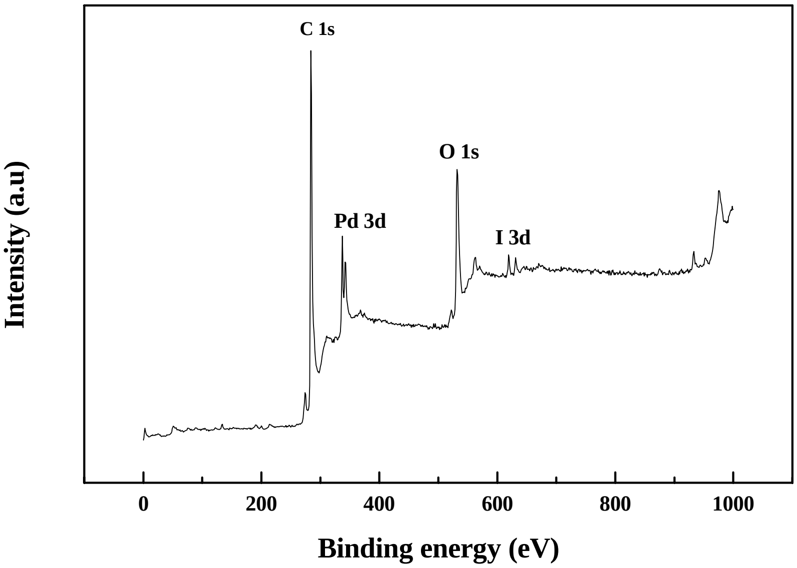
Appendix 4.1 Gas (H_2) consumed or gas (O_2) evolved in the conversion of H_2O_2 (at 27 ºC) over the Pd/C catalyst under static H_2 in acidic (0.03 H H_3PO_4) reaction medium with or without containing halide anions (concentration of halide = 2.7 mmol.dm^{-3})



Appendix 4.2 Representative XPS spectra of the Pd/C catalyst (KCl was added in the reaction medium).



Appendix 4.3 Representative XPS spectra of the Pd/C catalyst (KBr was added in the reaction medium).



Appendix 4.4 Representative XPS spectra of the Pd/C catalyst (KBr was added in the reaction medium).

CHAPTER-5

DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION /HYDROGENATION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/ALUMINA CATALYST:

INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

CHAPTER-5

DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION /HYDROGENATION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/ALUMINA CATALYST: INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTER IN THE MEDIUM

5.1 GENERAL INTRODUCTION-BACKGROUND AND OBJECTIVES

Demand for low cost H_2O_2 for the synthesis of bulk chemicals and wastewater treatments has been increasing day-by-day. The liquid phase direct oxidation of H_2 to H_2O_2 is an attractive alternative to the anthraquinone process for the production of low cost H_2O_2. Therefore, efforts have been made since long to produce H_2O_2 by the direct H_2 oxidation route. The process is covered in several patents [1-23]. Also, recently a large number of publications on the direct oxidation of H_2 to H_2O_2 over Pd catalysts have been appeared in the literature [24-36], indicating both the scientific and technological importance of the direct H_2 oxidation process. At present, some success has been achieved in the H_2-to-H_2O_2 oxidation with the Pd catalysts, especially when halides are used as promoters in the reaction. Bromides are especially effective as demonstrated by Gosser et al [22-23]. The main problem associated with the direct H_2-to-H_2O_2 oxidation is the poor selectivity for H_2O_2 because of the simultaneously occurring non-selective H_2-to-water oxidation and H_2O_2 decomposition/hydrogenation reactions. Since H_2O_2 is an intermediate product formed in the consecutive reactions ($H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O$), the H_2O_2 selectivity in the process is strongly dependent upon the H_2O_2 decomposition and hydrogenation activities of the Pd catalysts. It is, therefore, of both practical and scientific interest to reduce the H_2O_2 decomposition and/or hydrogenation activity of a Pd-catalyst and arrest the direct H_2-to-water oxidation over a Pd catalyst so that selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation can be drastically improved.

The present work was undertaken with the objective of investigating the factors strongly affecting the performance of Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition and/or hydrogenation reactions. The influence of different reaction mediums, presence of halide (viz. F^-, Cl^-, Br^- or I^-) and its concentration in the reaction medium, Pd oxidation state in the catalyst etc. on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions has been thoroughly investigated. The influence of different halides and their concentrations in the reaction medium on the H_2O_2 hydrogenation has also been studied.

5.2 DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION OF H_2O_2 OVER COMMERCIAL Pd (5%)/Al_2O_3 CATALYST

5.2.1 Influence of Reaction Medium

Results showing the effect of different reaction mediums on the performance of reduced Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 5.1. The results reveal the following important observations:

- In the absence of any acid in the aqueous medium, the catalyst shows no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation but very high activity for H_2O_2 decomposition.
- The H_2O_2 decomposition activity of the catalyst is reduced markedly in the presence of acid in the aqueous medium.
- The catalyst shows appreciable selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation in aqueous HBr or HCl medium.
- In the HI medium, both the H_2 conversion and H_2O_2 decomposition are drastically reduced over the catalyst.

The observed higher H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation in the aqueous halogen acid (viz. HCl or HBr) medium as compared to the aqueous oxyacid (viz. H_3PO_4, H_2SO_4 or HNO_3) medium is attributed to the presence of halide (Cl^- or Br^-) anions. The halogen acid present in the reaction medium results both the acidic type (reducing the H_2O_2 decomposition activity of the catalyst) and halide type (directing the H_2/O_2 reaction to H_2O_2, rather than H_2O) promotions on the H_2- to-H_2O_2 oxidation leading to the net formation of H_2O_2. The presence of protons (H^+ ions) in the reaction medium is essential for obtaining the H_2O_2 yield in the H_2-to-H_2O_2 oxidation; otherwise, H_2O_2 formed would be disappeared by its decomposition over the catalyst. The acidic reaction medium (except aqueous H_3PO_4), however, has a detrimental effect on the catalyst, causing significant dissolution of Pd from the catalyst in the reaction medium. H_3PO_4 is an ideal choice as an acid for the reaction medium, since no Pd leaching from the catalyst during the reaction is observed. Also H_3PO_4 acts a stabilizer for H_2O_2 (phosphates are generally used for H_2O_2 stabilizer).

Table 5.1 Results of direct H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/Al_2O_3 catalyst in different reaction mediums (at 27 ºC).

Reaction medium	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity (at 27 ºC) $k_d \times 10^4$ (min $^{-}$
	Conversion of H_2 (%)		H_2O_2 selectivity (%)	
	Total	To H_2O_2		
Distilled water [a]	47.9	0.0	0.0	375.2
0.1 N H_3PO_4 [a]	55.7	0.0	0.0	45.7
0.1 N H_2SO_4 [b]	50.5	1.7	3.3	40.6
0.1 N HNO_3 [b]	49.3	0.0	0.0	34.6
0.1 N HCl [b]	43.9	6.7	15.3	7.8
0.1 N HBr [b]	18.8	5.9	31.4	2.3
0.1 N HI [a]	< 1.0	0.0	-	0.7

[a] *No Pd leaching detected.* [b] *Significant leaching of Pd in the reaction.* [c] *Pseudo first order H_2O_2 decomposition rate constant.*

5.2.2 Influence of Presence of Different Halides in Reaction Medium

Results showing the influence of different halides (viz. F^-, Cl^-, Br^- or I^-, halides are introduced in the reaction medium as potassium halide) present in the aqueous acidic (0.03 M H_3PO_4 or 0.05 M H_2SO_4) reaction medium on the performance of the reduced Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 5.2. From the results the following important observations can be made:

- In the presence of potassium bromide in the acidic reaction medium, the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation are drastically increased, whereas the H_2O_2 decomposition activity of the catalyst is reduced markedly.
- The presence of potassium chloride, bromide or iodide in the reaction medium causes a large decrease in the H_2O_2 decomposition activity of the catalyst but the fluoride results in an increase in the H_2O_2 decomposition activity.

- The presence of potassium iodide causes almost a complete deactivation of the catalyst for both the H_2 oxidation and H_2O_2 decomposition reactions.

Table 5.2 Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/Al_2O_3 catalyst in aqueous acidic reaction mediums with or without containing different halides (concentration of halide in reaction medium = 0.94 $mmol.dm^{-3}$).

Alkali halide in the reaction medium	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity (at 27 ºC)
	Conversion of H_2 (%)		H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1}) [c]
	Total	To H_2O_2		
Reaction medium = 0.03 M H_3PO_4				
None [a]	54.0	0.0	0.0	46.5
KF [a]	59.2	0.0	0.0	141.5
KCl [a]	52.7	5.7	10.8	10.9
KBr [a]	43.8	25.8	58.9	3.6
KI [a]	2.4	0.2	8.7	0.6
Reaction medium = 0.05 M H_2SO_4				
None [b]	50.5	1.7	3.3	40.6
KF [b]	56.3	0.3	0.8	131.6
KCl [b]	50.8	4.6	9.1	14.6
KBr [a]	45.7	23.8	52.1	5.3
KI [a]	3.8	0.0	0.0	0.3

[a] *No Pd leaching detected.* [b] *Significant leaching of Pd in the reaction.* [c] *Pseudo first order H_2O_2 decomposition rate constant.*

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 and decomposition/hydrogenation of H_2O_2 to water 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 ($H_2 + 0.5\ O_2 \rightarrow H_2O$) oxidation and H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and hydrogenation ($H_2O_2 + H_2 \rightarrow 2H_2O$) reactions should therefore be minimized simultaneously. The presence of acid reduces the H_2O_2 decomposition over the Pd catalyst. The presence of halide anions (except F^-) in the acidic reaction medium results a further large decrease in the H_2O_2 decomposition over the catalyst (Figure 5.1).

A following probable mechanism for the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition and hydrogenation reactions in the presence of bromide or chloride anions in the acidic reaction medium, involving elementary ionic and free radical reactions, is proposed.

$S + X^- \rightarrow S.X^-$ ------------------- (5.1)

$2\ S + H_2 \rightarrow 2\ S.H$ ----------------- (5.2)

$S + O_2 \rightarrow S.O_2$ ---------------- (5.3)

$S.\ O_2 + S.X^- \rightarrow S.O_2^- + S.X$ --------- (5.4)

$S.O_2^- + S.H \rightarrow S.HO_2^- + S$ ---------- (5.5)

$S.HO_2^- + H^+ \rightarrow S.H_2O_2$ ----------- (5.6)

$S.H_2O_2 + S \rightarrow 2\ S.OH$ ------------- (5.7)

$S.H_2O_2 + S.H \rightarrow S.OH + H_2O + S$ ------- (5.8)

$S.OH + S.H \rightarrow H_2O + 2\ S$ ----------- (5.9)

$2\ S.OH \rightarrow S.H + H_2O + S$ ---------- (5.10)

$S.O_2^- + H^+ \rightarrow S.HO_2$ -------------- (5.11)

$S.HO_2 + S.H \rightarrow S.\ H_2O_2$ ---------- (5.12)

$S.H_2O_2 \rightarrow S + H_2O_2$ ------------- (5.13)

$S.X + S.H \rightarrow S.X^- + H^+ + S$ -------- (5.14)

(S = Adsorption site, X = Br or Cl)

In the presence of acid, since the pH of the reaction medium is lower than the isoelectric point of the catalyst support (e.g. Al_2O_3), only the halide anions from the reaction medium are adsorbed on the catalyst. Therefore, the cations associated with the halide anions do not modify the catalytic active sites. The modification of the catalysts through a change in the electronic environment on their surface due to the adsorbed halide anions is mostly responsible for the observed effects on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions (the adsorbed halide anions were detected by the XPS and EDX analysis of the used catalysts). Both the adsorbed halide anions (particularly Br^-) and protons (from the acid) are taking part in the H_2-to-H_2O_2 oxidation according to reactions – 5.4, 5.6 and 5.11 and likely to be regenerated by reaction 5.14.

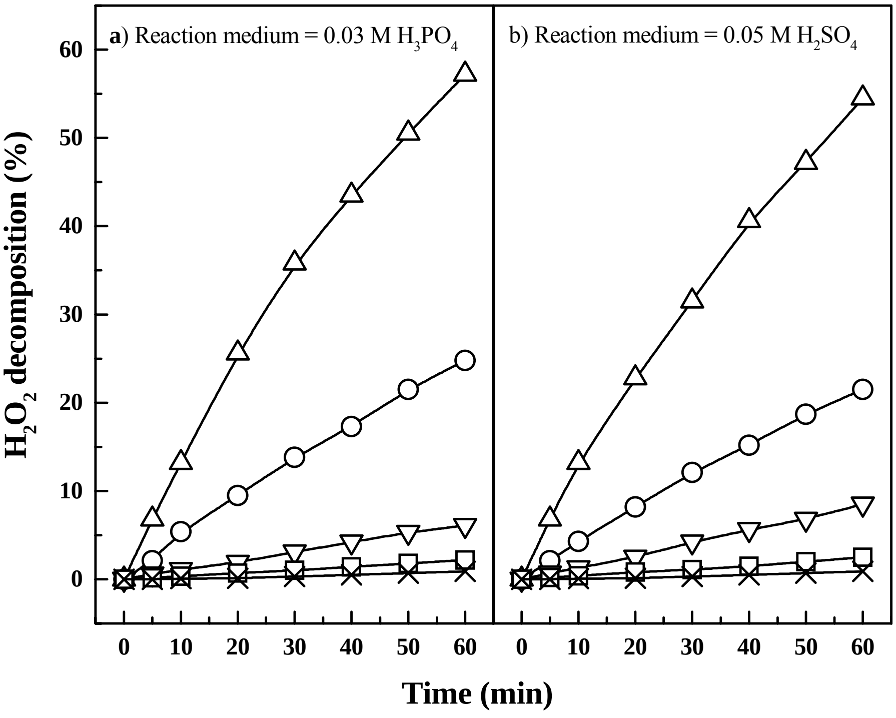


Figure 5.1 Influence of the presence of different halides (0.94 $mmol.dm^{-3}$) in aqueous acidic (a) 0.03 M H_3PO_4 and (b) 0.05 M H_2SO_4 reaction mediums on the H_2O_2 decomposition (at 27 ºC) over the reduced Pd/Al_2O_3 catalyst [halides in the reaction medium: without halide (O), KF (Δ), KCl (∇), KBr (□) and KI (×)].

In the absence of the Br^- anions, oxygen is likely to undergo dissociative adsorption on Pd, leading to complete hydrogen combustion. It may be noted that during the formation of H_2O_2 in the H_2-to-H_2O_2 oxidation, the oxygen-oxygen bond must be intact. Once oxygen-oxygen bond is broken water should be the only product of H_2 oxidation. Hence, the inhibition of oxygen-oxygen bond cleavage will increase the H_2O_2 formation. Because of the adsorbed bromide anions/radicals not only the activity of the catalyst is reduced due to blockage of a part of the catalytic active sites but also Pd surface is expected to be electron deficient, not favouring H_2O_2 adsorption and/or favouring non-dissociative O_2 adsorption, and thereby increasing the H_2O_2 yield and reducing the H_2O_2 conversion activity of the catalyst. However, the electronegativity of the halogens does not have a linear effect on the strength of their promotion for the H_2O_2 selectivity, since both the fluoride and chloride are found less effective promoters than bromide. In the absence of acid, the dissociation of H_2O_2 (which is a weak acid) by water ($H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$) and reverse reaction 5.6 are favoured, leading to the destruction of more and more H_2O_2.

5.2.3 Influence of Different Bromide Precursors Present in Reaction Medium

Results showing the influence of different bromide-containing compounds added in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the reduced Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 5.3. The results obtained with the different bromide compounds are comparable, emphasizing the importance of the Br^- ions over the associated cations; the cations (except H^+ ions) play a little or no role for influencing the H_2O_2 decomposition and H_2-to-H_2O_2 oxidation reactions. In the presence of acid, since the pH of the reaction medium is lower than the isoelectric point of the catalyst support (Al_2O_3), only the Br^- ions from the reaction medium is adsorbed on the catalyst. Therefore, the cations associated with the Br^- ions do not modify the catalytic active sites. The modification of the catalyst through a change in the electronic environment on its surface due to the adsorbed Br^- ions is mostly responsible for the observed effects on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions. A similar result was found for the Pd/C catalyst (Chapter 4); the different chloride-containing compounds result the same level of promotion on both the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the Pd/C catalyst.

Table 5.3 Results of the direct H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions (at 27 ºC) over the Pd/Al_2O_3 catalyst in aqueous acidic (0.03 M H_3PO_4) reaction medium containing different bromide compounds (concentration of = 0.94 $mmol.dm^{-3}$).

Bromide compound added in the reaction medium	H_2–to–H_2O_2 oxidation			H_2O_2 decomposition activity
	H_2 conversion (%)	H_2O_2 yield (%)	H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
HBr	43.7	26.3	60.2	3.2
NaBr	45.4	23.8	52.4	3.7
KBr	43.8	25.8	58.9	3.6
NH_4Br	46.2	24.2	52.4	3.8

5.2.4 Comparison of Reduced and Oxidized Pd/Al_2O_3 Catalysts

Results in Table 5.4 show a strong influence of the Pd oxidation state in the Pd/Al_2O_3 catalyst on its performance in both the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions. The surface and bulk properties of the oxidized and reduced Pd/Al_2O_3 catalysts are presented in Table 5.5. XRD spectra of the reduced and oxidized catalysts are shown in Figure 5.3. The reduced catalyst shows much higher H_2 conversion and H_2O_2 decomposition activities than the oxidized catalyst. The oxidized catalyst shows much higher H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation than the reduced catalyst. The observed high H_2O_2 decomposition activity (Figure 5.2) with no H_2O_2 selectivity for the reduced catalyst suggests that, in the H_2 oxidation over the reduced catalyst, H_2O_2 most likely an intermediate product formed in the consecutive reaction ($H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O + 0.5\ O_2$), but as soon as it is formed it is decomposed to water. However, for both the reduced and oxidized catalysts, the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation is increased in the presence Br^- ions in the reaction medium. The higher H_2 conversion activity of the reduced catalyst is attributed to the presence of metallic Pd (dissociative chemisorptions of H_2 more readily takes place on the metallic Pd surface as compared to the PdO surface) in the catalyst.

Table 5.4 Influence of Pd oxidation state in the Pd/Al_2O_3 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in acidic (0.03 M H_3PO_4) reaction medium with or without containing KBr (at 27 ºC).

Form of Pd/Al_2O_3 (reduced/ oxidized)	Concentration of KBr in the reaction medium	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition rate constant
		Conversion of H_2 (%)		H_2O_2 selectivity (%)	$k_d \times 10^4$ (min^{-1})
		Total	To H_2O_2		
Reduced	None	54.7	0.5	0.9	43.8
Oxidized [a]	None	20.8	8.5	40.9	5.3
Reduced	0.94	43.8	25.8	58.9	3.6
Oxidized [a]	0.94	15.6	8.7	55.8	1.9

[a] *The oxidized catalyst was prepared by calcining the reduced catalyst in static air at 500 ºC for 3h.*

Table 5.5 Surface and bulk properties of Pd/Al_2O_3 catalyst

Form of Pd/Al_2O_3 (oxidized/reduced)	XRD phase (Pd^o or PdO)	Surface area ($m^2\ g^{-1}$)	Binding energy (eV)			
			O (2s)	Pd ($3d_{3/2}$)	Pd ($3d_{5/2}$)	Al 2p
Oxidized	PdO	173.5	531.8	342.2	336.9	74.7
Reduced	Pd^o	198.0	531.6	340.4	335.1	74.5

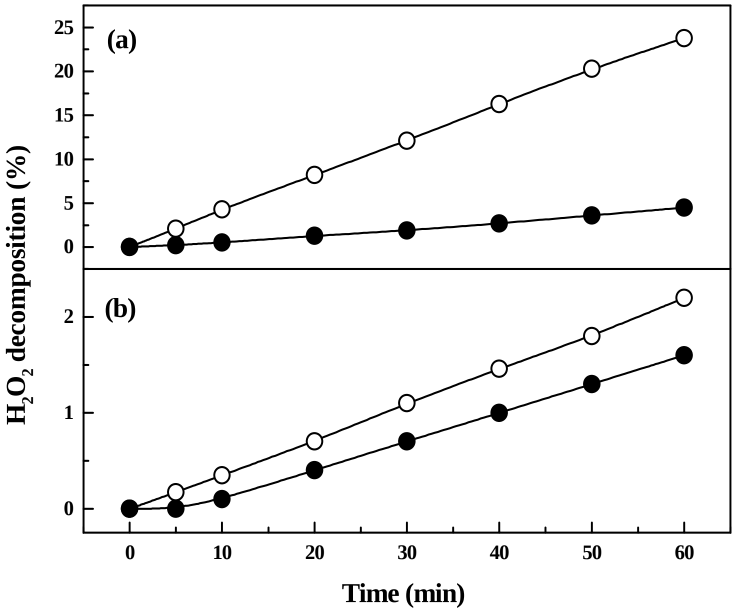


Figure 5.2 Effect of Pd oxidation state [Pdº (o) and PdO (•)] in the Pd/Al_2O_3 catalyst on the H_2O_2 decomposition in aqueous acidic (0.03M H_3PO_4) reaction medium in (a) absence and (b) presence of KBr (0.94 mmol.dm^{-3}).

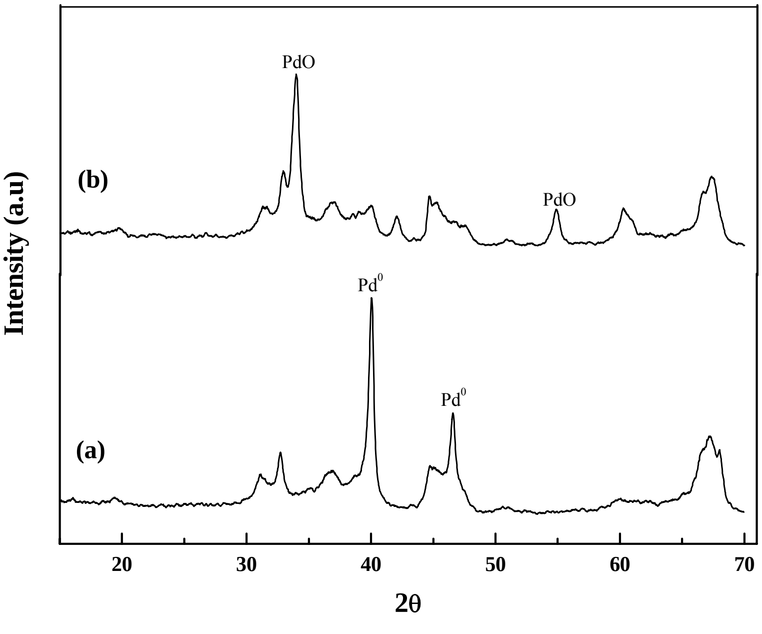


Figure 5.3 XRD spectra of (a) reduced and (b) oxidized Pd/Al_2O_3 catalysts.

5.2.5 Influence of Concentration of Bromide Anions in Reaction Medium

Results showing the influence of Br^- concentration in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the reduced Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Figure 5.4. Both the H_2 conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition over the catalyst are decreased with the increase in the Br^- concentration in the reaction medium, whereas the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is sharply increased and then passed through a maximum. Thus, for the highest H_2O_2 yield in the H_2-to-H_2O_2 oxidation, an optimum concentration of Br^- is necessary. The observed decrease in the H_2 conversion and H_2O_2 decomposition activities of the catalyst with increase in the Br^- concentration is due to the blockage of more and more catalytic active sites.

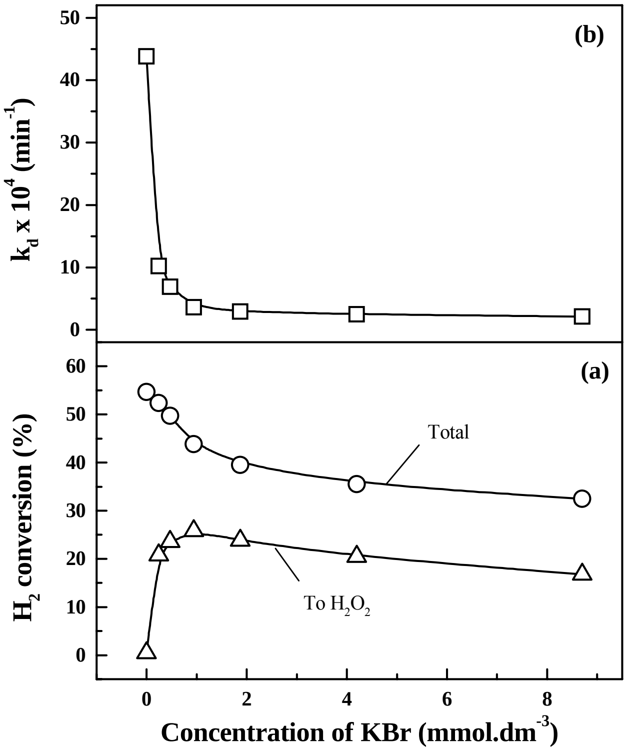


Figure 5.4 Influence of KBr concentration in aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the Pd/Al_2O_3 catalyst in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 °C) [k_d = pseudo first order H_2O_2 decomposition rate constant].

5.2.6 Effect of Concentration of Chloride Anions in Reaction Medium

Results in Table 5.6 show that, with increasing the chloride concentration in the reaction medium, the H_2O_2 decomposition activity of the catalyst is reduced but the H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation is passed through a maximum. The H_2 conversion activity of the catalyst is also reduced, particularly at the higher Cl^- concentrations. The beneficial effect of chloride anions as compared to that of bromide anions for the Pd/Al_2O_3 catalyst is much smaller. The Cl^- ions, unlike the Br^- ions, probably do not reduce the dissociative adsorption of O_2 on the catalyst and therefore plays a little role for reducing the initial H_2/O_2 reaction to H_2O. It may be noted that the presence of acid in the reaction medium is essential for reducing the H_2O_2 decomposition activity of the catalyst. The presence of Cl^- in the aqueous reaction medium in the absence of an acid causes a drastic increase in the H_2O_2 decomposition activity of the catalyst.

Table 5.6 Influence of chloride concentration in acidic (0.03 M H_3PO_4) reaction medium on the performance of reduced Pd/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions (at 27 ºC).

Concentration of KCl in reaction medium (mmol.dm^{-3})	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition rate constant $k_d \times 10^4$ (min^{-1})
	Conversion of H_2 (%)		H_2O_2 selectivity (%)	
	Total	To H_2O_2		
0.47 [a]	54.2	5.2	9.6	14.3
0.94 [a]	52.7	5.7	10.8	10.9
1.4 [a]	58.5	5.2	8.9	10.2
2.8 [a]	57.8	4.2	7.2	7.3
4.2 [b]	53.7	2.7	5.0	5.9
8.4 [b]	44.9	3.5	7.8	4.5
4.2 [c]	40.3	0.0	0.0	394.3

[a] *No Pd leaching detected.* [b] *Significant leaching of Pd in the reaction.* [c] *Reaction medium = distilled water.*

5.2.7 Influence of Iodide Concentration in Reaction Medium

Results in Figure 5.5 show a strong influence of the iodide concentration in the acidic reaction medium (0.03 M H_3PO_4) on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the catalyst. Both the H_2 conversion and H_2O_2 decomposition over the catalyst are reduced markedly with a slight increase in the iodide concentration (at the lower concentrations) in the reaction medium. The large deactivation in both the H_2 conversion and H_2O_2 decomposition activities of the catalyst due to the presence of iodide ions indicates a strong poisoning of the catalyst due to the adsorbed iodide ions.

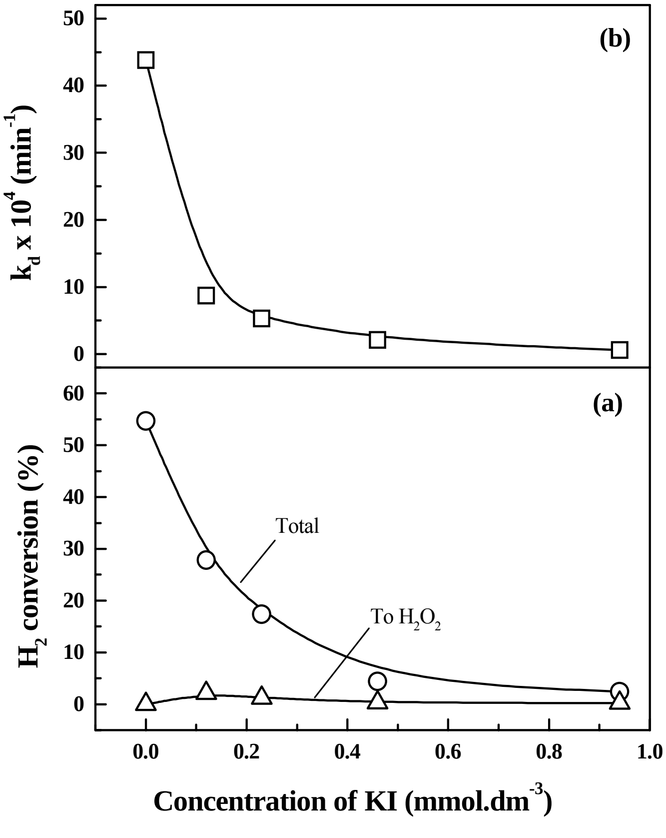


Figure 5.5 Influence of the concentration of KI in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the Pd/Al_2O_3 catalyst in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 ºC).

5.2.8 Influence of Fluoride Concentration in Reaction Medium

Results showing the influence of the fluoride concentration in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/Al_2O_3 catalyst are presented in Figure 5.6. The H_2O_2 decomposition activity of the catalyst is increased sharply with increase in the fluoride concentration in the reaction medium. Because of this, the catalyst shows a little or no H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation in the presence of F^- anions in the reaction medium.

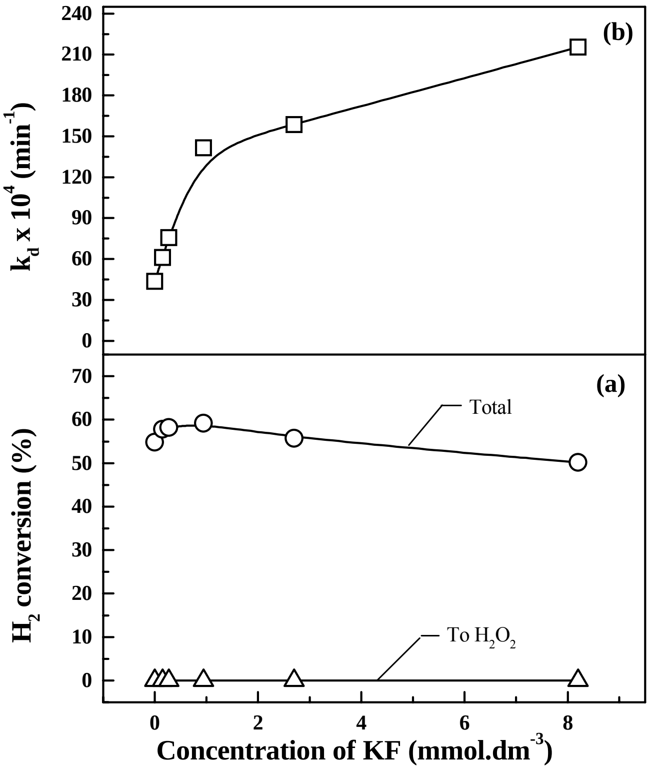


Figure 5.6 Influence of the concentration of KF in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the Pd/Al_2O_3 catalyst in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 ºC).

5.2.9 Influence of Concentration of Acid in Reaction Medium Containing Bromide Ions

Results showing the influence of acid (H_3PO_4) concentration in the aqueous reaction medium containing Br^- (0.94 mmol.dm^{-3}) on the H_2-to-H_2O_2 oxidation and H_2O_2

decomposition reactions over the reduced Pd/Al_2O_3 catalyst are presented in Table 5.7. Both the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation are increased and then pass through a maximum with increase in the acid concentration in the reaction medium. However, the H_2O_2 decomposition activity of the catalyst is reduced with increase in the acid concentration in the reaction medium. The high acid concentration in the reaction medium has, however, a detrimental effect on the catalyst, leading to the Pd leaching from the catalyst in the reaction medium. In the presence of bromide ions in the aqueous reaction medium, there is no formation of H_2O_2, indicating the presence of acid is essential for the net formation of H_2O_2 in the H_2-to-H_2O_2 oxidation.

Table 5.7 Results of the direct oxidation of H_2 to H_2O_2 and H_2O_2 decomposition over the reduced Pd/Al_2O_3 catalyst in aqueous medium containing H_3PO_4 at different concentrations and KBr (0.94 $mmol.dm^{-3}$).

Concentration of H_3PO_4 ($mol.dm^{-3}$)	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition rate constant $k_d \times 10^4$ (min^{-1})
	Conversion of H_2 (%)		H_2O_2 selectivity (%)	
	Total	To H_2O_2		
0.0 [a]	37.7	0.0	0.0	284.6
0.01 [a]	42.2	20.5	48.6	5.8
0.03 [a]	43.8	25.8	58.9	3.6
0.1 [a]	47.5	26.5	55.8	3.2
0.3 [a]	54.5	27.8	51.1	2.3
1.0 [b]	42.3	20.8	49.2	1.8
3.0 [b]	36.5	14.8	40.5	1.2

[a] *No Pd leaching detected.* [b] *Significant leaching of Pd in the reaction.*

5.3 H_2O_2 CONVERSION OVER Pd (5%)/Al_2O_3 CATALYST IN PRESENCE OF H_2

5.3.1 H_2O_2 Conversion Under Static H_2

5.3.1.1 Influence of Different Halides in Reaction Medium

Results showing the influence of different halides present in an acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 conversion over the Pd/Al_2O_3 catalyst in the presence of hydrogen are presented in Figure 5.7. In the presence of hydrogen, the H_2O_2 is destroyed over the catalyst by its decomposition and/or hydrogenation. Interestingly, also in the presence of H_2, the H_2O_2 conversion is markedly decreased because of the presence of halide, particularly the Cl^-, Br^- and I^- in the reaction medium. The influence of the different halides on the H_2O_2 conversion is in the following order: $F^- > Cl^- > Br^- >>> I^-$. In the presence of I^-, the conversion of H_2O_2 was negligibly small (< 1.0 % in 0.5h). However, in the presence of other halides or in their absence, the H_2O_2 conversion was complete between 3 and 30 min, depending upon the halide (Figure 5.7).

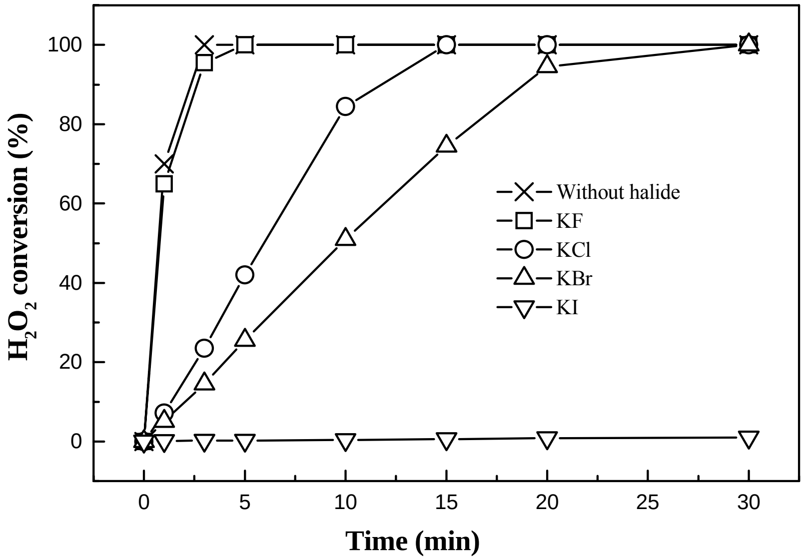


Figure 5.7 Influence of the presence of different halides (2.7 mmol.dm^{-3}) in the acidic reaction medium (0.03 M H_3PO_4) on the H_2O_2 conversion in the reaction of H_2O_2 over the Pd/Al_2O_3 catalyst (at 27 ºC) in the presence of hydrogen.

The observed much higher H_2O_2 destruction activity of the catalyst in the presence of hydrogen, as compared to that for the H_2O_2 decomposition in the absence of hydrogen (Figure 5.1) is because of the hydrogenation of H_2O_2 over the catalysts to a very large extent (Table 5.8) and also to some extent due to elimination of surface oxidation of the Pd by H_2O_2 (oxidized Pd surface has much lower H_2O_2 decomposition activity).

The results in Table 5.8 reveal that, in the absence of any halide anions or in the presence of F^- anions, the H_2O_2 destruction in the presence of H_2 is mainly due to the H_2O_2 decomposition and also the H_2O_2 decomposition rate is much higher than that observed in the absence of H_2 (Figure 5.1). However, in the presence of the Cl^- or Br^- anions, only the H_2O_2 hydrogenation reaction is responsible for the H_2O_2 destruction, thus revealing its importance over the H_2O_2 decomposition in the presence of H_2 for these halide anions.

Table 5.8 Influence of the presence of different halides (2.7 mmol.dm^{-3}) on the conversion of H_2O_2 by its decomposition and/or hydrogenation in the reaction of H_2O_2 over the Pd/Al_2O_3 catalyst in aqueous acidic (0.03 M H_3PO_4) reaction medium under H_2 (static) atmosphere at 27 ºC (reaction period = 0.5 h).

Halide added to the reaction medium	H_2O_2 conversion (%) [a]	
	By decomposition	By hydrogenation
None	≥ 65.0	≤ 35.0
KF	≥ 60.0	≤ 40.0
KCl	0.0	100
KBr	0.0	100

[a] *The H_2O_2 conversion by the individual H_2O_2 decomposition and hydrogenation reactions were evaluated from the amount of gas consumed in the hydrogenation or evolved in the decomposition (measured volumetrically) in the complete conversion of H_2O_2 to water and the stoichiometry of the reactions ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$ and $H_2O_2 + H_2 \rightarrow 2H_2O$).*

5.3.1.2 Influence of Chloride Concentration in Reaction Medium

Results showing the influence of chloride concentration in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 hydrogenation activity of the Pd/Al_2O_3 catalyst are presented in Figure 5.8. The H_2O_2 hydrogenation activity of the catalyst is decreased with increase in the Cl^- concentration in the reaction medium. Blockage of active sites in the catalyst (due to the adsorption of chloride anions from the reaction medium) probably increases with increase in the Cl^- concentration in the reaction medium. Interestingly, both the H_2O_2 decomposition and hydrogenation activities of the catalyst are reduced with increase in the chloride concentration in the reaction medium, indicating Cl^- ions adsorbed from the reaction medium poison some of the active sites in the catalyst responsible for H_2O_2 decomposition and hydrogenation.

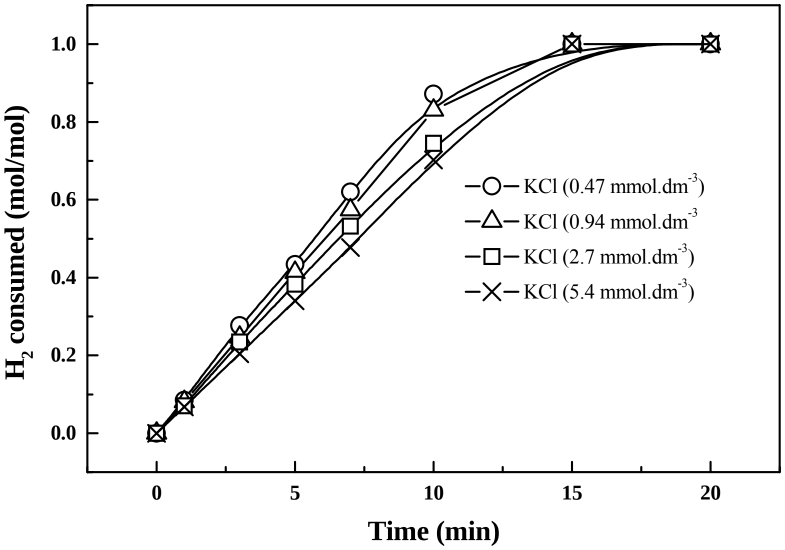


Figure 5.8 Effect of the concentration of KCl in aqueous acidic (0.03 M H_3PO_4) reaction medium on the rate of H_2 consumption in the hydrogenation of H_2O_2 over the reduced Pd/Al_2O_3 catalyst (at 27 ºC).

5.3.1.3 Influence of Bromide Concentration in Reaction Medium

Results showing the influence of concentration of Br^- ions in the aqueous acidic (0.03 M H_3PO_4) reaction medium on the conversion of H_2O_2 in the presence of H_2 over the reduced Pd/Al_2O_3 catalyst are presented in Figure 5.9. The results reveal that the time required for half the H_2O_2 destruction in the presence of H_2 over the catalyst is sharply increased and then leveled off with increasing the Br^- concentration in the reaction medium.

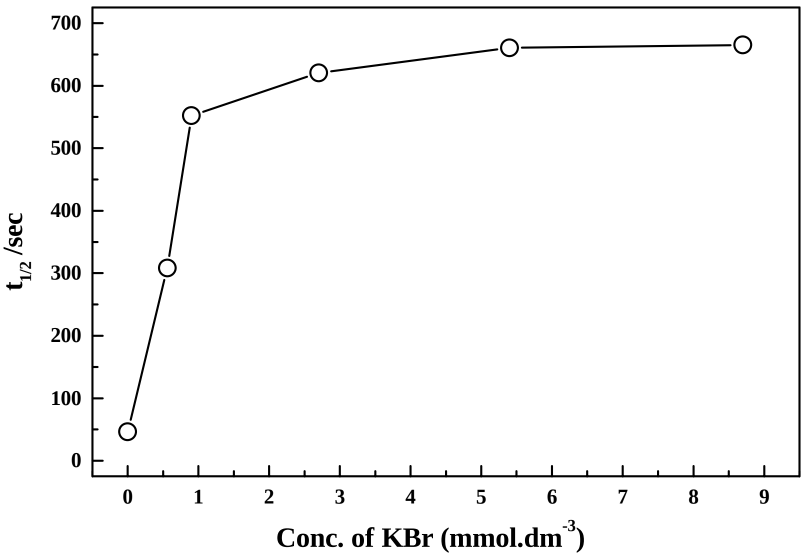


Figure 5.9 Influence of the concentration of KBr in the acidic reaction medium (0.03 M H_3PO_4) on the time required for half the H_2O_2 conversion reaction [$t_{½}$] on the Pd/Al_2O_3 catalyst (at 27 ºC) in the presence of H_2.

5.3.2 H_2O_2 Conversion in Presence of Flowing H_2

5.3.2.1 H_2O_2 Conversion Under Different Gases Flowing through Reaction Medium

Results showing the conversion of H_2O_2 in an aqueous acidic (0.03 M H_3PO_4) reaction medium with or without containing KBr (0.94 $mmol.dm^{-3}$) over the reduced Pd/Al_2O_3 catalyst under different gases (viz. O_2, N_2 and H_2) flowing through the reaction medium are presented in Figure 5.10. The H_2O_2 conversion is very small under the flowing N_2 or O_2, whereas H_2O_2 is destroyed very rapidly under the flowing H_2. The observed much higher H_2O_2 conversion under the flowing H_2 is because of the hydrogenation of H_2O_2. On the other hand, the H_2O_2 conversion takes place only by its decomposition under the flowing N_2 or O_2. This reveals that the H_2O_2 is more stable in the presence of O_2 or N_2, but is reduced by H_2 to H_2O in the presence of H_2. The H_2O_2 conversion under the flowing H_2 in the absence of Br^- in the reaction medium is found to be much higher as compared to that in the presence of Br^- in the reaction medium. In the presence of H_2, the catalyst becomes highly active for the H_2O_2 decomposition because of the elimination of surface/sub-surface PdO in the catalyst. It may be noted that the presence of Br^- not only decreases the H_2O_2

conversion (in the presence of H_2) activity of the catalyst but also makes the process less hazardous. In the absence of Br^- in the reaction medium, the H_2 (present in the system) and O_2 (produced from the decomposition of H_2O_2) form a gas mixture in the explosive range (4-94 % H_2 in O_2) and the catalyst, particularly in dry state, on the reactor wall initiates an explosive H_2 oxidation, as noted by us.

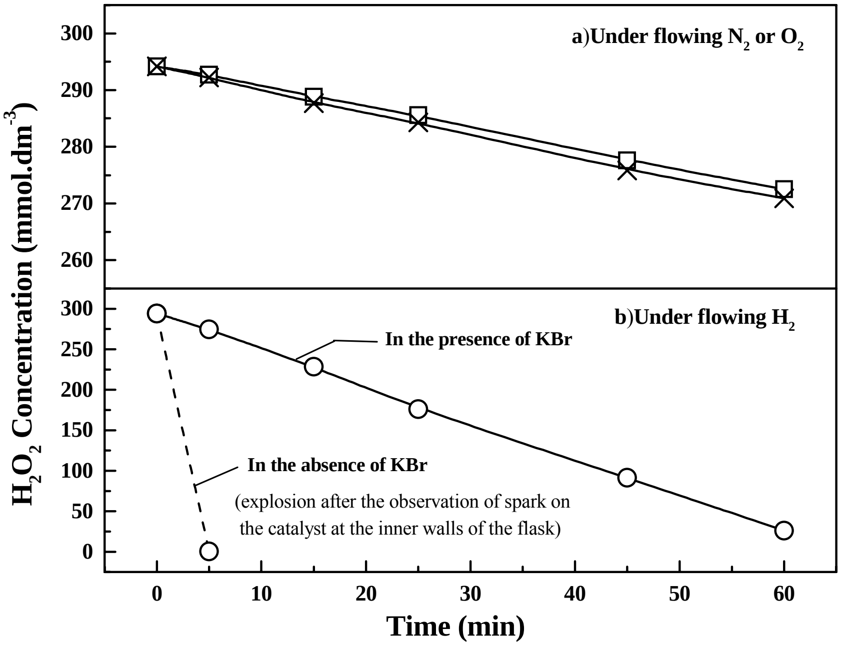


Figure 5.10 Conversion of H_2O_2 in aqueous acidic (0.03 M H_3PO_4) reaction medium containing KBr (concentration = 0.94 $mmol.dm^{-3}$) over the reduced Pd/Al_2O_3 catalyst at 25 ºC under different gases [H_2 (o), O_2 (□) or N_2 (×)] flowing through the reaction medium [other reaction conditions: amount of catalyst = 0.2 g, volume of reaction medium = 150 cm^3, amount of H_2O_2 = 44 mmol, H_2 flow rate = 30 $cm^3.min^{-1}$].

5.3.2.2 Influence of Chloride Concentration in Reaction Medium on H_2O_2 Conversion Under Flowing H_2

Results showing the influence of Cl^- concentration in an aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 conversion under flowing H_2 are presented in Figure 5.11. The results reveal that, at the lower Cl^- concentrations, the H_2O_2 is converted mostly by its decomposition. However, at the higher Cl^- concentrations, only the H_2O_2

hydrogenation is responsible for the H_2O_2 conversion over the catalyst. Both the H_2O_2 decomposition and H_2O_2 hydrogenation activities of the catalyst are reduced with increasing the Cl^- concentration in the reaction medium.

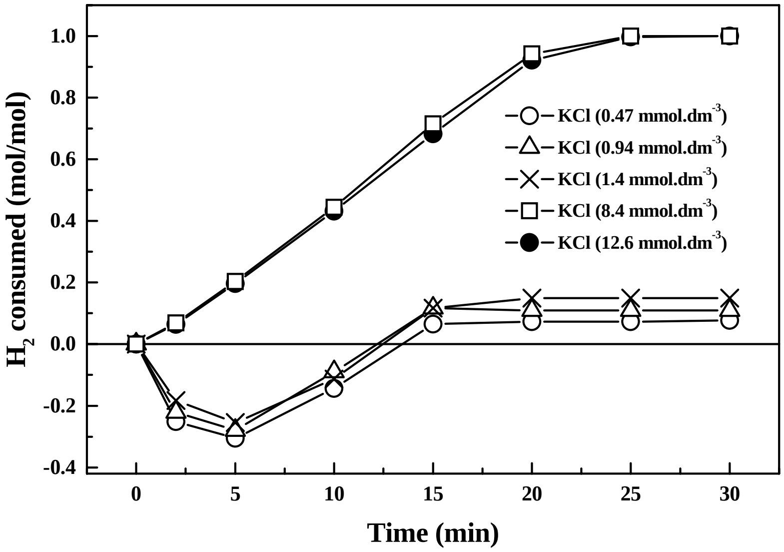


Figure 5.11 Effect of KCl concentration in acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 conversion over the reduced Pd/Al_2O_3 catalyst at 25 ºC under H_2 flowing through the reaction medium [other reaction conditions: amount of catalyst = 0.2 g, volume of reaction medium = 150 cm^3, amount of H_2O_2 = 3 ml of 30 w/v%, H_2 flow rate = 30 cm^3.min^{-1}].

5.3.2.3 Influence of Bromide Concentration in Reaction Medium on H_2O_2 Conversion Under Flowing H_2

Results showing the influence of the Br^- concentration in the acidic reaction medium on the conversion of H_2O_2 under flowing H_2 over the catalyst are presented in Figure 5.12. In the presence of Br^- anions (0.47-6.7 mmol.dm^{-3}), the H_2O_2 is converted only by its hydrogenation. The rate of H_2O_2 hydrogenation over the catalyst is decreased with increasing bromide concentration in the reaction medium. It is found that at the Cl^- concentration of 0.94 mmol.dm^{-3}, the H_2O_2 conversion (under flowing H_2) over the catalyst takes place mostly by its decomposition (Figure 5.11) whereas, at the same Br^- concentration, the hydrogenation of H_2O_2 is responsible for its conversion over the catalyst. This indicates that the Br^- ions cause more reduction of the catalytic for H_2O_2 destruction as compared to that observed in case of the Cl^- ions.

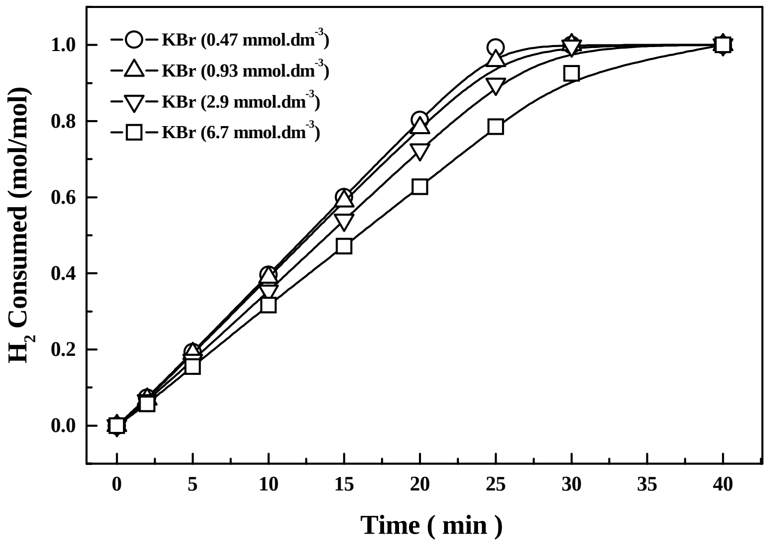


Figure 5.12 Effect of KBr concentration in acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 conversion over the reduced Pd/Al_2O_3 catalyst at 25 ºC under H_2 flowing through the reaction medium [other reaction conditions: amount of catalyst = 0.2 g, volume of reaction medium = 150 cm^3, amount of H_2O_2 = 3 ml of 30 w/v %, H_2 flow rate = 30 $cm^3.min^{-1}$].

5.4 GENERAL REMARKS

In the direct oxidation of H_2 to H_2O_2 over the Pd catalyst, along with the H_2O_2 formation, water is formed in the process in both the parallel (reaction II) and consecutive (reactions III and IV) reactions (Figure 5.13). Since, H_2O_2 is an intermediate product formed in the consecutive reactions and also thermodynamically much less stable than H_2O, the selectivity for H_2O_2 in the process depends on the H_2O_2 decomposition and hydrogenation activities of the catalyst and also on the H_2 combustion (direct H_2-to-water oxidation) activity of the catalyst, as per the reaction scheme.

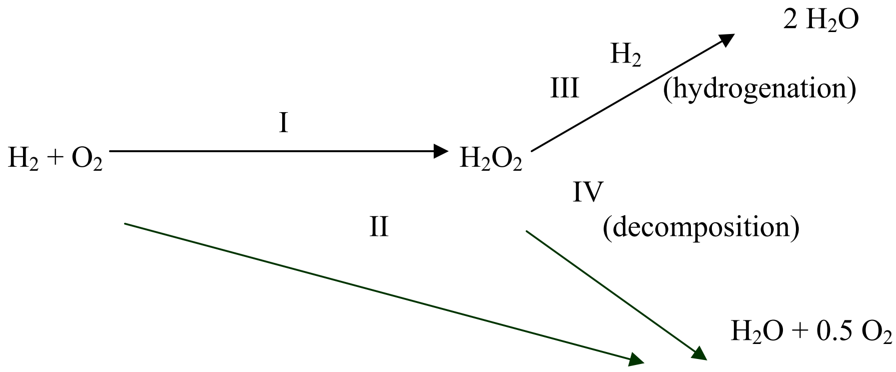


Figure 5.13 Reaction scheme for the direct oxidation of H_2 to H_2O_2 over Pd catalyst.

The parallel oxidation of H_2 to H_2O (reaction I) alone cannot be studied because of the formation of water also by the consecutive reactions. Also, the H_2O_2 decomposition or hydrogenation reaction can be studied at the identical temperature and also using the same reaction medium but not at the same feed gas composition used in the H_2-to-H_2O_2 oxidation. Nevertheless, the results obtained from the H_2O_2 decomposition and/or hydrogenation reactions are useful for developing a better catalyst for the process. The above results reveal that the catalyst showing lower H_2O_2 decomposition and/or hydrogenation activity show better performance in the H_2-to-H_2O_2 oxidation.

5.5 CONCLUSIONS

From the present studies on the direct oxidation of H_2 to H_2O_2 and decomposition/hydrogenation of H_2O_2 over the Pd/Al_2O_3 catalyst, the following important conclusions have been drawn:

1. The selective H_2O_2 and non-selective water forming reactions takes place simultaneously in the reaction between H_2 and O_2 over the catalyst. The H_2O_2 formed in the reaction undergoes decomposition and/or hydrogenation of to water via consecutive reactions. Hence, to obtain good selectivity for H_2O_2 in the process both the non-selective H_2O forming reaction and decomposition/hydrogenation of H_2O_2 over the catalyst should be minimized simultaneously.
2. The presence of acid in the aqueous reaction medium reduces the H_2O_2 decomposition activity of the catalyst. The presence of halide-containing acid in the reaction medium results both the acidic type (reducing H_2O_2 decomposition) and halide type (selective formation of H_2O_2) promotions in the H_2-to-H_2O_2 oxidation.
3. The reduced Pd catalyst is more active both for the H_2 conversion and H_2O_2 decomposition reactions but less selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation as compared to the corresponding oxidized Pd catalyst.
4. The presence of Br^- in the acidic reaction medium increases the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation by drastically reducing both the H_2O_2 decomposition and hydrogenation activities of the catalyst. The improved H_2O_2 selectivity in the presence of Br^- in the reaction medium is attributed to the poisoning and/or modification of the active sites in the catalyst responsible for dissociative chemisoption of O_2 and/or H_2O_2 decomposition.

5. The associated cations of the halide anions play a very little or no role for influencing the H_2O_2 decomposition and/or the promotion of H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. The different bromide-containing compounds give approximately the same H_2O_2 yield in the H_2-to-H_2O_2 oxidation.
6. The presence of F^- in the reaction medium increases the H_2O_2 decomposition activity of the catalyst.
7. The presence of I^- in the reaction medium causes a large deactivation of the catalyst for both the H_2 oxidation and H_2O_2 decomposition reactions.
8. An optimum concentration of halide (Br^- or Cl^-) in the reaction medium is essential for achieving the highest H_2O_2 yield in the H_2-to-H_2O_2 oxidation. The H_2O_2 yield in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition activity of the catalyst largely depend upon the halide concentration in the reaction medium. The H_2O_2 decomposition and hydrogenation activities of the catalyst decrease with increasing the halide concentration (except F^-) in the reaction medium.
9. The rate of H_2O_2 conversion in the presence of H_2 is much higher as compared to that in the absence of H_2 mainly because of the hydrogenation of H_2O_2 over the catalyst to a very large extent. In the absence of any halide anions or in the presence of F^- or Cl^- (at the lower concentrations) in the reaction medium, the H_2O_2 is destroyed over the catalyst mostly by its decomposition whereas in the presence of Br^- or Cl^- (at the higher concentrations) the H_2O_2 hydrogenation is only responsible for the destruction of H_2O_2 over the catalyst.

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CHAPTER-6

INFLUENCE OF HALIDE PROMOTER PRESENT IN REACTION MEDIUM ON THE H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION OVER OXIDIZED AND REDUCED Pd/Ga_2O_3, Pd/ZrO_2 AND Pd/CeO_2 CATALYSTS

CHAPTER-6

INFLUENCE OF HALIDE PROMOTER PRESENT IN REACTION MEDIUM ON THE H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION OVER OXIDIZED AND REDUCED Pd/Ga_2O_3, Pd/ZrO_2 AND Pd/CeO_2 CATALYSTS

6.1 GENERAL INTRODUCTION-BACKGROUND AND OBJECTIVES

The liquid phase direct oxidation of H_2 to H_2O_2 is generally carried out over the supported Pd catalysts and the most popular supports are alumina, silica and carbon [1]. Titanium dioxide is also mentioned in a number of patents as being a suitable support for Pd for the synthesis of H_2O_2 from H_2 and O_2 [2-5]. Solid super acid such as tungsten oxide on zirconia is also reported as a support for Pd in the synthesis of H_2O_2 [6]. Ga_2O_3, ZrO_2 and CeO_2 supported Pd catalysts have also been employed for the synthesis of H_2O_2 in the direct oxidation of H_2 [7-8]. Inspite of the large efforts made so far, the direct oxidation process is far away from its commercialization. This State-of art of the direct process is mainly because of two reasons - first, a highly hazardous nature of the process due to the presence of H_2 and O_2 gas mixture in the flammable/explosion range, and second, a poor H_2O_2 selectivity because of the simultaneously occurring undesirable H_2-to-water oxidation and consecutive H_2O_2 decomposition and hydrogenation reactions ($H_2 + O_2 \rightarrow H_2O_2$, $H_2O_2 \rightarrow H_2O + 0.5\ O_2$ and $H_2O_2 + H_2 \rightarrow 2H_2O$). The H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation over Pd catalyst can be improved by using halides as catalyst promoter in the reaction [9-15].

The present work was undertaken with the objective of investigating the influence of different halides (viz. F^-, Cl^-, Br^- and I^-) added to an aqueous acidic reaction medium on the performance of oxidized and reduced Pd/Ga_2O_3, Pd/ZrO_2 and Pd/CeO_2 catalysts [which showed promising results in the earlier work in our group (7,8)] in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions. Influence of the concentration of Br^- ions in the acidic reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition over the reduced Pd catalysts has also been investigated.

6.2 H_2-TO-H_2O_2 OXIDATION AND DECOMPOSITION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/Ga_2O_3 CATALYSTS

6.2.1 Influence of Different Halides Present in Reaction Medium

Results showing the influence of different halide anions (halides are added to the reaction medium as potassium halides) present in an acidic (0.03 M H_3PO_4) reaction medium on the performance of the oxidized and reduced Pd/Ga_2O_3 catalysts in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 6.1. From the results the following important observations can be made:

- The presence of Cl^- or Br^- ions in the reaction medium increases drastically the selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation over both the oxidized and reduced catalysts. However, H_2 conversion activity of both the oxidized and reduced catalysts is decreased due to the presence of Cl^- or Br^- ions in the reaction medium. The H_2O_2 decomposition activity of both the oxidized and reduced catalysts is also reduced drastically due to the presence of Cl^- or Br^- ions in the reaction medium. Br^- is found more effective than Cl^- (at the same halide concentration) for the selective formation of H_2O_2 in the H_2-to-H_2O_2 oxidation over both the oxidized and reduced catalysts.
- The presence of F^- ions in the reaction medium increases the H_2O_2 yield/ selectivity in the H_2-to-H_2O_2 oxidation over the oxidized catalyst but decreases over the reduced catalyst.
- The addition of I^- ions to the reaction medium causes a drastic reduction in both the H_2 conversion and H_2O_2 decomposition over the oxidized and reduced catalysts, indicating a strong poisoning of the catalyst due to the presence of I^- ions in the reaction medium.

The improved H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation due to the interaction of catalyst with the Cl^- or Br^- ions in the reaction medium is mainly attributed to the partial inhibition to the non-selective H_2-to-water oxidation and also a large decrease in the H_2O_2 decomposition (Figure 6.1) over the catalyst. The H_2O_2 decomposition activity of the catalyst largely depends upon the Pd oxidation state in the catalyst and also the nature of halide ions added to the reaction medium. The oxidized (i.e. PdO containing) catalyst shows much lower H_2O_2 decomposition activity than the reduced (Pd^o containing) catalyst and the addition of Cl^-, Br^- or I^- ions in the reaction medium causes a further large decrease in the H_2O_2 decomposition activity of both the oxidized and reduced catalysts. However, the H_2O_2 decomposition activity of the reduced catalyst is increased markedly due to presence of F^-

ions in the reaction medium. The modification of the catalysts through a change in the electronic environment on their surface due to the interaction of catalyst with the halide anions in the reaction medium is mostly responsible for the observed beneficial effects on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the catalysts due to the presence of halide anions in the reaction medium.

Table 6.1 Results of the direct oxidation of H_2 to H_2O_2 over the oxidized and reduced Pd (2.5%)/Ga_2O_3 catalysts in acidic (0.03 M H_3PO_4) reaction medium containing different potassium halides (concentration = 0.94 mmol.dm^{-3}) [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, concentration of H_2 in O_2 = 4.6 mol%, pressure = 0.95 atm, temperature = 25 ºC and reaction period = 3h].

Potassium halide in reaction medium	Form of catalyst (oxidized/ reduced)[a]	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	Oxidized	24.6	9.9	40.3	4.7
None	Reduced	50.0	5.4	10.8	42.2
KF	Oxidized	26.4	10.7	40.5	4.3
KF	Reduced	50.7	2.7	5.3	75.7
KCl	Oxidized	27.5	14.3	51.9	3.2
KCl	Reduced	47.8	11.3	23.4	5.2
KBr	Oxidized	14.7	12.0	78.9	1.5
KBr	Reduced	39.8	22.8	56.9	2.9
KI	Oxidized	<1.0	0.0	0.0	0.9
KI	Reduced	2.1	0.2	9.5	1.5

X, Y and S are conversion, yield and selectivity, respectively. [a] *Oxidized (as PdO) and reduced (as Pd°) forms of the catalyst were confirmed by XRD.* [b] *k_d = Pseudo first order H_2O_2 decomposition rate constant.*

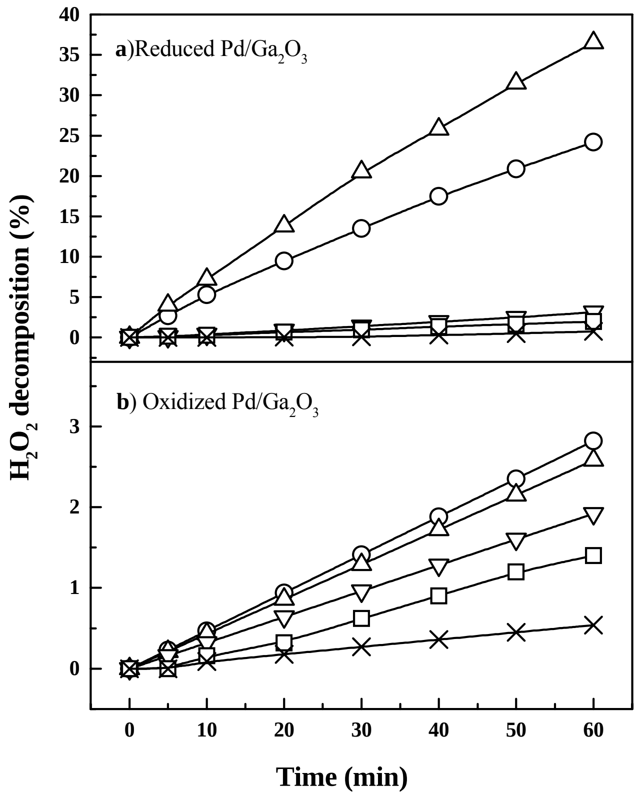

Figure 6.1 Effect of different potassium halides present in acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 decomposition (at 25 ºC) over the (a) reduced and (b) oxidized Pd/Ga_2O_3 catalysts [Potassium halide in the reaction medium: none (o), KF (Δ), KCl (∇), KBr (□), KI (×)].

6.2.2 Influence of Br^- Concentration in Reaction Medium on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions Over Reduced Pd/Ga_2O_3 Catalyst

Results showing the influence of Br^- concentration in an aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the reduced Pd/Ga_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Figure 6.2. The H_2O_2 yield in the H_2-to-H_2O_2 oxidation is sharply increased (particularly at the lower Br^- concentrations) and then passed through a maximum with increasing the Br^- concentration in the reaction medium. However, the H_2 conversion over the catalyst is decreased continuously with increasing the Br^- concentration in the reaction medium. The H_2O_2 decomposition activity of the catalyst is also decreased continuously with increasing the Br^- concentration in the reaction medium. The observed lower H_2 conversion and H_2O_2 decomposition activities of the catalyst at the higher Br^- concentrations is probably due to the blockage of more and more active sites in the catalyst responsible for H_2 dissociation and /or H_2O_2 decomposition.

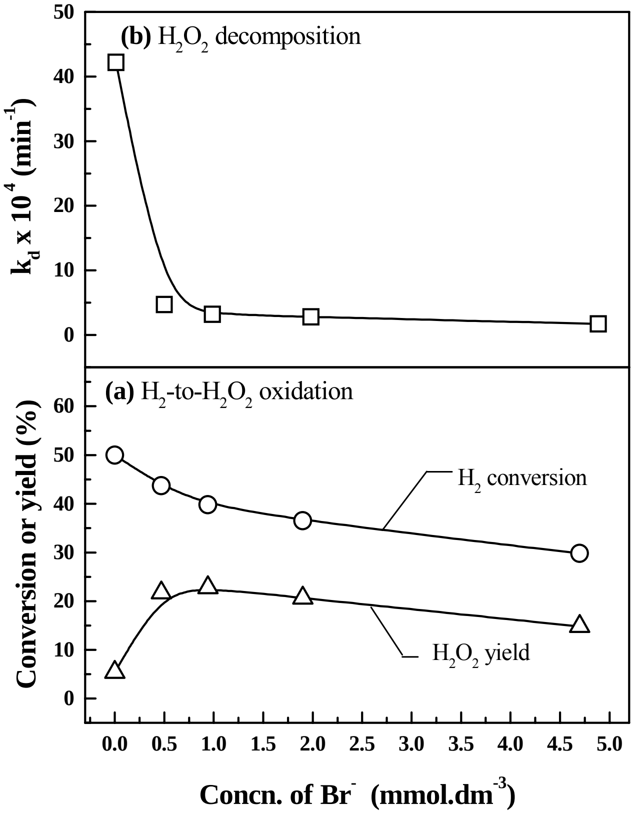

Figure 6.2 Effect of the concentration of Br^- in acidic (0.03 M H_3PO_4) reaction medium on the performance of the reduced Pd/Ga_2O_3 catalyst in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 25 ºC).

6.2.3 Effect of Different Reaction Mediums on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions over Reduced Pd/Ga_2O_3 Catalyst

Results showing the influence of different reaction mediums containing Br^- ions (1.87 $mmol.dm^{-3}$) on the performance of the reduced Pd/Ga_2O_3 catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 6.2. The H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation is strongly dependent upon the presence of protons (H^+ ions) in the reaction medium. In the presence of Br^- ions in the aqueous medium, there is no formation of H_2O_2 in the H_2-to-H_2O_2 oxidation due to the very high H_2O_2 decomposition activity of the catalyst, indicating the presence protons (i.e. H^+ ions) in the reaction medium is must for obtaining H_2O_2. The observed low H_2 conversion over the catalyst in aqueous HCl medium is due to the high Cl^- concentration.

Table 6.2 Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition over the reduced Pd/Ga_2O_3 catalyst in different reaction mediums containing Br^- (1.87 $mmol.dm^{-3}$) [H_2-to-H_2O_2 oxidation reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, concentration of H_2 in O_2 = 4.6 mol %, pressure = 0.95 atm, temperature = 25 ºC and reaction period = 3h].

Reaction medium	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity
	X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
Distilled water	31.3	0.0	0.0	143.9
0.1 N H_3PO_4	34.8	22.7	65.8	3.4
0.1 N H_2SO_4	32.3	17.1	53.3	3.2
0.1 N HCl	25.4	17.5	68.9	2.1

6.2.4 Conversion of H_2O_2 in Presence of H_2 over Reduced Pd/Ga_2O_3 Catalyst

A comparison of H_2O_2 conversion over the reduced Pd/Ga_2O_3 catalyst in the presence and absence of H_2 (Figure 6.3) reveals that H_2O_2 is destroyed more rapidly in the presence of H_2 than in absence of H_2 (i.e. in the presence of air). The observed much higher rate of H_2O_2 conversion in the presence of H_2 as compared to the H_2O_2 decomposition in the presence of air is because of the hydrogenation of H_2O_2 over the catalyst to a very large extent. Interestingly, the H_2O_2 hydrogenation activity of the catalyst, like the H_2O_2 decomposition activity is also reduced due to the presence of Cl^- or Br^- ions in the reaction medium. The decrease in both H_2O_2 decomposition and hydrogenation activities of the catalyst due to presence of Cl^- or Br^- ions indicates that Cl^- or Br^- ions poison some of the active sites in the catalyst responsible for H_2 dissociation and H_2O_2 decomposition/hydrogenation.

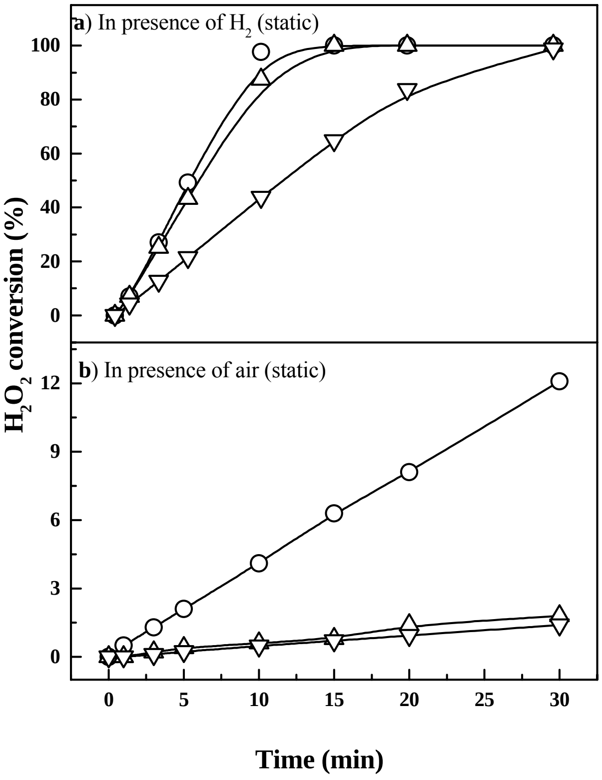

Figure 6.3 Conversion of H_2O_2 (at 25 ºC) in presence of (a) H_2 and (b) air over the reduced Pd/Ga_2O_3 catalyst in acidic (0.03 M H_3PO_4) reaction medium with or without containing potassium halides (0.94 $mmol.dm^{-3}$) [Potassium halide in reaction medium: none (o), KCl (Δ) and KBr (∇)].

6.3 H_2-TO-H_2O_2 OXIDATION AND DECOMPOSITION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/ZrO_2 CATALYSTS

6.3.1 Influence of Potassium Halides Present in Reaction Medium

Results showing the influence of different potassium halides added to the aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced and oxidized Pd/ZrO_2 catalysts in are presented in Table 6.3. The H_2O_2 yield and/or selectivity in the H_2-to-H_2O_2 oxidation over both the oxidized and reduced catalysts are drastically increased because of the presence of Cl^- or Br^- ions in the reaction medium. However, the presence of F^- ions in the reaction medium caused a decrease in the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation over both the oxidized and reduced catalysts. The presence of I^- ions in the reaction medium drastically reduces the H_2 conversion over the catalyst. The presence of F^- ions in the reaction medium increased the H_2O_2 decomposition activity of the catalyst whereas I^- ions caused a large inhibition for the H_2O_2 decomposition over the catalyst (Figure 6.4).

Table 6.3 Results of the direct oxidation of H_2 to H_2O_2 over the oxidized and reduced Pd/ZrO_2 catalysts in aqueous acidic (0.03 M H_3PO_4) reaction medium containing different potassium halides (concentration = 0.94 $mmol.dm^{-3}$) [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, concentration of H_2 in O_2 = 4.6 mol%, pressure = 0.95 atm, temperature = 25 ºC and reaction period = 3h].

Potassium halide in reaction medium	Form of catalyst (oxidized/ reduced) [a]	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
None	Oxidized	31.9	12.1	37.7	2.3
None	Reduced	43.7	3.9	8.9	38.0
KF	Oxidized	34.1	8.9	26.1	4.5
KF	Reduced	45.9	3.5	7.6	43.8
KCl	Oxidized	28.9	12.8	44.3	1.8
KCl	Reduced	38.7	12.6	32.6	4.6
KBr	Oxidized	23.7	18.5	78.1	1.5
KBr	Reduced	36.2	23.8	65.7	2.7
KI	Oxidized	2.3	0.0	0.0	0.6
KI	Reduced	8.9	0.0	0.0	0.9

X, Y and S are conversion, yield and selectivity, respectively. [a] *Oxidized (as PdO) and reduced (as Pd°) forms of the catalyst were confirmed by XRD.*

The improved H_2O_2 selectivity due to presence of Cl^- or Br- ions in the reaction medium is attributed to the drastic reduction in the H_2O_2 decomposition and hydrogenation activities of the catalyst. The non-selective H_2-to-water oxidation may also be inhibited due to the interaction of Cl^- or Br- ions with the catalyst in the reaction medium.

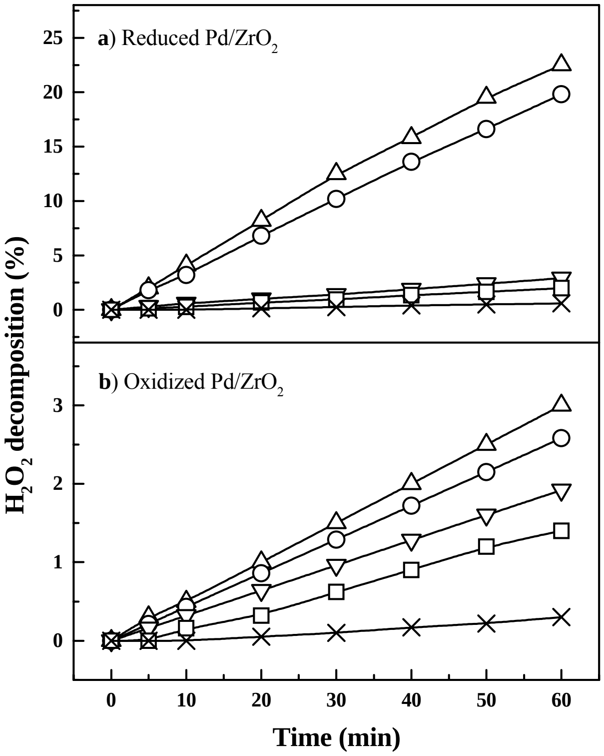

Figure 6.4 Effect of different potassium halides (concentration = 0.94 mmol.dm^{-3}) present in aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 decomposition (at 25 ºC) over the (a) reduced and (b) oxidized Pd/ZrO_2 catalysts [Potassium halide in reaction medium: none (o), KF (Δ), KCl (∇), KBr (□), KI (×)].

6.3.2 Influence of Br^- Concentration in Reaction Medium on the Performance of Reduced Pd/ZrO_2 Catalyst in H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

Results in Figure 6.5 show a strong influence of the Br^- concentration in reaction medium (0.03 M H_3PO_4) on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/ZrO_2 catalyst in. Both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation are increased and then passed through a maximum with increasing the Br^-

concentration in the reaction medium. Thus, an optimum concentration of Br$^-$ in the reaction medium is essential for achieving the maximum H_2O_2 yield in the reaction. The H_2 conversion and H_2O_2 decomposition activities of the catalyst are reduced with increasing the Br$^-$ concentration in the reaction medium.

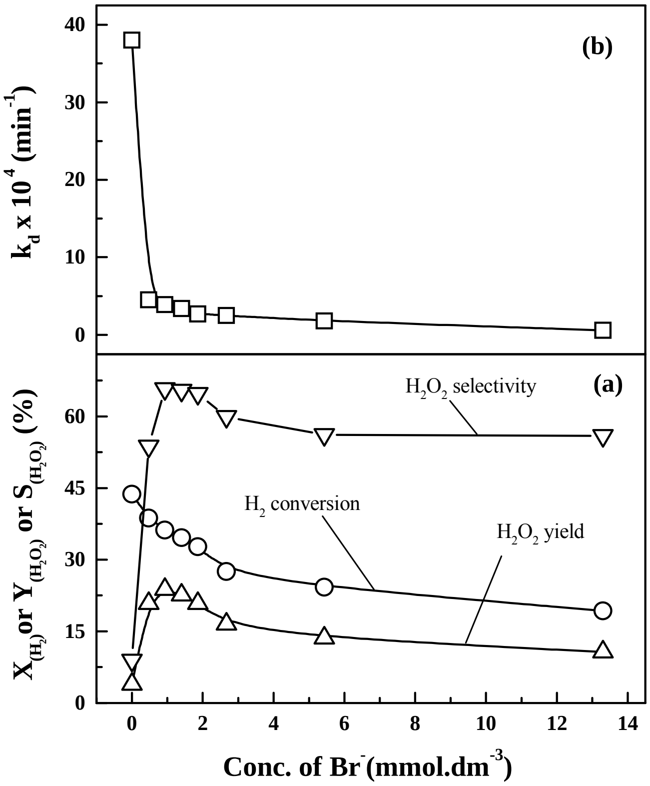

Figure 6.5 Effect of the concentration of Br$^-$ in aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of the reduced Pd/ZrO_2 catalyst in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 25 °C).

6.3.3 Influence of Concentration of Cl$^-$ in Reaction medium on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition over Reduced Pd/ZrO_2 Catalyst

Results showing influence of Cl$^-$ concentration in the acidic (0.03 M H_3PO_4) reaction medium on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/ZrO_2 catalyst are presented in Figure 6.6. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are decreased with increasing the Cl$^-$ concentration in the reaction medium. However, the H_2O_2 yield is increased and then passed through a maximum with increasing the Cl^- concentration. It may be noted that of an optimum concentration of Cl^- ions in the reaction medium like Br- ions, results the maximum formation of H_2O_2 in the H_2-to-H_2O_2 oxidation.

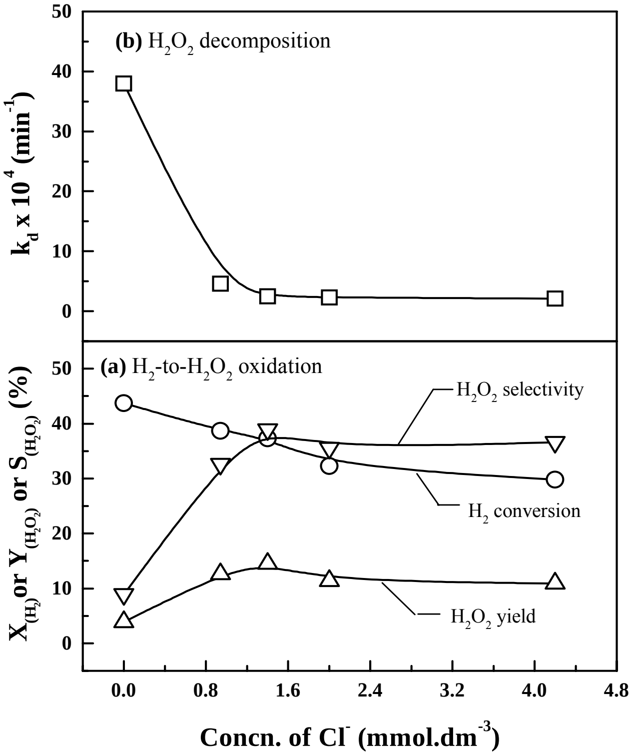

Figure 6.6 Effect of the concentration of Cl^- in acidic (0.03 M H_3PO_4) reaction medium on the (a) H_2-to-H_2O_2 oxidation (b) and H_2O_2 decomposition reactions over the reduced Pd/ZrO_2 catalyst (at 25 ºC).

6.4 H_2-TO-H_2O_2 OXIDATION AND DECOMPOSITION OF H_2O_2 OVER OXIDIZED AND REDUCED Pd/CeO_2 CATALYSTS

6.4.1 Influence of Different Halides Present in Reaction Medium

Results showing the influence of different halides (viz. F^-, Cl^-, Br^- and I^-) added to an aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the oxidized and reduced Pd/CeO_2 catalysts are presented Table 6.4. The performance of both the oxidized and reduced catalysts in the H_2-to-H_2O_2 oxidation are dramatically improved due to the presence of Cl^- or Br^- ions in the reaction medium. However, the presence of F^- ions in the reaction medium decreased the H_2O_2 selectivity for both the oxidized and reduced catalysts. The presence of I^- ions in the reaction medium caused a large deactivation for both the H_2 conversion and H_2O_2 decomposition reactions over the catalyst due to poisoning of the catalytic active sites.

Table 6.4 Results of the direct oxidation of H_2 to H_2O_2 over the oxidized and reduced Pd (2.5%)/CeO_2 catalysts in an aqueous acidic (0.03 M H_3PO_4) reaction medium containing different potassium halides (concentration = 0.94 mmol.dm^{-3}) [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, concentration of H_2 in O_2 = 4.6 mol%, pressure = 0.95 atm, temperature = 25 ºC and reaction period = 3h].

Potassium halide in reaction medium	Form of catalyst (oxidized/reduced) [a]	H_2- to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
None	Oxidized	23.8	8.9	37.4	5.2
None	Reduced	51.8	6.9	13.6	40.3
KF	Oxidized	37.3	8.5	23.3	6.8
KF	Reduced	56.5	3.1	5.5	52.8
KCl	Oxidized	30.1	12.1	40.1	3.4
KCl	Reduced	50.7	12.8	25.3	13.2
KBr	Oxidized	24.1	16.9	70.7	3.2
KBr	Reduced	37.3	21.5	57.8	3.7
KI	Oxidized	2.3	0.0	0.0	1.0
KI	Reduced	7.1	0.0	0.0	2.7

X, Y and S are conversion, yield and selectivity, respectively. [a] *Oxidized (as PdO) and reduced (as Pd°) forms of the catalyst were confirmed by XRD.*

The improved H_2O_2 selectivity of both the oxidized and reduced catalyst in the presence of Cl^- or Br- ions is attributed to the large decrease in the H_2O_2 decomposition reaction over the catalysts. However, H_2 conversion activity of both the oxidized and reduced catalyst is decreased due to the presence of Cl^- or Br^- in the reaction medium. The H_2 conversion and H_2O_2 decomposition activities of both the oxidized and reduced Pd/CeO_2 catalysts are however, increased due to the presence of F^- ions in the reaction medium. This may be due to the activation of some catalytic sites (adsorption of electronegative species make the Pd surface more electron deficient, facilitating the adsorption of hydrogen). However, the interaction of the other halide anions with the catalyst decreased both the H_2 conversion and H_2O_2 decomposition activities of the catalyst, indicating these halides block and/or poison some of the active sites in the catalyst responsible for H_2 dissociation and H_2O_2 decomposition.

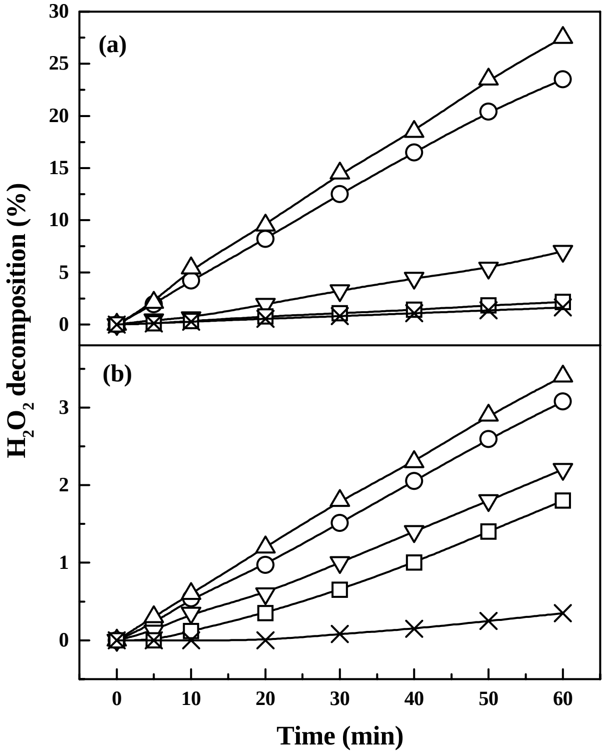

Figure 6.7 Influence of the different potassium halides (0.94 $mmol.dm^{-3}$) present in aqueous acidic (0.03 M H_3PO_4) reaction medium on the H_2O_2 decomposition (at 25 ºC) over the (a) reduced and (b) oxidized Pd/CeO_2 catalysts [Potassium halide in reaction medium: None (o), KF (Δ), KCl (∇), KBr (□), KI (×)]

It may be noted that, Br^- is especially effective promoter in the H_2-to-H_2O_2 oxidation over the metal oxide (viz. Al_2O_3, Ga_2O_3, ZrO_2, CeO_2 etc.) supported Pd catalysts. The ability of the Br^- ions for promoting the H_2O_2 selectivity in the direct oxidation of H_2 to H_2O_2 is mostly attributed to the inhibition to the dissociative chemisorption of O_2 on the catalyst thereby reducing the non-selective/undesirable direct H_2-to-water oxidation and also to the reduction in the H_2O_2 decomposition over the catalyst.

6.4.2 Effect of Pd loading in Reduced Pd/CeO_2 Catalyst on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

Results showing the influence of Pd loadings in the reduced Pd/CeO_2 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium in the absence of any halide are presented in Figure 6.8.

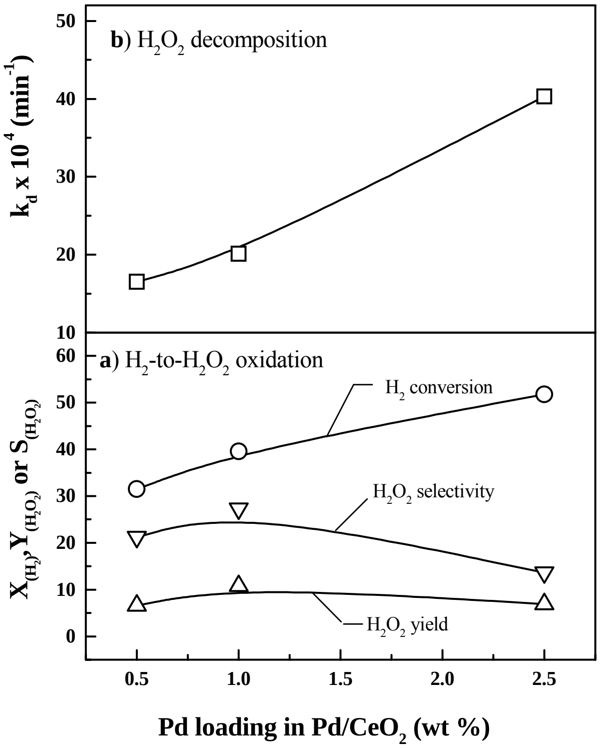

Figure 6.8 Effect of Pd loading in the reduced Pd/CeO_2 catalyst on its performance in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 ºC).

Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are increased with increasing the Pd loading in the catalyst but the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation passed through a maximum. The increased Pd loading in the catalyst caused an increase in the H_2O_2 decomposition activity of the catalyst and consequently the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is decreased.

Results in Figure 6.9 show influence of the Pd loading in the Pd°/CeO_2 catalyst on its activity/selectivity in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reaction in an aqueous acidic (0.03 M H_3PO_4) reaction medium containing Br^- ions (0.94 $mmol.dm^{-3}$). In this case also both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are increased with increasing Pd loading in the catalyst. However, the H_2O_2 selectivity is increased and then passed through a maximum with increasing Pd loading in the catalyst. The H_2O_2 yield is increased with increasing the Pd loading from 0.5 to 1.0 wt% but remained almost constant when the Pd loading is increased from 1 to 2.5 wt%.

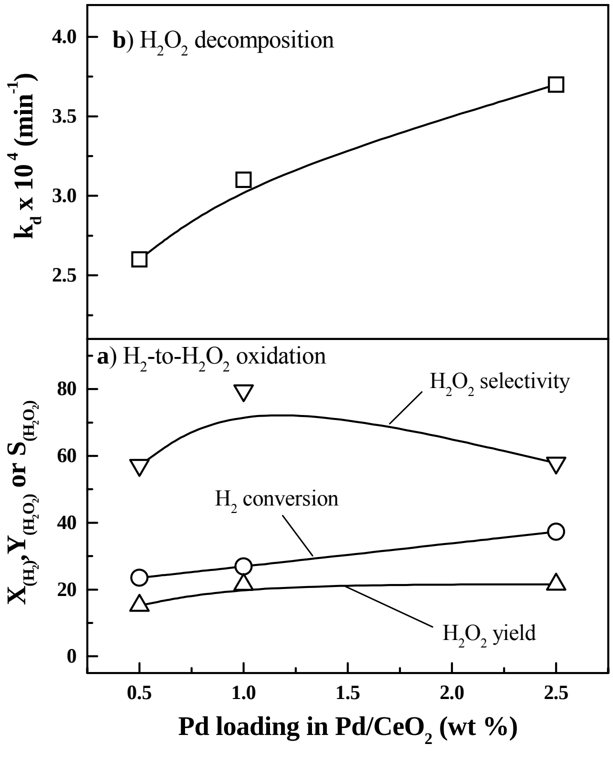

Figure 6.9 Effect of Pd loading in the reduced Pd/CeO_2 catalyst on its performance in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium containing Br^- ions (0.94 $mmol.dm^{-3}$) (at 25 °C).

The observed influence of the Pd loading may be attributed to the increase in the Pd surface and/or particle size. Further detailed investigation is necessary for understanding the Pd loading effect.

6.4.3 Influence of Concentration of Br^- in Reaction Medium on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions over Reduced Pd (1%)/CeO_2 Catalyst

Results showing the influence of concentration of Br^- ions in acidic reaction medium (0.03 M H_3PO_4) on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced Pd/CeO_2 catalyst are presented in Figure 6.10.

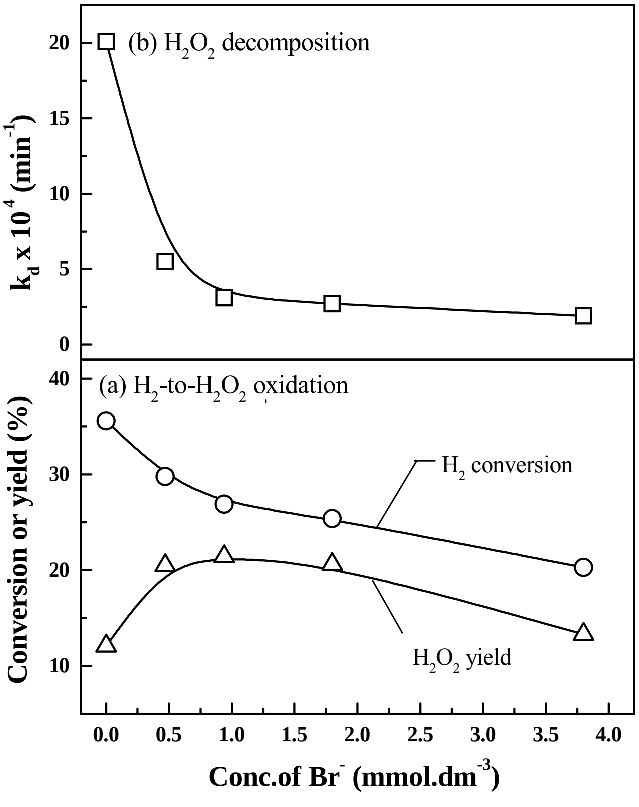

Figure 6.10 Effect of Br^- concentration in acidic (0.03 M H_3PO_4) reaction medium on the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions over the reduced Pd (1%)/CeO_2 catalyst (at 25 ºC).

Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are reduced with increasing Br^- concentration in the reaction medium. However, the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is increased and then passed through a maximum with increasing the Br^- concentration in the reaction medium. Thus, an optimum concentration of Br^- ions is essential for achieving maximum H_2O_2 yield in the H_2-to-H_2O_2 oxidation over the catalyst.

6.5 CONCLUSIONS

The following important conclusions have been drawn from this investigation:

1. In absence of any halide ions or in the presence of F^- ions in the reaction medium, the reduced Pd catalysts show very little or no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation due to their very high H_2O_2 decomposition activity. However, the corresponding oxidized (PdO containing) catalysts are selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation, even in the absence of any halide.
2. The H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation are drastically increased over both the oxidized and reduced Pd-catalysts due to presence of Br^- ions in the acidic reaction medium; the increase is drastic for the reduced catalysts. Cl^- also promotes the H_2O_2 formation in the H_2-to-H_2O_2 but it is less effective than Br^-. An optimum concentration of Br^- (or Cl^-) in the acidic reaction medium is essential for obtaining the maximum H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation.
3. Both the H_2 conversion and H_2O_2 decomposition activities of the Pd-catalysts are reduced due to the interaction of halide anions (except for F^-) with the Pd catalyst.
4. The presence of I^- ions in the reaction medium causes a large deactivation for both the H_2 conversion and H_2O_2 decomposition reactions over the catalyst.
5. With increasing the Pd loading in the catalyst, both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are increased but the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation in the presence or absence ob Br^- anions in the acidic reaction medium is passed through a maximum.
6. The H_2O_2 hydrogenation activity of the Pd/Ga_2O_3 catalyst is higher than its H_2O_2 decomposition activity. It is reduced markedly due to the addition of bromide anions in the acidic reaction medium.

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CHAPTER-7

INFLUENCE OF HALIDE PROMOTER IN SUPPORTED Pd CATALYSTS ON THEIR ACTIVITY/SELECTIVITY IN THE DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION/HYDROGENATION OF H_2O_2

CHAPTER-7

INFLUENCE OF HALIDE PROMOTER IN SUPPORTED Pd CATALYSTS ON THEIR ACTIVITY/SELECTIVITY IN THE DIRECT OXIDATION OF H_2 TO H_2O_2 AND DECOMPOSITION / HYDROGENATION OF H_2O_2

7.1 GENERAL INTRODUCTION- BACKGROUND AND OBJECTIVES

The direct oxidation of H_2 to H_2O_2 over different supported Pd catalysts in acidic reaction medium employing halide promoters are reported in a number of patents [1-6] and literatures [7-10]. However, the acidic reaction medium containing halide ions has a detrimental effect on the catalyst and results a complex aqueous reaction mixture from which the isolation of H_2O_2 and the catalyst recovery becomes a difficult task. This detrimental effect (i.e. presence of halide ions in the acidic reaction medium) has been eliminated by incorporating halide ions (which promote the Pt-group metal) as an insoluble form (using organo silane precursor) into the solid [11]. Halogenated material (viz. halogenated resin) has also been employed as a support for Pd in the H_2-to-H_2O_2 oxidation [12]. Halogenated metal oxide (viz. fluorinated γ-Al_2O_3, chlorinated γ-Al_2O_3 and fluorinated ZrO_2 etc.) [13] and halogenated zeolite (viz. fluorinated H-β, H-ZSM-5 etc.) [14] supported Pd catalysts have also been used in the direct oxidation of H_2 to H_2O_2. Recently, we have shown that incorporation of bromide ions in the supported Pd catalysts drastically increases the selectivity for H_2O_2 formation in the H_2-to-H_2O_2 oxidation [15].

The present study was undertaken with the objective of investigating the performance of different supported Pd catalysts (viz. Pd/Al_2O_3, Pd/Ga_2O_3, Pd/CeO_2, Pd/ZrO_2, Pd/SiO_2, Pd/Hβ, Pd/C) in the direct oxidation of H_2 to H_2O_2, after incorporating different halide ions (F^-, Cl^-, Br^- and I^-) into them. Influence of the different halides and their concentration in the catalysts and pretreatment of the halogenated Pd catalysts on their activity/selectivity in the H_2-to-H_2O_2 oxidation has been studied in details. Procedures for the incorporation of different halide anions in the supported reduced or oxidized Pd catalysts have been described earlier (Chapter 2). Influence of the above factors on the H_2O_2 decomposition and/or hydrogenation activity of the supported Pd catalysts has also been studied.

7.2 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/Al_2O_3 CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION AND HYDROGENATION REACTIONS

7.2.1 H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition over Pd or PdO Supported on Prehalogenated γ-Al_2O_3 Catalysts

7.2.1.1 Influence of Halide Promoter on H_2-to-H_2O_2 Oxidation

Results showing the performance of PdO and Pd^o (2.5 wt% Pd) catalysts supported on γ-Al_2O_3 and halogenated γ-Al_2O_3, in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.1. The results show a strong influence of the halide ions incorporated into the support and Pd oxidation state in the catalyst on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions.

Table 7.1 Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition in aqueous acidic (0.03 M H_3PO_4) reaction medium over Pd^o and PdO supported on γ–Al_2O_3 with or without its prehalogenation (halide loading = 5 wt% and Pd loading = 2.5 wt%) (at 27 ºC).

Halide deposited on γ–Al_2O_3	Form of Pd [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	PdO	24.7	8.6	34.9	5.6
None	Pd^o	49.8	0.25	0.5	35.8
F	PdO	13.5	8.6	63.5	2.4
F	Pd^o	63.5	0.0	0.0	193.9
Cl	PdO	21.3	5.4	25.5	1.8
Cl	Pd^o	63.9	1.6	2.5	61.4
Br	PdO	20.9	17.1	81.7	0.2
Br	Pd^o	31.5	19.4	61.8	6.5

X, Y and S = conversion, yield and selectivity, respectively. [a] XRD phase. [b] Pseudo first order H_2O_2 decomposition rate constant (at 27 ºC).

The halogenation of γ-Al_2O_3 support was done by impregnating the support with ammonium halide by the incipient impregnation technique, followed by drying and calcining the impregnated support. The reduced (i.e. Pd^o containing) catalyst (without any halide in the support) shows very high H_2 conversion activity but very little or no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. However, after the incorporation of Br^- ions into γ-Al_2O_3, the Pd^o/brominated γ-Al_2O_3 catalyst becomes highly selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The corresponding PdO/brominated γ-Al_2O_3 catalyst also shows very high H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. It may be noted that the PdO/fluorinated γ-Al_2O_3 and PdO/chlorinated γ-Al_2O_3 catalysts show good selectivity for H_2O_2 formation in the H_2-to-H_2O_2 oxidation but the corresponding reduced (Pd^o containing) catalysts are less selective for H_2O_2 formation, most probably because of their high H_2O_2 decomposition activity, indicating the importance of the Pd oxidation state in these catalysts. The incorporation of F^- or Cl^- anions in the γ-Al_2O_3 increases the H_2 conversion activity for the supported Pd^o catalysts but it causes a decrease in the H_2 conversion activity for the corresponding supported PdO catalyst. Both the halide ions (incorporated into the support) and Pd oxidation state in the catalyst strongly influence the activity/selectivity of the catalyst in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions.

The highly improved performance of Pd^o or PdO/brominated γ-Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation seems to be attributed to the drastic decrease in its H_2O_2 decomposition activity due to the bromination of the support. The non-selective direct H_2-to-water oxidation ($H_2 + 0.5\ O_2 \rightarrow H_2O$) may also be inhibited due to the Br^- ions in the catalyst.

7.2.1.2 Influence of Halide Promoter on H_2O_2 Decomposition

Results showing the influence of different halides present in the catalyst support on the H_2O_2 decomposition activity of the catalyst in acidic (0.03 M H_3PO_4) and aqueous mediums are presented in Figures 7.1 and 7.2, respectively. The results show that the H_2O_2 decomposition activity of the catalyst depends on the nature of the halide present in the catalyst support, Pd oxidation state in the catalyst and also on the presence of protons (H^+ ions) in the reaction medium. The PdO containing catalysts show much lower H_2O_2 decomposition activity than the corresponding metallic Pd (i.e. Pd^o) containing catalysts.

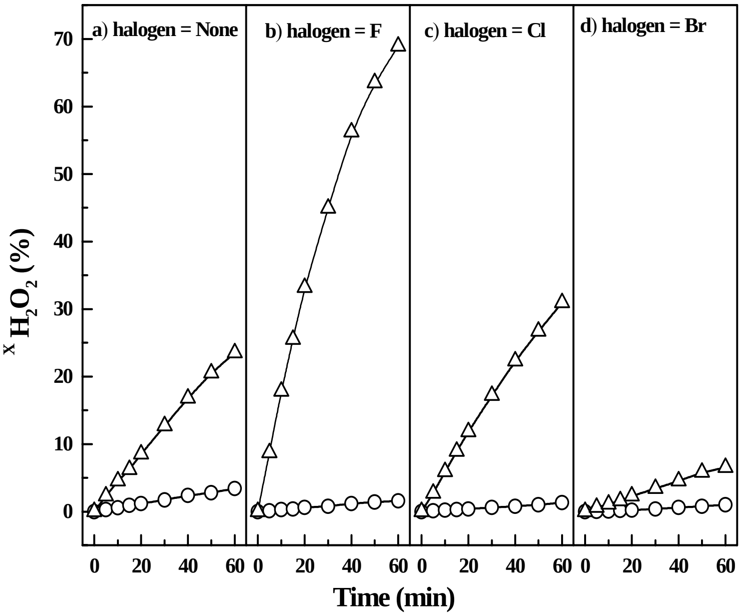

Figure 7.1 H_2O_2 decomposition in aqueous acidic (0.03 M H_3PO_4) medium over the reduced (Δ) and oxidized (O) Pd/γ-Al_2O_3 catalysts with or without containing halide in the support (loading of halide = 0 or 5 wt% and loading of Pd = 2.5 wt%).

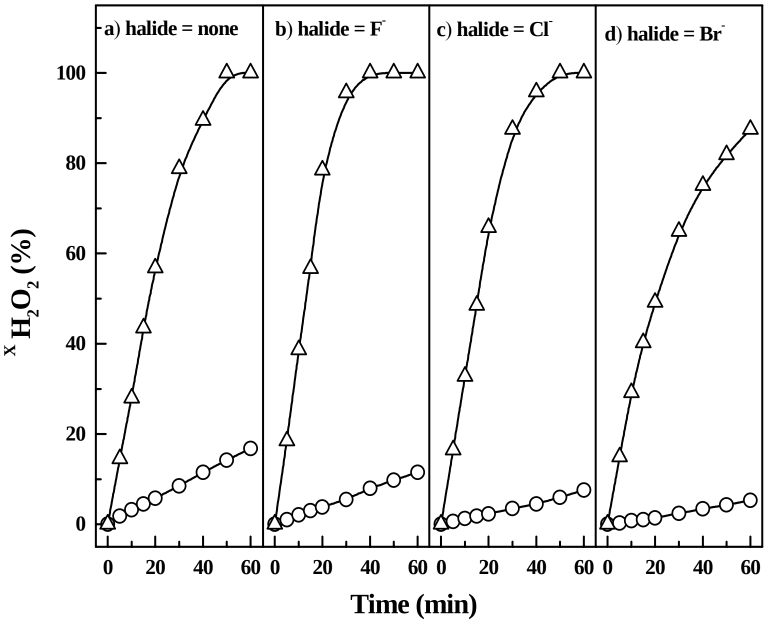

Figure 7.2 H_2O_2 decomposition in pure water over the Pd^o (Δ) or PdO (O) supported on γ-Al_2O_3 with or without containing halide in the support (loading of halide = 0 or 5 wt% and loading of Pd = 2.5 wt%).

The Pd^o/fluorinated γ-Al_2O_3 and Pd^o/chlorinated γ-Al_2O_3 catalysts show high activity for H_2O_2 decomposition in both the aqueous non-acidic (i.e. pure water) and acidic mediums. However, Pd^o/brominated γ-Al_2O_3 catalyst shows very low activity for H_2O_2 decomposition. The rate of H_2O_2 decomposition over the catalysts in the non-acidic aqueous (pure water) medium is much higher than in the aqueous acidic medium, revealing the importance of H^+ ions on the H_2O_2 decomposition over the catalyst. The Br^- ions present in the catalyst support reduce the H_2O_2 decomposition activity of the catalyst probably because of poisoning and/or modification of the active sites, responsible for H_2O_2 decomposition, in the catalyst.

7.2.2 H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition/Hydrogenation Reactions over Halogenated Pd/Al_2O_3 Catalyst Containing Pd in Oxidized or Reduced Form

The Pd (5 wt%)/Al_2O_3 used in this work a commercially available catalyst obtained from Lancaster, UK.The catalyst was halogenated by impregnating it with ammonium halide by incipient wetness technique followed by its calcination under N_2 or air.

7.2.2.1 Influence of Halide Promoter in the Catalyst on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

Results showing the influence of different halides (viz. F^-, Cl^-, Br^- and I^-) incorporated into the Pd/Al_2O_3 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium at room temperature (27 ºC) are presented in Table 7.2.

The results in Table 7.2 can be summarized as follows:

- After bromination of the Pd/Al_2O_3 catalyst, its selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation is drastically increased, whereas its activity for H_2O_2 decomposition is drastically reduced. The total H_2 conversion over the catalyst is also decreased but to a smaller extent.
- The incorporation of iodide in the Pd/Al_2O_3 catalyst results in a marked decrease both in its H_2 conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition activities.
- The incorporation of F^- or Cl^- ions in the catalyst caused an increase in the H_2 conversion but no improvement in the H_2O_2 yield and/or selectivity in the H_2-to-H_2O_2 oxidation. Because of the fluorination or chlorination, the H_2O_2 decomposition activity of the catalyst is increased markedly.

Table 7.2 Performance of the reduced Pd (5 wt%)/Al_2O_3 catalyst with or without its halogenation in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%. After the halogenation by ammonium halide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide incorporated in the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X_{H_2} (%)	$Y_{H_2O_2}$ (%)	$S_{H_2O_2}$ (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	Pd^o	54.7	0.5	0.9	43.8
F	Pd^o	62.3	0.0	0.0	398.8
Cl	Pd^o	63.4	0.0	0.0	368.2
Br	Pd^o	48.9	29.7	60.8	5.8
I	Pd^o	9.3	3.4	33.3	1.9

[a] *Confirmed by XRD*

The highly improved performance of the Pd/Al_2O_3 catalyst after its bromination is attributed to the inhibition caused by the Br^- ions (present in the catalyst) to the H_2O_2 decomposition (Figure 7.3) and/or hydrogenation (discussed later), responsible for the water formation in the consecutive reaction ($H_2 \rightarrow H_2O_2 \rightarrow H_2O$) and also to the parallel H_2-to-H_2O oxidation.

It may be noted that the presence of Br^- ions either in the catalyst support (Al_2O_3) (Table 7.1) or in the catalyst (Table 7.2) improves the performance of the catalyst in the H_2-to-H_2O_2 oxidation. It is interesting to note that the catalyst could be reused without a significant loss in its activity in the reaction. Also, no leaching of Pd from the catalyst during the reaction is observed, indicating long catalyst life. The presence of I^- ions in the catalyst causes a large deactivation for both the H_2 conversion and H_2O_2 decomposition over the catalyst. It may also be noted that the results obtained in the H_2-to-H_2O_2 oxidation with the halogenated reduced Pd/Al_2O_3 catalysts are consistent to the results obtained with the reduced Pd/Al_2O_3 catalyst in the presence of corresponding halides in the acidic reaction medium (Chapter 5).

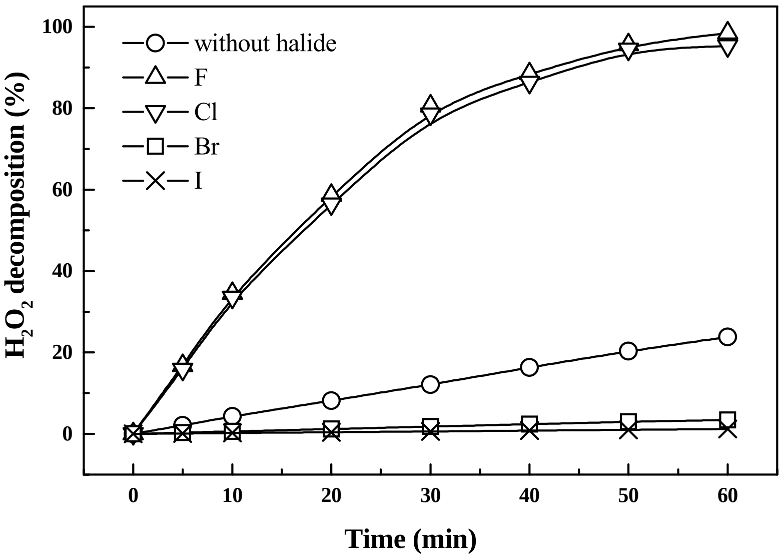

Figure 7.3 H_2O_2 decomposition (under static air) over the reduced Pd (5 wt%)/Al_2O_3 catalyst with or without containing halide in aqueous acidic (0.03 M H_3PO_4) reaction medium (concentration of halide in the halogenated catalyst = 1.0 wt%).

7.2.2.2 Influence of Halide Present in the Pd/Al_2O_3Catalyst on the Conversion of H_2O_2 in Presence of H_2

Results showing the influence of different halides incorporated into the Pd/Al_2O_3 catalyst on its activity for H_2O_2 conversion in aqueous acidic (0.03 M H_3PO_4) reaction medium in the presence H_2 are presented in Figure 7.4. A comparison of H_2O_2 conversion in presence of H_2 (Figure 7.4) to that in absence of H_2 (Figure 7.3) reveals that the rate of H_2O_2 conversion is much higher in the presence H_2 than that in the absence of H_2 (or in the presence of air).

This observed much higher rate of H_2O_2 destruction over the Pd catalyst with or without its halogenation in the presence of hydrogen, as compared to that for the H_2O_2 decomposition in the presence of air, is because of the hydrogenation of H_2O_2 over the catalysts to a very large extent. Interestingly, even in the presence of H_2, the H_2O_2 conversion is markedly decreased because of the presence of halide, particularly the, Br^- and I^- anions, in the catalyst. In the presence of I^- in the catalyst, the conversion of H_2O_2 was negligibly small (< 1.0 % in 0.5h). However, in the absence of any halide or in the presence other halides (F^-, Cl^-, Br^-), the H_2O_2 is completely destroyed over the catalyst in a short period by its decomposition and/or hydrogenation, depending upon the halide present in the catalyst (Figure 7.4 and Table 7.3).

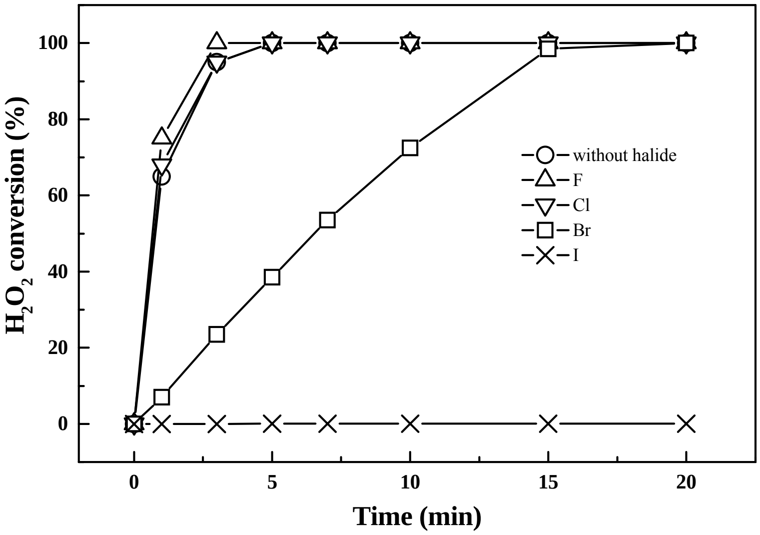

Figure 7.4 Influence of the presence of different halides (1 wt%) in thePd/Al_2O_3 catalyst on the H_2O_2 conversion in the reaction of H_2O_2 over the Pd/Al_2O_3 catalyst (at 27 ºC) in acidic reaction medium (0.03 M H_3PO_4) in the presence of hydrogen.

Table 7.3 Extent of hydrogenation and decomposition of H_2O_2 in the presence of H_2 (static) over the reduced Pd (5 wt%)/Al_2O_3 catalyst (with or without containing halide ions) in aqueous acidic (0.03 M H_3PO_4) reaction medium (concentration of halide in halogenated catalyst = 1.0 wt%). [reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.1 g, amount of H_2O_2 = 1 ml 30 w/v% and temperature = 27 ºC].

Halide incorporated in the catalyst	Conversion of H_2O_2 (%) [a]		Time for complete conversion (min)
	By decomposition	By hydrogenation	
None	≥ 65	≤ 35.0	3.0
F	≥ 75	≤ 25.0	2.0
Cl	≥ 70	≤ 30.0	2.5
Br	0.0	100.0	15.0

[a] *The H_2O_2 conversion by the individual H_2O_2 decomposition and hydrogenation reactions were evaluated from the amount of gas consumed in the hydrogenation or evolved in the decomposition (measured volumetrically) in the complete conversion of H_2O_2 to water and the stoichiometry of the reactions ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$ and $H_2O_2 + H_2 \rightarrow 2H_2O$).*

In absence of any halide or in the presence of fluoride or chloride in the catalyst, the H_2O_2 is destroyed mostly by its decomposition (Table 7.3) over the catalyst. The very high H_2O_2 destruction activity of the catalyst in the presence of H_2 is attributed to the activation of the catalyst due to elimination of surface PdO by H_2 in the catalyst.

7.2.2.3 Influence of Gas Atmosphere employed during Calcination of Halogenated Pd/Al_2O_3 Catalyst on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

Results showing the influence of gas atmosphere employed during calcination of different ammonium halides impregnated the Pd/Al_2O_3 (with its Pd in metallic form) catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.4. From the results, the following important observations can be made:

- The calcination of the ammonium halide impregnated Pd/Al_2O_3 catalyst either in the flowing or static air (at 400 ºC) results the oxidation of metallic Pd to PdO. However, when the calcination is carried out in an inert (N_2) gaseous atmosphere (at 400 ºC), the metallic Pd phase in the catalyst is retained.
- The ammonium fluoride and chloride impregnated Pd/Al_2O_3 catalysts calcined in flowing N_2 show high H_2 conversion activity but no selectivity for H_2O_2 in the H_2-to- H_2O_2 oxidation and also show very high H_2O_2 decomposition activity. However, the corresponding fluoride and chloride impregnated catalysts calcined in flowing or static air show much higher selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation. Both the H_2 conversion and H_2O_2 decomposition activities of the halogenated catalysts are decreased after their calcination in air.
- The bromide incorporated Pd/Al_2O_3 catalyst calcined either in air or N_2 shows high selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation but shows very low activity for the H_2O_2 decomposition.

The oxidation of bulk and/or sub-surface Pd^o to PdO in the catalyst results a drastic reduction in the H_2O_2 decomposition activity (Figure 7.5) of the halogenated catalysts. The H_2 conversion is also reduced due to the PdO phase in the catalyst. It may be noted that the Pd oxidation state and the halide ions present in the catalyst cooperatively control the H_2O_2 decomposition activity of the catalyst. For the fluorinated or chlorinated Pd/Al_2O_3 catalyst calcined in air, the PdO phase in the catalyst largely determines H_2O_2 decomposition activity of the catalyst. Interestingly, the brominated catalyst calcined either in oxidizing (air) or inert (N_2) gaseous atmosphere shows very low H_2O_2 decomposition activity, indicating the Br^- anions present in the catalyst drastically reduces the catalytic activity for H_2O_2 decomposition irrespective to the Pd oxidation state in the catalyst.

Table 7.4 Influence of gas atmosphere used for the calcination of halogenated reduced Pd (5 wt%)/Al_2O_3 catalyst on its performance in the H_2-to-H_2O_2 oxidation and on its H_2O_2 decomposition activity (at 27 ºC) in aqueous acidic (0.03 M H_3PO_4) reaction medium (flow rate of air or N_2 = 30 cm^3. g^{-1}catalyst. min^{-1}).

Gas atmosphere used in calcination of halogenated catalyst (at 400 ºC for 1h)	Form of Pd (Pd° or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition rate constant $k_d \times 10^4$ (min^{-1})
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	
Catalyst halogenated by NH_4F (5 wt% F)					
Static air	PdO	24.2	8.2	33.7	4.7
Flowing air	PdO	38.9	11.7	29.9	8.7
Flowing N_2	Pd°	67.1	0.0	0.0	1847
Catalyst halogenated by NH_4Cl (5 wt% Cl)					
Static air	PdO	28.8	14.2	49.2	2.6
Flowing air	PdO	35.8	17.6	49.9	4.6
Flowing N_2	Pd°	60.9	0.0	0.0	1987
Catalyst halogenated by NH_4Br (5 wt% Br)					
Static air	PdO	34.9	16.9	48.3	2.9
Flowing air	PdO	32.8	18.6	53.8	2.8
Flowing N_2	Pd°	45.8	23.9	52.2	4.1

[a] *Confirmed by XRD.*

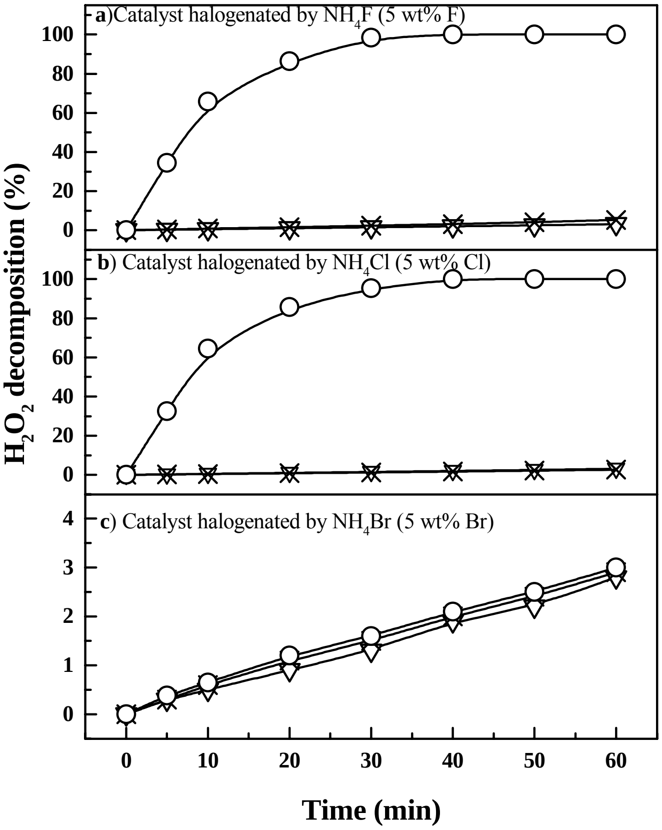

Figure 7.5 Influence of gas atmosphere [static air (×), flowing air (Δ) and flowing N_2 (O)] used for the calcination of halogenated reduced Pd (5 wt%)/Al_2O_3 catalyst on its performance in the H_2O_2 decomposition in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 27 ºC).

7.2.2.4 Influence of Halide Concentration in Reduced Catalyst on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

a) Influence of Concentration of Fluoride Anions

Results showing the influence of fluoride concentration in the fluorinated Pd/Al_2O_3 catalyst (calcined in flowing N_2 at 400 ºC) on its activity in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Figure 7.6. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are increased with increasing the F^- concentration in the catalyst. The F^- incorporated Pd/Al_2O_3 catalyst calcined in N_2 shows no selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation but a drastic increase in the H_2O_2 decomposition activity of the catalyst after its fluorination.

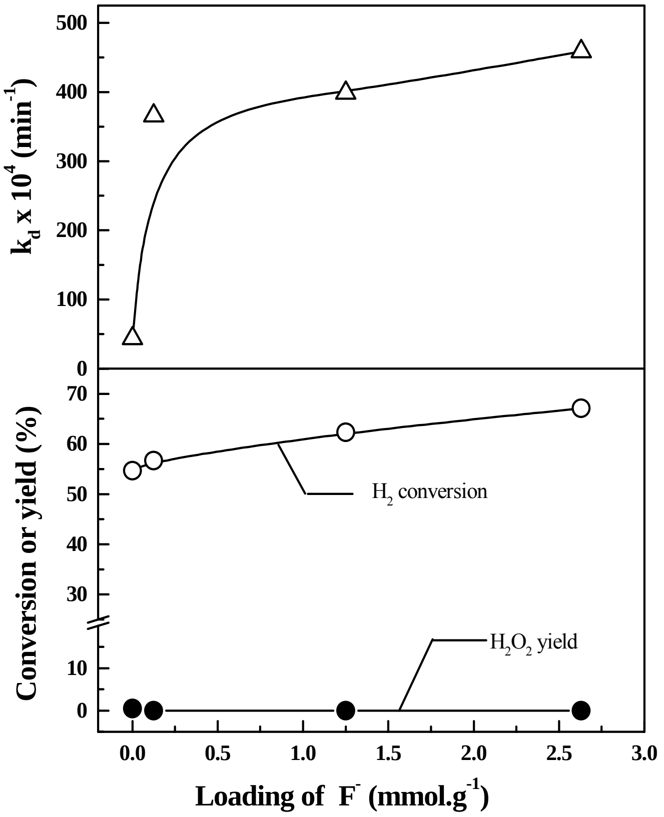

Figure 7.6 Influence of fluoride concentration in the fluorinated Pd/Al_2O_3 catalysts on the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition rate constant (k_d) (at 27 °C) [after fluorination by ammonium fluoride, the catalyst was calcined in flowing N_2 at 400 °C for 1h].

b) Influence of Concentration of Chloride Anions

Results in Figure 7.7 show that the H_2O_2 decomposition activity of the catalyst is increased and then passed through a maximum with increasing the chloride loading in the catalyst; there is no improvement for the H_2O_2 yield in the H_2-to-H_2O_2 oxidation. The chlorinated Pd/Al_2O_3 catalyst shows only a little or no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation most probably due to its very high H_2O_2 decomposition activity.

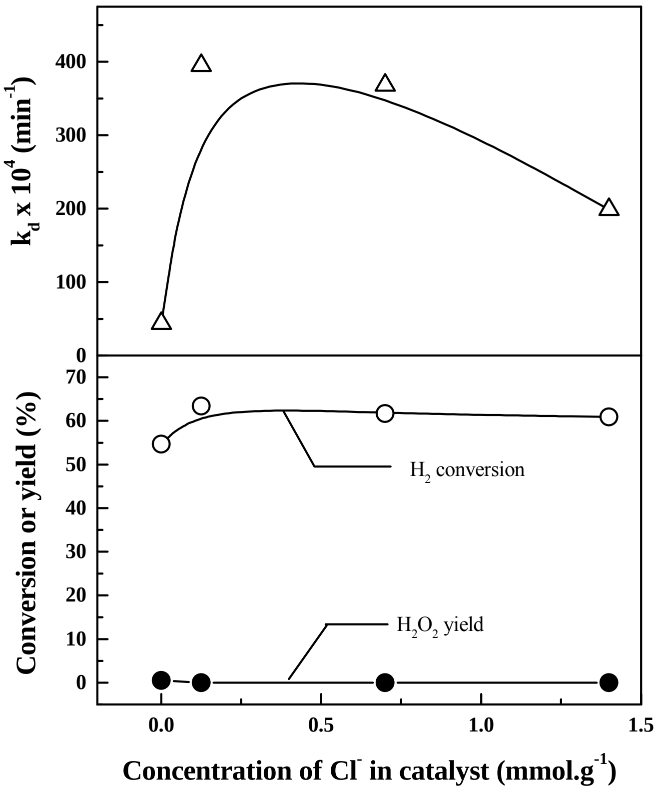

Figure 7.7 Influence of chloride concentration in the chlorinated Pd/Al_2O_3 catalyst on the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition rate constant (k_d) (at 27 °C) [after chlorination by ammonium chloride, the catalyst was calcined in flowing N_2 at 400 °C for 1h].

c) Influence of Concentration of Bromide Anions

Results showing the influence of Br^- concentration in the brominated Pd/Al_2O_3 catalyst (calcined in N_2) on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Figure 7.8. The H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation are increased and then passed through maxima with increasing the Br^- concentration in the catalyst. Therefore, an optimum concentration of Br^- ($\approx$ 0.2 $mmol.g^{-1}$) in the Pd/Al_2O_3 catalyst is essential for achieving the highest H_2O_2 yield (i.e. H_2-to-H_2O_2 conversion) in the H_2-to-H_2O_2 oxidation. The H_2 conversion is, however, decreased to a small extent and the H_2O_2 decomposition activity of the catalyst is decreased sharply with the increase in the Br^- concentration in the catalyst. The improved H_2O_2 selectivity and yield of the catalyst after incorporation of the Br$^-$ ions is expected mostly due to the modification and/or poisoning of the catalytic active sites, responsible for H_2 combustion and/or H_2O_2 destruction.

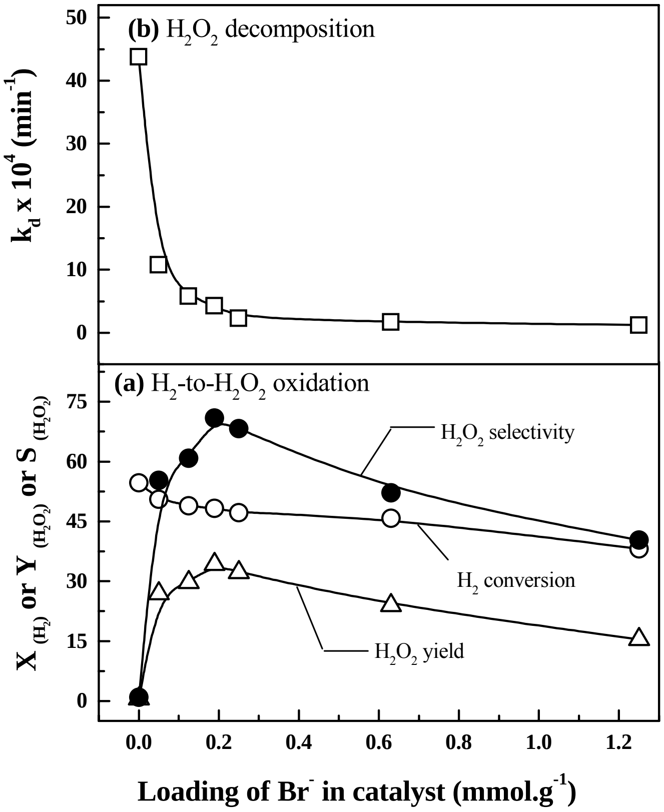

Figure 7.8 Influence of Br$^-$ concentration in the brominated Pd/Al_2O_3 catalyst on its performance in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 °C) [after bromination by ammonium bromide, the catalyst was calcined in flowing N_2 at 400 °C for 1h].

7.2.2.5 Influence of different Bromine Compounds used in the Bromination of Pd/Al_2O_3 Catalyst on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions

Results showing the influence of different bromide-compounds incorporated into the Pd/Al_2O_3 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.5. The incorporation of bromide from ammonium bromide results more H_2O_2 yield in the H_2-to-H_2O_2 oxidation as compared to the other bromide-containing compounds. The catalyst performance for the different bromides is in the following order: NH_4Br > HBr > NaBr > KBr. For the H_2O_2 decomposition, the order is reversed; the H_2O_2 yield/selectivity is increased with the decrease in the H_2O_2 decomposition activity of the catalyst. It may be noted that, the ammonium bromide impregnated catalyst calcined in flowing N_2 at 400 ºC results the deposition of bromine in the catalyst by the thermal decomposition of ammonium bromide ($NH_4Br \rightarrow NH_3 + HBr$). This *in situ* formation of HBr and NH_3 from NH_4Br probably makes the catalyst more selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The ammonia produced is expected to reduced PdO, if any, present in the catalyst during calcination of the NH_4Br impregnated catalyst in N_2. This is not the case for the other bromide. The observed lower H_2O_2 selectivity/yield of the KBr or NaBr impregnated catalyst may also be due to the presence of Na^+ or K^+ cations, which are retained in the catalysts after the calcination.

Table 7.5 Results of H_2-to-H_2O_2 oxidation and H_2O_2 decomposition over brominated Pd (5%)/Al_2O_3 catalyst (concentration of Br = 0.63 mmol.g^{-1}) in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 27 ºC) showing influence of the different bromide compounds used for the bromination of catalyst.

Bromide compound used [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
	X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
HBr	47.0	20.5	43.6	6.7
NaBr	39.4	16.5	41.9	6.5
KBr	38.5	14.5	37.5	7.2
NH_4Br	45.8	23.9	52.2	4.1

[a] *After the impregnation of bromide compound, the catalyst was calcined in a flow of N_2 at 400 ºC for 1h.*

7.2.2.6 *Influence of the Presence of Bromide Anions in Acidic Reaction Medium on H_2-to-H_2O_2 Oxidation and H_2O_2 Decomposition Reactions over Halogenated Pd^o/Al_2O_3 and PdO/Al_2O_3 Catalysts*

Results in Table 7.6 reveal that a strong influence of the presence of Br^- ions in the acidic (0.03 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the halogenated Pd^o and PdO containing catalysts.

Table 7.6 Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition at 27ºC over halogenated Pd^o (or PdO)/Al_2O_3 catalyst (halogen loading = 5 wt%) in acidic medium (0.03 M H_3PO_4) containing bromide anions (concentration of Br^- = 0.94 mmol. dm^{-3}). [values in the square brackets correspond to that obtained in the absence of bromide anions in the same acidic reaction medium].

Halide present in catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition rate constant $k_d \times 10^4$ (min^{-1})
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	
Catalyst calcined under flowing N_2 at 400 ºC					
None	Pd^o	47.8 [54.7]	21.8 [0.5]	45.6 [0.9]	3.6 [43.8]
F	Pd^o	56.5 [67.1]	20.4 [0.0]	36.2 [0.0]	1.3 [1847]
Cl	Pd^o	43.5 [60.9]	20.4 [0.0]	46.9 [0.0]	1.3 [1987]
Br	Pd^o	44.3 [45.8]	23.7 [23.9]	53.5 [52.2]	0.7 [4.1]
Catalyst calcined under static air at 400 ºC					
None	PdO	15.6 [20.8]	8.7 [8.5]	55.8 [40.9]	1.9 [5.3]
F	PdO	14.2 [24.2]	5.4 [8.2]	38.4 [33.7]	2.7 [4.7]
Cl	PdO	23.2 [28.8]	11.2 [14.2]	48.2 [49.2]	2.5 [2.6]
Br	PdO	27.1 [34.9]	14.2 [16.9]	52.2 [48.3]	0.5 [2.9]

[a] *Confirmed by XRD.*

For the fluorinated and chlorinated Pd^o/Al_2O_3 catalysts having no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation, their H_2O_2 selectivity is dramatically improved after the addition of bromide ions in the reaction medium. However, the H_2 conversion is decreased due to the addition of Br^- ions in the reaction medium. The observed high H_2O_2 selectivity for the fluorinated and chlorinated Pd^o/Al_2O_3 catalysts due to the presence of Br^- in the reaction medium is attributed to a drastic decrease in their H_2O_2 decomposition activity. However, the addition of Br^- ions in the reaction medium causes only a small change in the H_2O_2 yield over the halogenated PdO/Al_2O_3 catalysts.

7.3 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/Hβ CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.3.1 Effect of Presence of Halide in Reduced Pd/Hβ Catalyst

Results showing the influence of different halides incorporated in the reduced Pd/Hβ catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.7.

Table 7.7 Performance of the reduced Pd (2.5 wt%)/Hβ catalyst with or without containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium (at 27 ºC) [concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h].

Halide added to the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity $k_d \times 10^4$ (min^{-1})
		X_{H_2} (%)	$Y_{H_2O_2}$ (%)	$S_{H_2O_2}$ (%)	
None	Pd^o	60.5	0.0	0.0	134.0
F	Pd^o	54.1	0.0	0.0	608.0
Cl	Pd^o	51.3	0.0	0.0	305.0
Br	Pd^o	56.3	26.4	46.9	4.0

[a] *Confirmed by XRD.*

The selectivity of the catalyst for H_2O_2 formation in the H_2-to-H_2O_2 oxidation is dramatically improved whereas its activity for H_2O_2 decomposition (Figure 7.9) is reduced very markedly due to the incorporation of Br^- ions in the catalyst. However, the incorporation of F^- or Cl^- ions in the catalyst causes a drastic increase in the H_2O_2 decomposition activity of the catalyst.

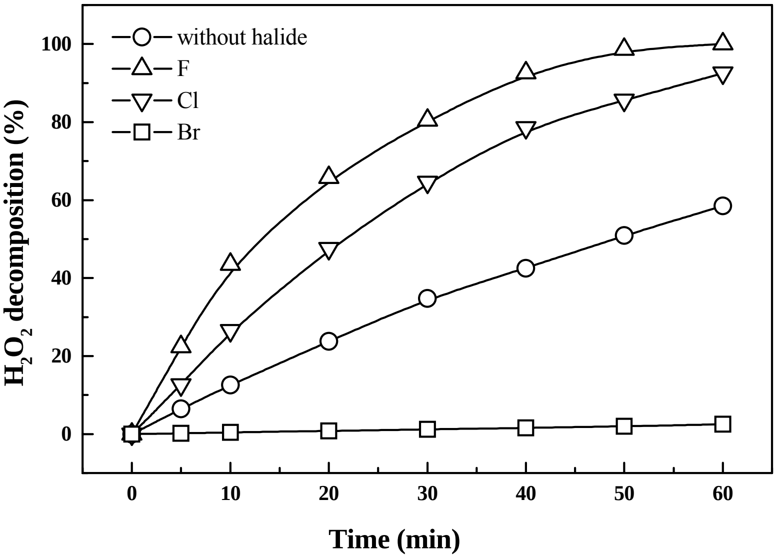

Figure 7.9 H_2O_2 decomposition (at 27 ºC) in aqueous acidic (0.03 M H_3PO_4) medium over the reduced Pd (2.5 wt%)/Hβ catalyst with or without containing halide (concentration of halide in halogenated catalyst = 1.0 wt%. After the halogenation the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

7.3.2 Effect of Oxidation of Halogenated Pd/Hβ Catalyst

A comparison of results in Table 7.7 and 7.8 reveals that the fluorinated and chlorinated Pd°/Hβ catalysts show no H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation but the corresponding fluorinated and chlorinated catalyst after oxidation (i.e. PdO/Hβ) becomes selective for the H_2O_2 formation. Both the H_2 conversion and H_2O_2 decomposition activities of the halogenated PdO/Hβ catalysts are found much lower than the corresponding halogenated Pd°/Hβ catalysts. For the ammonium halide impregnated Pd°/Hβ catalyst, the metallic Pd phase in the catalyst is oxidized to PdO during its calcination in air (static or flowing) at 400 ºC, whereas the same catalyst calcined in inert gaseous atmosphere (N_2), the metallic Pd phase in the catalyst remains intact (Fig. 7.10). The introduction of PdO phase in the halogenated catalyst due to the calcination in air drastically reduces the H_2O_2

decomposition activity of the catalyst while the halide anions present in the catalyst reduces the non-selective H_2-to-water oxidation activity of the catalyst, possibly by poisoning/blocking active sites in the catalyst. It is may be noted that the Pd^o-F or Pd^o-Cl interaction in the catalyst causes a drastic increase in the H_2O_2 decomposition activity of the catalyst. However, PdO-F or PdO-Cl interaction shows very low H_2O_2 decomposition activity for the catalyst. Bromine promoter is however, unique for reducing the H_2O_2 decomposition activity of the catalyst irrespective to the Pd oxidation state in the catalyst.

Table 7.8 Performance of the oxidized Pd (2.5 wt%)/Hβ catalyst with containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing and/or static air 400 ºC for 1h).

Halide present in catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
Halogenated catalyst calcined under static air at 400 ºC					
F	PdO	43.9	9.7	17.4	2.9
Cl	PdO	46.4	11.9	25.6	1.2
Br	PdO	47.4	19.1	40.7	0.9
Halogenated catalyst calcined under flowing air at 400 ºC					
F	PdO	31.5	10.9	34.6	3.2
Cl	PdO	27.4	11.5	41.9	2.1
Br	PdO	36.1	18.7	51.7	1.5

. [a] *Confirmed by XRD.*

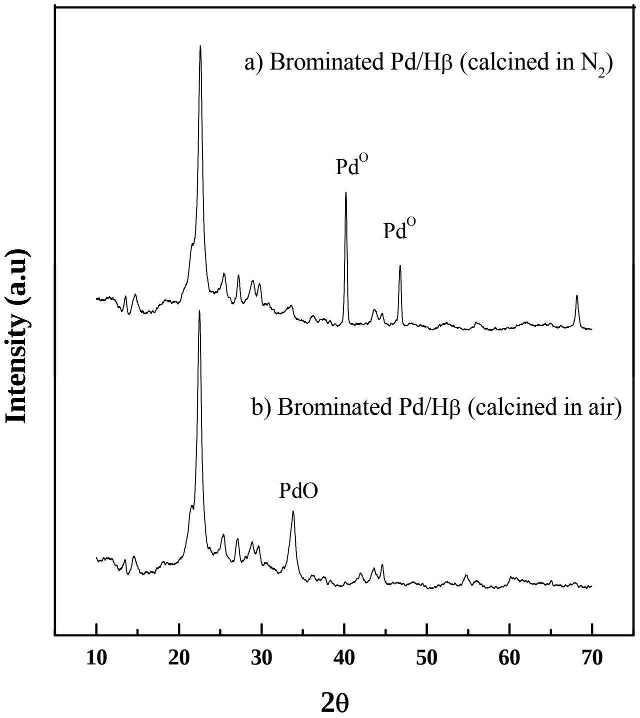

Figure 7.10 XRD spectra of the brominated Pd/Hβ (1 wt % Br) catalyst calcined in flowing N_2 (a) and static air (b) at 400 ºC.

7.3.3 Effect of Bromide Concentration in Reduced Pd/Hβ Catalyst

Results showing the influence of Br^- concentration in the reduced Pd/Hβ catalyst on its performance in the direct oxidation of H_2 to H_2O_2 and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Fig. 7.11. The H_2O_2 yield in the H_2-to-H_2O_2 oxidation is increased and then passed through a maximum with increasing Br^- concentration in the catalyst. The H_2O_2 yield is increased particularly at the lower bromide concentration in the catalyst. However, at the higher Br^- concentrations, both the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation are reduced appreciably. The H_2O_2 decomposition activity of the catalyst is, however, decreased continuously with increasing the Br^- concentration in the catalyst. At the very high Br^- concentration, probably most of the catalytic active sites are blocked, inhibiting the H_2 conversion over the catalyst, and consequently the H_2O_2 yield in the H_2-to-H_2O_2 oxidation is reduced.

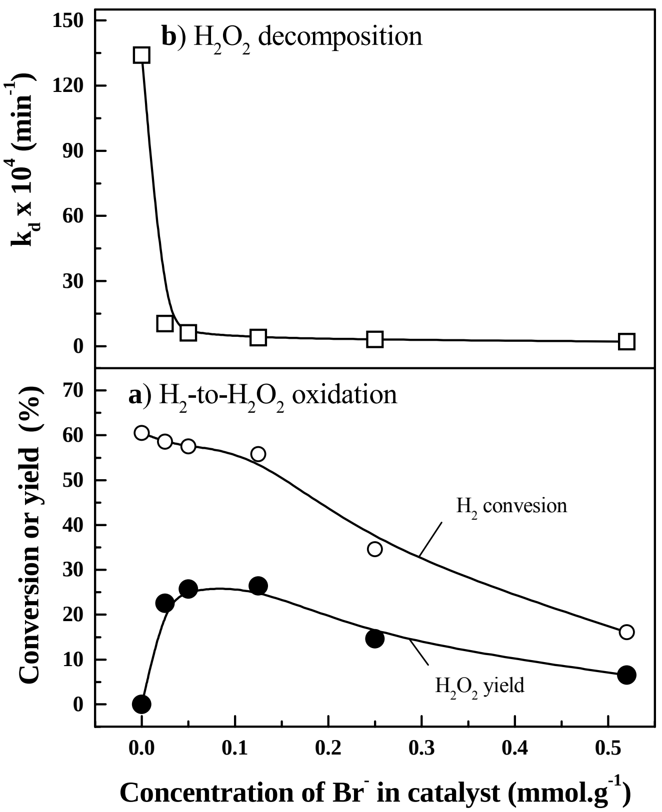

Figure 7.11 Influence of the concentration of Br^- incorporated in Pd/Hβ catalyst on its performance in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 °C) in aqueous acidic (0.03 M H_3PO_4) reaction medium (after bromination by ammonium bromide the catalyst was calcined in flowing N_2 at 400 °C for 1h).

7.4 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/ZrO$_2$ CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.4.1 Effect of Presence of Halide in Reduced Pd/ZrO$_2$ Catalyst

Results showing the performance of different halides containing Pd°/ZrO$_2$ catalysts in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.9. The incorporation of Br^- in the catalyst causes an increase in both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation. However, the fluorination or chlorination of the catalyst causes an increase in the H_2 conversion but no improvement for the H_2O_2 yield in the H_2-to-H_2O_2 oxidation; after the fluorination, the catalyst becomes less or non-selective for the H_2O_2 formation. The H_2O_2 decomposition activity of the catalyst is drastically reduced due to the incorporation of Br^- ions, while incorporation of F^- in the catalyst caused a drastic increase in the H_2O_2 decomposition activity. The chlorination of the catalyst, however, caused a small decrease in the H_2O_2 decomposition activity of the catalyst.

Table 7.9 Performance of the reduced Pd (2.5 wt%)/ZrO_2 catalyst with or without containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide added to the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
None	Pd^o	43.7	3.9	8.9	38.0
F	Pd^o	51.8	0.0	0.0	57.0
Cl	Pd^o	50.5	3.6	7.1	27.0
Br	Pd^o	37.3	25.6	68.8	2.5

[a] *Confirmed by XRD*

7.4.2 Effect of Oxidation of Halogenated Pd/ZrO_2 Catalyst

A comparison of the results in Tables 7.9 and 7.10 reveals that the fluorinated and chlorinated Pd/ZrO_2 catalysts calcined in flowing N_2 are much less selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation than the corresponding halogenated catalysts calcined in air (static or flowing). The much higher H_2O_2 selectivity of the fluorinated and chlorinated catalysts calcined in air is attributed to the presence of PdO in the catalyst. However, the incorporation of bromide in the catalyst drastically improved the H_2O_2 selectivity of both the Pd^o and PdO containing catalysts.

Table 7.10 Performance of the oxidized Pd (2.5 wt%)/ZrO_2 catalyst with containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing and/or static air 400 ºC for 1h).

Halide present in catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
Halogenated catalyst calcined under static air at 400 ºC					
F	PdO	16.2	3.4	20.8	2.6
Cl	PdO	29.3	10.6	36.1	0.6
Br	PdO	33.1	22.6	68.2	0.6
Halogenated catalyst calcined under flowing air at 400 ºC					
F	PdO	24.6	10.9	44.2	2.3
Cl	PdO	36.3	10.4	28.7	0.84
Br	PdO	35.8	24.5	68.4	0.58

[a] *Confirmed by XRD*

7.4.3 Effect of Bromide Concentration in Reduced Pd/ZrO_2 Catalyst

Results in Figure 7.12 show that, with increase in the Br^- concentration in the catalyst, the H_2O_2 yield is increased (particularly at the lower concentrations) and then passed through a maximum. Thus an optimum concentration of Br^- in the catalyst is essential for achieving maximum H_2O_2 yield in the process. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are decreased with increasing the Br^- concentration in the catalyst; the decrease in the later is drastic, particularly in the lower Br^- concentrations.

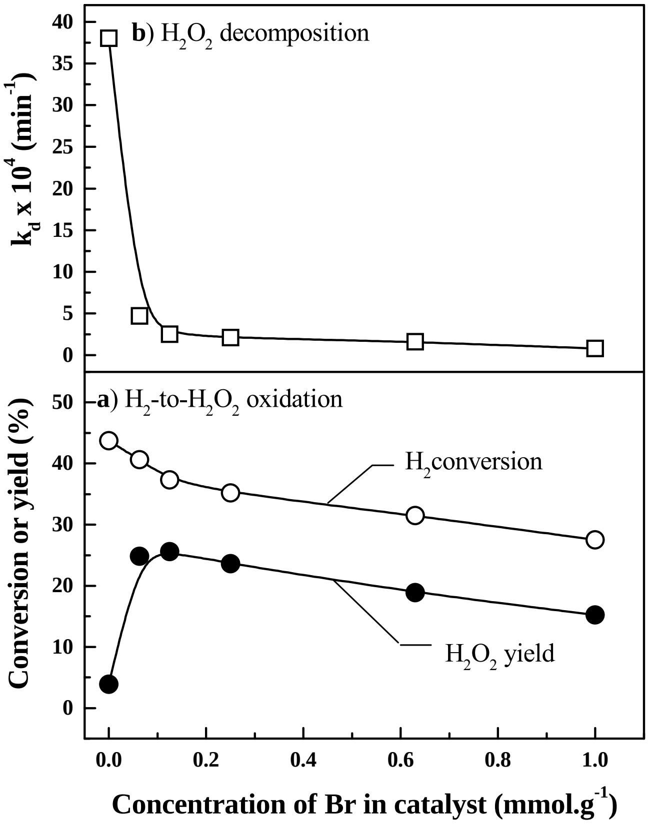

Figure 7.12 Influence of the concentration of Br^- added to Pd/ZrO_2 catalyst on its activity in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 ºC) (after bromination by ammonium bromide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

7.5 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/Ga_2O_3 CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.5.1 Effect of Halides in Reduced Pd/Ga_2O_3 Catalyst

Results in Table 7.11 reveal that there is a strong influence of the halides incorporated in the catalyst on its performance both in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions. The incorporation of Br^- in the catalyst caused an increase in the H_2O_2 yield/ selectivity in the H_2-to-H_2O_2 oxidation and a drastic reduction in the H_2O_2 decomposition activity of the catalyst. However, the fluorination of the catalyst caused an increase in both the H_2 conversion and H_2O_2 decomposition activities of the catalyst. The chlorination of the catalyst however caused a decrease in the H_2O_2 decomposition activity of the catalyst but there is no improvement of the H_2O_2 yield and/or selectivity of the catalyst in the H_2-to-H_2O_2 oxidation. It may be noted that Cl^- ions present in the catalyst probably block some active sited that are responsible for H_2O_2 decomposition but have little influence on directing the H_2 oxidation reaction to H_2O_2.

Table 7.11 Performance of the reduced Pd (2.5 wt%)/Ga_2O_3 catalyst with or without containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide added to the catalyst	Form of Palladium (Pdº or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	Pdº	50.0	5.4	10.8	42.2
F	Pdº	55.5	2.2	3.9	57.0
Cl	Pdº	41.4	3.6	8.9	27.0
Br	Pdº	38.5	24.8	64.5	3.8

X, Y and S = conversion, yield and selectivity, respectively. [a] *confirmed by XRD.* [b] *Pseudo first order H_2O_2 decomposition rate constant (at 27 ºC).*

7.5.2 Effect of Oxidation of Halogenated Pd/Ga_2O_3 Catalyst

Results showing the performance of halogenated PdO/Ga_2O_3 catalysts in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.12. All the halogenated PdO/Ga_2O_3 catalysts show H_2O_2 selectivity in the process. However, the brominated catalyst is found the most selective one for the H_2O_2 formation. The increased H_2O_2 selectivity for the chlorinated or fluorinated catalyst calcined in air, as compared to the corresponding catalyst calcined in N_2 (Table 7.11), is attributed to the oxidation of the metallic Pd from the catalyst to PdO during its calcination in air.

Table 7.12 Performance of the oxidized Pd (2.5 wt%)/Ga_2O_3 catalyst with containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing and/or static air 400 ºC for 1h).

Halide present in catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X_{H_2} (%)	$Y_{H_2O_2}$ (%)	$S_{H_2O_2}$ (%)	$k_d \times 10^4$ (min^{-1}) [b]
Halogenated catalyst calcined under static air at 400 ºC					
F	PdO	15.9	4.8	30.2	2.3
Cl	PdO	23.2	6.9	29.7	2.6
Br	PdO	30.6	20.5	66.9	0.6
Halogenated catalyst calcined under flowing air at 400 ºC					
F	PdO	22.5	6.5	28.9	2.6
Cl	PdO	28.2	9.8	34.7	1.8
Br	PdO	32.1	23.5	73.2	0.7

X, Y and S = conversion, yield and selectivity, respectively. [a] *confirmed by XRD.* [b] *Pseudo first order H_2O_2 decomposition rate constant (at 27ºC).*

7.5.3 Effect of Bromide Concentration in Reduced Pd/Ga_2O_3 Catalyst

Results showing the influence of Br^- concentration in the brominated Pd/Ga_2O_3 catalyst on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an acidic (0.03 H_3PO_4) reaction medium are presented in Figure 7.13. The H_2O_2 yield and selectivity in H_2-to-H_2O_2 oxidation are first increased with the increase in the Br^- concentration (particularly, at the lower concentrations) in the catalyst and then passed through a maximum. This reveals that for obtaining maximum H_2O_2 yield an optimum concentration of Br^- in the catalyst is essential. Both the H_2 conversion and H_2O_2 decomposition activities of the catalyst are decreased with increasing Br⁻ concentration in the catalyst; the decrease in the later is very large, particularly at the lower Br⁻ concentrations.

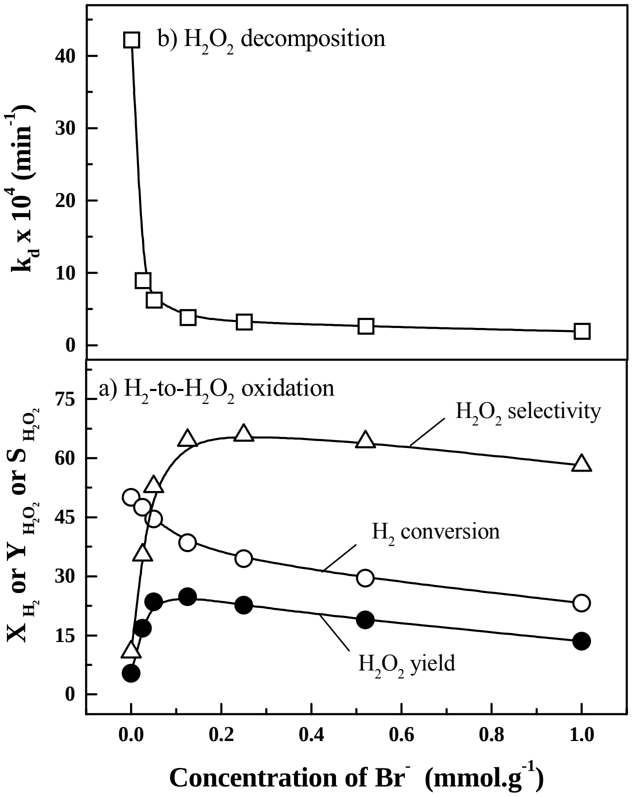

Figure7.13 Influence of the concentration of Br⁻ incorporated in the Pd/Ga_2O_3 catalyst on its activity in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 °C) (after bromination by ammonium bromide, the catalyst was calcined in flowing N_2 at 400 °C for 1h).

7.6 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/CeO_2 CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.6.1 Effect of Presence of Halides in Reduced Pd/CeO_2 Catalyst

Results showing the influence of different halide anions incorporated in the reduced Pd/CeO_2 catalysts on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions are presented in Table 7.13. Interestingly, the H_2O_2 yield in the H_2-to-H_2O_2

oxidation is increased after the incorporation of F^- or Cl^- anions in the catalyst. It may be noted that fluorinated or chlorinated Pd/Al_2O_3, Pd/ZrO_2 or Pd/Ga_2O_3 catalyst showed no selectivity for H_2O_2 formation but the fluorinated or chlorinated Pd/CeO_2 catalyst showed high H_2O_2 selectivity in the H_2 to H_2O_2 oxidation. This indicates that the catalyst support plays an important role in the Pd-halogen interaction in the catalyst. In this case also, the Br^- incorporated catalyst showed the highest H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation and lowest H_2O_2 decomposition activity.

Table 7.13 Performance of the reduced Pd (2.5 wt%)/CeO_2 catalyst with or without containing different halogen in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide added to the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	Pd^o	51.8	6.9	13.6	40.3
F	Pd^o	46.4	15.4	33.2	3.5
Cl	Pd^o	42.7	19.1	44.6	2.4
Br	Pd^o	35.6	19.5	54.8	1.4

[a] *Confirmed by XRD.* [b] *Pseudo first order H_2O_2 decomposition rate constant (at 27 ºC).*

7.6.2 Effect of Oxidation of Halogenated Pd/CeO_2 Catalyst

A comparison of the results in Table 7.13 and 7.14 reveals that the halogenated Pd/CeO_2 catalysts calcined in N_2 are more active for the H_2 conversion in the H_2-to-H_2O_2 oxidation as compared to the corresponding halogenated catalysts calcined in air. The lower H_2 conversion activity of the halogenated catalysts calcined in air is due to the resulting PdO phase. Among the halogenated PdO/CeO_2 catalysts, the brominated PdO/CeO_2 catalyst showed the highest H_2O_2 yield in the H_2-to-H_2O_2 oxidation

Table 7.14 Performance of the oxidized Pd (2.5 wt%)/CeO_2 catalyst with containing halogen in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing and/or static air 400 ºC for 1h).

Halide present in catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
<u>Halogenated catalyst calcined under static air at 400 ºC</u>					
F	PdO	27.3	8.9	32.7	1.6
Cl	PdO	31.3	10.9	34.8	1.7
Br	PdO	31.5	17.5	55.5	2.1
<u>Halogenated catalyst calcined under flowing N_2 at 400 ºC</u>					
F	PdO	31.5	10.9	34.6	3.2
Cl	PdO	27.4	11.5	41.9	2.1
Br	PdO	33.8	17.1	50.6	2.1

[a] *Confirmed by XRD.*

7.7 INFLUENCE OF HALIDE PROMOTER PRESENT IN Pd/SiO_2 CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.7.1 Influence of Halide Present in Reduced Pd/SiO_2 Catalyst

Results showing the influence of different halide anions incorporated in the reduced Pd/SiO_2 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium are presented in Table 7.13. After incorporation of Br^- in the catalyst, the H_2O_2 selectivity of the catalyst in the H_2-to-H_2O_2 oxidation is drastically increased. However, the incorporation of F^- or Cl^- in the catalyst caused no improvement in the H_2O_2 selectivity/yield but a large increase in the

H_2O_2 decomposition activity of the catalyst. The H_2 conversion activity is also increased due to the fluorination or chlorination, while bromination causes a reduction in the H_2 conversion activity of the catalyst.

Table 7.15 Performance of the reduced Pd (2.5 wt%)/SiO_2 catalyst with or without containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions (at 27 ºC) in aqueous acidic (0.03 M H_3PO_4) reaction medium (concentration of halide in halogenated catalyst = 1.0 wt%, after the halogenation by ammonium halide the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide added to the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1}) [b]
None	Pd^o	50.3	0.0	0.0	542.0
F	Pd^o	54.7	0.0	0.0	1023
Cl	Pd^o	58.4	0.0	0.0	887.0
Br	Pd^o	38.5	23.3	60.5	7.3

[a] *Confirmed by XRD.*

7.7.2 Effect of Bromide Concentration in Reduced Pd/SiO_2 Catalyst

Results in Figure 14 show a strong influence of the Br^- concentration in the brominated Pd/SiO_2 catalyst on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions. The H_2 conversion activity of the catalyst is decreased with increasing the Br^- concentration in the catalyst. The H_2O_2 yield in the H_2-to-H_2O_2 oxidation is passed through a maximum with increasing the Br^- concentration in the catalyst. The H_2O_2 decomposition activity of the catalyst is decreased with increasing the Br^- concentration in the catalyst.

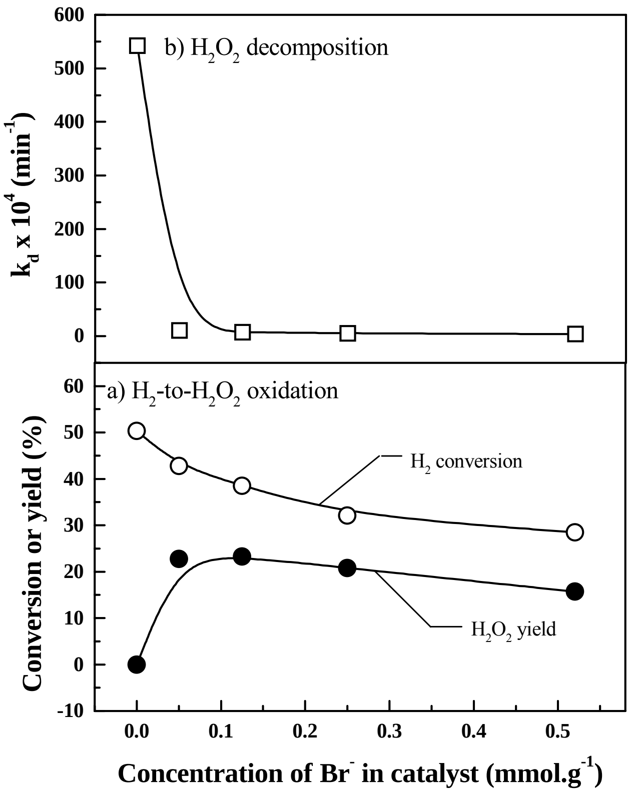

Figure 7.14 Influence of the concentration of Br^- added to Pd/SiO_2 catalyst on its activity in the (a) H_2-to-H_2O_2 oxidation and (b) H_2O_2 decomposition reactions (at 27 ºC) (after bromination by ammonium bromide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

7.8 INFLUENCE OF HALIDE PRESENT IN Pd/C CATALYST ON ITS PERFORMANCE IN H_2-TO-H_2O_2 OXIDATION AND H_2O_2 DECOMPOSITION REACTIONS

7.8.1 Effect of Presence of Halide in Reduced Pd/C Catalyst

Results showing the influence of different halide incorporated into the reduced Pd/C catalysts on its activity/selectivity in the H_2-to-H_2O_2 oxidation are presented in Table 7.14. The incorporation of Cl^- or Br^- in the catalyst causes a drastic reduction in the H_2O_2 decomposition activities of the catalyst but there is only a little improvement of the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. The catalyst fluorination caused an increase in both the H_2 conversion and H_2O_2 decomposition activities of the catalyst. The incorporation of I^- in the catalyst caused a large deactivation of the catalyst in both the H_2 oxidation and H_2O_2

decomposition reactions over the catalyst, indicating strong poisoning of the catalyst due to the iodide ions.

It is interesting to note that the bromination of the metal oxide supported Pd-catalysts (viz. Pd/Al_2O_3, Pd/Ga_2O_3. Pd/ZrO_2, Pd/SiO_2, Pd/Hβ etc.) drastically improve their performance in the H_2-to-H_2O_2 oxidation. However, for the Pd/C catalyst, there is only a little improvement in its performance even after the bromination. This indicates the promoting effect of the halide ions for H_2O_2 formation in the H_2-to-H_2O_2 oxidation strongly depends upon the nature of the support in the Pd catalyst.

Table 7.16 Performance of the reduced commercial Pd (5 wt%)/C catalyst with or without containing halide in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions in aqueous acidic (0.03 M H_3PO_4) reaction medium at 27 ºC (concentration of halide in halogenated catalyst = 5.0 wt%, after the halogenation by ammonium halide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h).

Halide added to the catalyst	Form of Pd (Pd^o or PdO) [a]	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})
None	Pd^o	59.5	0.0	0.0	135.0
F	Pd^o	69.9	0.0	0.0	531.8
Cl	Pd^o	57.1	0.8	1.2	78.8
Br	Pd^o	15.5	0.8	4.8	24.3
I	Pd^o	0.6	0.2	25.0	4.5

[a] *Confirmed by XRD.*

7.9 CONCLUSIONS

Following important conclusions have been drawn from the above investigations:

1. Metal oxide supported Pd catalysts after their bromination become highly selective for H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The highly improved performance of the Pd catalyst in the H_2-to-H_2O_2 oxidation due to its bromination is at least partly attributed to the drastic reduction in its H_2O_2 decomposition and/or hydrogenation activity of the catalyst. The non-selective parallel H_2-to-water oxidation over the catalyst may also be reduced due to the bromination of the Pd catalyst. However, there is an optimum concentration of bromide in the supported Pd catalysts for obtaining the highest H_2O_2 yield in the direct H_2 to H_2O_2 oxidation. At very high bromine concentration both the H_2 conversion over the catalyst and H_2O_2 yield in the reaction are reduced.
2. The fluorination of the supported Pd^o catalysts (except Pd^o/CeO_2) causes an increase in their H_2O_2 decomposition activity and consequently their H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation is drastically reduced. However, the fluorinated PdO containing catalysts show high H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation, indicating the importance of the Pd oxidation state in the catalysts. The PdO containing halogenated catalysts show much lower activity for H_2O_2 decomposition than the corresponding Pd^o containing halogenated catalyst.
3. Incorporation of chlorine in the supported Pd^o catalysts influence causes similar to that shown by the fluorine incorporation. However, the chlorinated PdO supported catalysts are also selective in the H_2-to-H_2O_2 oxidation.
4. Incorporation of I^- in the Pd catalyst (e.g. Pd/Al_2O_3, Pd/C) causes a large deactivation in both the H_2 conversion and H_2O_2 decomposition activities of the catalysts due to poisoning of their active sites.
5. Like the presence of bromide anions in the acidic reaction medium, the presence of bromine promoter in the Pd/Al_2O_3 catalyst causes a large reduction in the H_2O_2 conversion/hydrogenation activity in the presence of hydrogen.

7.10 REFERENCES

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CHAPTER-8

H_2O_2 FORMATION IN THE INTERACTION OF O_2 WITH HYDRAZINE –REDUCED BORON CONTAINING SUPPORTED Pd CATALYSTS

AND IN THE OXIDATION BY O_2 OF HYDRAZINE HYDRATE/SALT OVER SUPPORTED Pd CATALYSTS:

INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTERS

CHAPTER-8

H_2O_2 FORMATION IN THE INTERACTION OF O_2 WITH HYDRAZINE–REDUCED BORON CONTAINING SUPPORTED Pd CATALYSTS AND IN THE OXIDATION BY O_2 OF HYDRAZINE HYDRATE / SALT OVER SUPPORTED Pd CATALYSTS: INFLUENCE OF REACTION MEDIUM AND HALIDE PROMOTERS

8.1 GENERAL INTRODUCTION AND OBJECTIVE OF THE PRESENT WORK

Demand for H_2O_2 (a versatile, clean oxidizing agent) in the pulp/paper and wastewater treatment industries as an eco-friendly alternative to chlorine has been increasing day-by-day. There is also a trend to use H_2O_2 as an environmentally oxidant in the synthesis of fine and bulk chemicals [1-4]. At present, H_2O_2 is produced commercially mainly by the anthraquinone process, which involves an indirect oxidation of hydrogen [5]. This process is not environmentally clean, requires very costly solvent system and also involves costly cyclic hydrogenation-oxidation and H_2O_2 processing/separation steps, thereby increasing the H_2O_2 production cost. This limits the use of H_2O_2 for the wastewater treatments and production of inexpensive chemicals in large quantities. Therefore, a lot of efforts have been made for developing alternative routes for the production of H_2O_2, such as liquid phase direct oxidation of H_2 to H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) using heterogeneous Pd catalysts [6-21] and oxidation of carbon monoxide and water to H_2O_2 ($CO + H_2O + O_2 \rightarrow H_2O_2 + CO_2$) using homogeneous Pd catalysts [22-28].

The H_2-to-H_2O_2 oxidation is environmentally clean process, producing only water as a side product. However, this process is highly hazardous because of the very wide flammability/explosion limits for a mixture of H_2 and O_2 (4 - 94 % H_2 in O_2). This has so far limited the commercial exploitation of the direct H_2 oxidation process; even-though it has been extensively investigated and patented during the last 2-3 decades [29-44]. However, the explosion limits for a mixture of CO and O_2 are narrower (15.5 to 94 % wet CO in O_2) and hence the (CO and H_2O)-to-H_2O_2 oxidation by O_2 is less hazardous but the H_2O_2 formation turnover rates are low and/or the stability of ligands of the homogeneous catalysts under strongly oxidizing condition is questionable. Moreover, there are serious problems associated with the separation and reuse of the homogeneous catalysts. Also the by-product (CO_2) is a green house gas, a direct release of which in the atmospheric would be restricted in the near future for avoiding the global warming. Hence, there is an urgent need for developing a new non-hazardous route for H_2O_2 production and also a new method for the generation of H_2O_2 in situ in the synthesis of fine/bulk chemicals. At present, the in situ H_2O_2 generation is done by two methods-one based on the direct oxidation of H_2 by O_2 [45-48] and second based on indirect oxidation of H_2 employing anthraquinone carrier [49].

A novel process for the formation of the H_2O_2 in high yields by the oxidation of hydrogen from hydrazine (N_2H_4) or hydrazine-salt in an aqueous acidic medium containing bromide promoters, using Pd catalyst at close to room temperature, without involvement of any explosive gas mixture, particularly for the in situ H_2O_2 generation, has been reported here for the first time. Moreover, in this novel process, only environmentally benign by-product (N_2) and side product (water) are formed.

The present study was undertaken with the objective of investigating the factors affecting the formation of H_2O_2 in the oxidation hydrazine or its salt by O_2 over the supported Pd catalysts. The first portion of this chapter deals with the investigation of the H_2O_2 formation in the interaction of O_2 with a hydrazine–reduced boron containing supported Pd catalysts (viz. Pd/Al_2O_3-B_2O_3, Pd/Ga_2O_3-B_2O_3, Pd/CeO_2-B_2O_3, Pd/ZrO_2-B_2O_3 and Pd/boron phosphate) in an aqueous reaction medium. The second portion of this chapter deals with the formation of H_2O_2 by a totally new route, which involves a liquid phase oxidation of hydrazine hydrate and hydrazine sulfate by O_2 over the supported Pd catalysts (viz. Pd/Al_2O_3, Pd/C and Pd/Ga_2O_3). The influence of the various factors viz. the presence of acid in the reaction medium; the different halides (present in the catalyst or in the reaction medium) and their concentrations on the formation of H_2O_2 in the oxidation of hydrazine and/or hydrazine sulfate have been investigated.

8.2 H_2O_2 FORMATION IN THE INTERACTION OF O_2 WITH HYDRAZINE-REDUCED BORON CONTAINING SUPPORTED Pd CATALYSTS

The supported Pd catalysts with Pd loading of 2.5 wt % (Table 8.1) were prepared by impregnating $PdCl_2$ from its acetonitrile solution on boron phosphate or respective metal oxide support (with or without containing boron) by incipient wetness technique, drying the impregnated mass in air oven at 100 ºC for 2h and then calcining it at 500 ºC under static air for 3h. The ZrO_2-B_2O_3, CeO_2-B_2O_3, TiO_2-B_2O_3 and Al_2O_3-B_2O_3 catalyst supports were prepared by mixing boric acid (H_3BO_3) with respective metal oxide [ZrO_2 (prepared from zirconyl nitrate by its hydrolysis to zirconium hydroxide, by ammonium hydroxide and calcining at 500 ºC for 2h), CeO_2 (Aldrich), TiO_2 (Loba) or Al_2O_3 (prepared from bohemite by its calcination at 500 ºC for 2h)] with the metal/boron mole ratio of 1.0 in the presence of deionised water just sufficient to form a thick paste, drying the wet mixture in air oven at 100 ºC for 2h and then calcining it in air at 600 ºC for 3h. Similarly, the boron phosphate was prepared from a mixture of boric acid and orthophosphoric acid (with B/P mole ratio of 1.0). The calcined catalyst was reduced by hydrazine by adding 3 ml hydrazine hydrate (98%) dropwise to the catalyst (3g) while mixing thoroughly the hydrazine-catalyst mixture at a room temperature for 5 min and drying the wet catalyst mass on water bath for 1h.

The catalyst–oxygen interaction was carried out in a magnetically stirred glass reactor (capacity = 250 cm^3), using 0.5 g fine particles of the prereduced catalyst in 150 cm^3 aqueous reaction medium with or without containing mineral acid and/or halide and passing O_2 (or air) through the reaction medium at a flow rate of 1.5 $dm^3.h^{-1}$ at 27 ºC. The H_2O_2 formed in the reaction was analyzed by the iodometric titration. Influence of the presence of B_2O_3 in the catalyst and also of the reduction of the catalyst by hydrogen (at 400 ºC) or aqueous sodium borohydride solution on the H_2O_2 formation has also been studied.

Results showing the formation of H_2O_2 in the interaction of O_2 with the different Pd (2.5 wt%) catalysts, with or without containing boron, in an aqueous reaction medium in the presence or absence of mineral acid (H_3PO_4 or H_2SO_4) and/or different halides (introduced as potassium halide) are presented in Table 8.1. Influence of the concentration of acid and Br^- ions present in the aqueous reaction medium and also of the reaction period on the H_2O_2 formation for the Pd/ZrO_2–B_2O_3 catalyst prereduced by hydrazine is shown in Figures 8.1 and 8.2.

The results in Table 8.1 show the formation of H_2O_2 in appreciable amounts but only when

– the catalyst contains boron in the support,

– the boron containing catalyst is prereduced by hydrazine, and

– the reaction medium contains both the acid and Br^- ions

Otherwise, there is only a little or no formation of H_2O_2. The H_2O_2 formation is markedly increased with increasing the concentration of acid (H_3PO_4) or Br^- ions in the reaction medium; the increase is predominant particularly at the lower concentrations (Figure 8.1). It is also increased with increasing the reaction period (Figure 8.2). The formation of H_2O_2 is more pronounced when pure oxygen is used instead of air (Figure 8.2). At the higher reaction periods, the H_2O_2 formation is leveled off, probably because of the simultaneous H_2O_2 decomposition over the Pd catalyst, nullifying the H_2O_2 formation.

Table 8.1 Results of the formation of H_2O_2 in the interaction of O_2 with different supported Pd catalysts in the aqueous reaction medium with or without containing mineral acid and/or halide [reaction conditions: amount of catalysts = 0.5 g, volume of reaction medium =150 cm^3, flow rate of O_2 = 1.5 $dm^3.h^{-1}$ and reaction temperature = 25 ºC]

Catalyst	Reaction medium	Halide promoter	Concn.of halide ($mmol.dm^{-3}$)	Reaction period (h)	H_2O_2 formed (mmol)
$Pd/ZrO_2–B_2O_3$ [a]	H_3PO_4 (0.03 M)	Br^-	0.94	3	2.90
$Pd/CeO_2–B_2O_3$ [a]	H_3PO_4 (0.03 M)	Br^-	0.94	1	0.96
$Pd/TiO_2–B_2O_3$ [a]	H_3PO_4 (0.03 M)	Br^-	0.94	1	0.57
$Pd/Al_2O_3–B_2O_3$ [a]	H_3PO_4 (0.03 M)	Br^-	0.94	1	0.53
Pd/BPO_4[a]	H_3PO_4 (0.03 M)	Br^-	0.94	3	2.89
Pd/ZrO_2 (or CeO_2, TiO_2, Al_2O_3)[a]	H_3PO_4 (0.03 M)	Br^-	0.94	3	0.0
PdO/ZrO_2 (or CeO_2, TiO_2, Al_2O_3)–B_2O_3 [b]	H_3PO_4 (0.03 M)	Br^-	0.94	3	0.0
Pd/ZrO_2 (or CeO_2, TiO_2, Al_2O_3)–B_2O_3 [c]	H_3PO_4 (0.03 M)	Br^-	0.94	3	0.0
$Pd/ZrO_2–B_2O_3$ [a]	H_2SO_4 (0.05 M)	Br^-	0.94	1	1.10
$Pd/ZrO_2–B_2O_3$ [a] or Pd^o/BPO_4[a]	Water (without mineral acid)	Br^-	0.94	3	< 0.38
$Pd/ZrO_2–B_2O_3$ [a] or Pd^o/BPO_4[a]	H_3PO_4 (0.03 M)	Without promoter	0.00	3	< 0.02
$Pd/ZrO_2–B_2O_3$ [a] or Pd^o/BPO_4[a]	H_3PO_4 (0.03 M)	Cl^- or I^-	0.94	3	< 0.01

[a] *Catalyst prereduced by hydrazine.*

[b] *Unreduced catalyst (with its Pd in oxidized form).*

[c] *Catalyst prereduced by hydrogen (at 400º C) or aqueous sodium borohydride solution.*

It is interesting to note that, H_2O_2 formation is not observed when the boron containing Pd catalysts were prereduced by hydrogen (at 400 ºC) or by aqueous sodium borohydride solution. Highly basic hydrazine chemisorbed on strongly acidic boron oxide may be playing an important role in the formation of H_2O_2 in the interaction of oxygen with the hydrazine-prereduced catalysts.

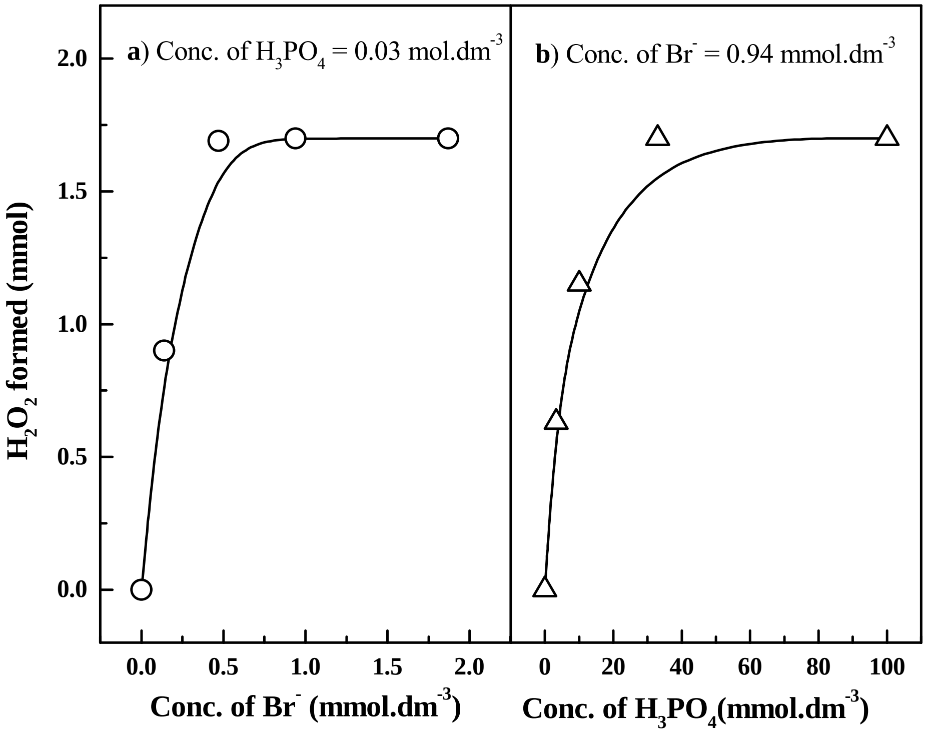
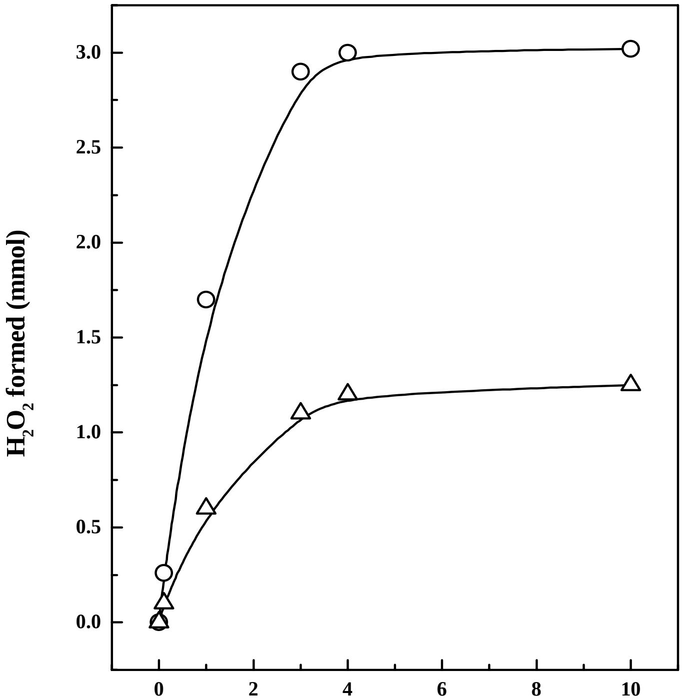


Figure 8.1 Effect of the concentration of Br^- ions (a) and phosphoric acid (b) in the reaction medium on the H_2O_2 formation for the hydrazine reduced Pd/ZrO_2-B_2O_3 catalyst at 25ºC (reaction period =1h).

The source of hydrogen for the H_2O_2 formation is very likely to be the chemisorbed hydrazine. However, the dissolved hydrogen in the palladium and/or the H^+ form in the acidic medium may be involved in the H_2O_2 formation.

Further detailed investigation is necessary for understanding the H_2O_2 formation and the role of the essential factors (viz. the presence of boron in the support, the catalyst prereduction by hydrazine, and the presence of mineral acid and Br^- anions in the reaction medium) having very strong influence on the formation of H_2O_2 in the interaction/reaction of O_2 with the supported Pd catalysts in an aqueous reaction medium. It may be noted that the formation of H_2O_2 in the present case is non-hazardous; unlike in the direct oxidation of H_2, there is no formation of explosive gas mixture.

The above interesting observations lead further investigation on the oxidation of hydrazine over different Pd catalysts was undertaken.



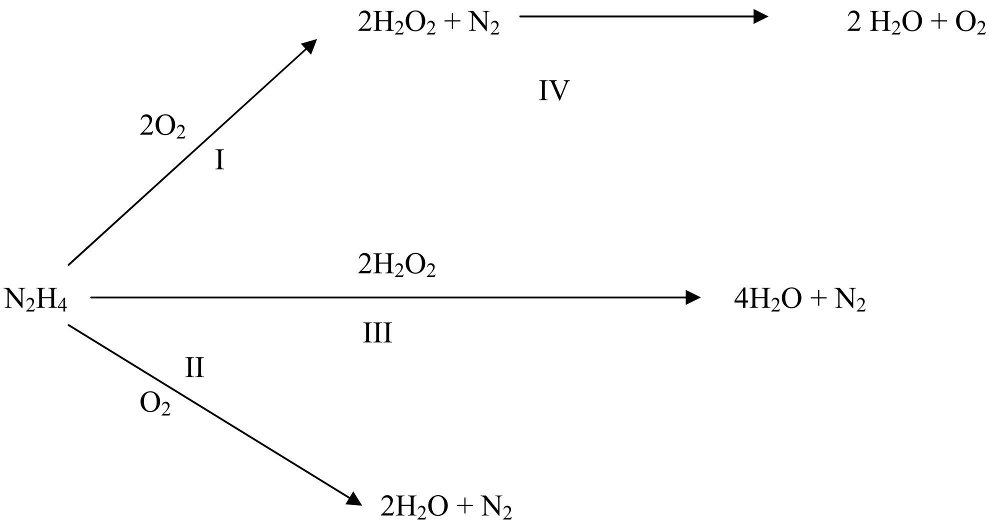
Reaction time (h)

Figure 8.2 Effect of the reaction time on the H_2O_2 formation in the interaction of molecular O_2 (o) or air (Δ) with hydrazine reduced Pd/ZrO_2-B_2O_3 catalyst (at 25 ºC).

8.3 OXIDATION OF HYDRAZINE HYDRATE TO H_2O_2 OVER Pd/Al_2O_3 CATALYST IN AQUEOUS REACTION MEDIUM

8.3.1 Influence of Acid and Halide in Reaction Medium

Results showing the influence of different reaction mediums (with or without containing different potassium halides) on the H_2O_2 formation in the oxidation of hydrazine (by O_2) over the reduced Pd/Al_2O_3 catalyst are presented in Table 8.2. The results show that in the absence of any acid in the aqueous reaction medium, there is no formation of H_2O_2; the hydrazine oxidation leads to the formation of water only. The presence of acid (i.e. H^+ ions) in the reaction medium is essential for obtaining H_2O_2 otherwise the H_2O_2 formed in the reaction is decomposed over the catalyst because of the very high H_2O_2 decomposition activity of the catalyst in the absence of acid in the reaction medium. It may be noted that, like in the direct H_2-to-H_2O_2 oxidation, in the N_2H_4-to-H_2O_2 oxidation, both the H_2O_2 and water forming consecutive and parallel reactions occur simultaneously over the catalyst (Scheme 8.1). In the absence of acid, the reaction between hydrazine (unconverted) and H_2O_2 in the bulk liquid medium (reaction III) is facilitated, leading to the destruction of the H_2O_2 formed.



Scheme 8.1 Reactions involves in the oxidation of N_2H_4 by O_2 to H_2O_2.

Table 8.2 Formation of H_2O_2 in the oxidation of hydrazine hydrate by O_2 (at 25 °C) over the reduced Pd (5%)/Al_2O_3 catalyst in aqueous medium with or without containing acid and/or halide [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine hydrate = 2.3 mmol, O_2 flow rate = 10 cm^3/min and reaction period = 0.5h]

Reaction medium (mol.dm^3) [a]	Potassium halide in reaction medium [mmol.dm^{-3}) [b]	Conversion of hydrazine (%)	H_2O_2 formed per mole of hydrazine consumed (mol/mol)	H_2O_2 yield [c] (%)
H_3PO_4 (0.1)	None [0.0]	100	0.0	0.0
H_3PO_4 (0.1)	KF [0.94]	1.00	0.0	0.0
H_3PO_4 (0.1)	KCl [0.94]	100	0.0	0.0
H_3PO_4 (0.1)	KBr [0.94]	100	0.85	42.5
H_3PO_4 (0.1)	KI [0.94]	10	0.0	0.0
H_2SO_4 (0.1)	KF or KCl [0.94]	100	0.0	0.0
H_2SO_4 (0.1)	KBr [0.94]	100	0.8	40.0
H_2SO_4 (0.1)	KI [0.94]	12	0.0	0.0
Pure water	None [0.0]	100	0.0	0.0
Pure water	KBr [0.94]	100	0.0	0.0

[a] *Value given in the round bracket corresponds to the concentration of acid in the reaction medium.* [b] *Value given in the square bracket corresponds to the concentration of halide in the reaction medium.* [c] *Yield of H_2O_2 is based on the hydrogen (from hydrazine) consumed in the reaction.*

Results in Table 8.2 reveal that in the absence of any halide or presence of KF or KCl in the aqueous acidic reaction medium, the hydrazine is oxidized with its 100% conversion to water ($N_2H_4 + O_2 \rightarrow 2H_2O + N_2$), without formation of H_2O_2. The addition of KI to the aqueous acidic (H_3PO_4 or H_2SO_4) reaction medium also leads to the similar results except that the hydrazine conversion is drastically reduced, indicating strong poisoning of the catalyst due to the presence of I^- ions. However, in the presence of KBr, the H_2O_2 yield is drastically increased from zero to 40% and 42.5% respectively, in the aqueous 0.1 M H_2SO_4 and 0.1 M H_3PO_4 reaction medium. The influence of protons and different halides on the H_2O_2 formation in the hydrazine oxidation can be explained as follows:

At the very low pH of the reaction medium, the catalyst surface is positively charged because of the much higher isoelectric point of the Al_2O_3. This facilitates the adsorption of only anions (viz. halide anions) from the acidic reaction medium on the catalyst, modifying its surface properties/active sites, depending upon the halide. Indeed, the strong adsorption of the halide anions was detected from the XPS and/or EDX analysis of the Pd/Al_2O_3 catalyst after its use in the hydrazine oxidation (Table 8.2). The observed highly positive effect of the Br^- (adsorbed in the catalyst) is expected most probably because of it intermediate reducing strength (electron donating ability). A following probable mechanism involving both the ionic and free radical reactions for the N_2H_4-to-H_2O_2 oxidation in the presence of protons and Br^- ions, is proposed.

$S + Br^- \rightarrow S.Br^-$ ----------------- (8.1)

$S + O_2 \rightarrow S.O_2$ ----------------- (8.2)

$S.O_2 + S.Br^- \rightarrow S.O_2^- + Br$ ------------- (8.3)

$4\ S + N_2H_4 \rightarrow 4\ S.H + N_2\uparrow$ -------- (8.4)

$S.O_2^- + S.H \rightarrow S.HO_2^- + S$ --------- (8.5)

$S.HO_2^- + H^+ \rightarrow S.H_2O_2$ --------- (8.6)

$S.H_2O_2 + S \rightarrow 2S.OH$ ------------ (8.7)

$S.H_2O_2 + S.H \rightarrow S.OH + H_2O + S$ ----- (8.8)

$S.OH + S.H \rightarrow H_2O + 2S$ ------------ (8.9)

$S.O_2^- + H^+ \rightarrow S.HO_2$ --------------- (8.10)

$S.HO_2 + S.H \rightarrow S.H_2O_2$ ---------- (8.11)

$S.O_2 + S \rightarrow 2\ S.O$ ----------- (8.12)

$S.O + 2\ S.H \rightarrow 3\ S + H_2O$ -------- (8.13)

$S.H_2O_2 \rightarrow S + H_2O_2$ -------------- (8.14)

$S.\ Br + S.H \rightarrow S.Br^- + H^+ + S$ -------- (8.15)

$N_2H_4 + H_2O_2 \rightarrow 4\ H_2O + N_2\uparrow$ ---------- (8.16)

(Where S = Adsorption site)

Thus, both the protons and adsorbed halide (Br$^-$) anions are expected to take part in the hydrazine oxidation according to reactions-8.1, 8.3, 8.6 and 8.10 and the two are regenerated in reaction 8.15. In the absence of Br$^-$ ions, reactions 8.12 and 8.13 are facilitated, leading to the formation of water alone. In the presence of both the acid and Br$^-$ ions, the H_2O_2 decomposition activity of the catalysts is drastically reduced (Chapter 5) thereby increasing the net formation of H_2O_2 in the hydrazine oxidation. However, in the absence of acid or in the basic medium, reaction 8.16 is facilitated in the bulk liquid medium leading to the destruction of H_2O_2 formed. The hydrazine probably reacts via its successive

($N_2H_4 \xrightarrow{-H} N_2H_3 \xrightarrow{-H} N_2H_2 \xrightarrow{-H} N_2H \xrightarrow{-H} N_2$) on the catalyst to overall

dissociative adsorption reaction 8.4. It is also interesting to note that the results and proposed reaction mechanism for the hydrazine oxidation are complementary/consistent to the earlier observed drastic increase in the H_2O_2 formation in the direct H_2-to-H_2O_2 oxidation over the supported Pd catalysts in the presence of acid and Br$^-$ ions. The influence of the presence of acid and halide anions on the H_2O_2 formation in the hydrazine oxidation is quite similar to that observed in the H_2-to-H_2O_2 oxidation (Chapter 5).

8.3.2 Influence of Halide Incorporated in Catalyst

Results showing the influence of different halides (F$^-$, Cl$^-$, Br$^-$ or I$^-$) incorporated in the Pd/Al_2O_3 catalyst on its performance in the oxidation of hydrazine to H_2O_2 in an aqueous acidic (0.1 M H_3PO_4) reaction medium are presented in Table 8.3. The results obtained are quite similar to that observed for the halides present in the reaction medium (Table 8.2). In both the cases, the formation of H_2O_2 in the hydrazine oxidation occurs only in the presence of Br$^-$ ions. The incorporation of the I$^-$ ions causes a drastic inhibition to the hydrazine conversion over the catalyst.

It may be noted that the incorporation of the F$^-$ or Cl$^-$ ions in the Pd/Al_2O_3 catalyst, drastically increases its activity for H_2O_2 decomposition. However, the Br$^-$ ions incorporated in the catalyst drastically reduce its activity for H_2O_2 decomposition. The Br$^-$ ions may also reduce the dissociative adsorption of O_2 on the catalyst thereby inhibiting the non-selective hydrazine-to-water ($N_2H_4 + O_2 \rightarrow 2H_2O + N_2$) oxidation.

Table 8.3 Performance of the reduced Pd (5%)/Al_2O_3 catalyst (with or without containing halide) in the oxidation of hydrazine hydrate by O_2 in aqueous acidic (0.1 M H_3PO_4) reaction medium (halide incorporated in the catalyst = zero or 1 wt%. After the halogenation by ammonium halide, the catalyst was calcined in flowing N_2 at 400 ºC for 1h) [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine = 4.0 mmol O_2 flow rate = 10 cm^3/min, reaction temperature = 25 ºC and reaction period = 1h].

Halogen added to the catalyst	Form of Pd (Pd^o or PdO) [a]	Conversion of hydrazine (%)	H_2O_2 formed per mol of hydrazine converted (mol/mol)	H_2O_2 yield [c] (%)
None	Pd^o	100	0.0	0.0
F	Pd^o	100	0.0	0.0
Cl	Pd^o	100	0.0	0.0
Br	Pd^o	100	0.7	35.0
I	Pd^o	8.5	0.0	0.0

[a] *Confirmed by XRD.* [b] *Yield of H_2O_2 is based on the hydrogen from hydrazine.*

8.4 OXIDATION OF HYDRAZINE SULFATE TO H_2O_2 OVER SUPPORTED Pd CATALYSTS IN AQUEOUS REACTION MEDIUM

8.4.1 Influence of Halide Added to Reaction Medium

Results showing the influence of different halides added to the aqueous medium on the oxidation of hydrazine from hydrazine sulfate over the reduced Pd/Al_2O_3 and Pd/C catalysts are presented in Table 8.4. The results show that the formation of H_2O_2 in the oxidation of hydrazine (from hydrazine sulfate) takes place only in the presence of Br^- ions in the reaction medium. Indeed, the influence of the different halides on the oxidation of hydrazine (from hydrazine sulfate) is similar to that observed in the oxidation of hydrazine from hydrazine hydrate (Table 8.2). In the presence of I^- ions the hydrazine conversion over the catalyst is drastically reduced, indicating strong poisoning effect of the I^- ions to the catalyst. The presence of Cl^- or F^- in the reaction medium leads mostly to the formation of water, with only a little (in case of Cl^- for the Pd/C) or no formation of any H_2O_2 in the oxidation of hydrazine.

Table 8.4 Results of the formation of H_2O_2 in the oxidation of hydrazine sulfate by O_2 over the reduced Pd (5%)Al_2O_3 and Pd (5%)/C catalysts in aqueous medium (pure water) with or without containing different alkali halides (concentration of halide in the reaction medium = 0.94 mmol/dm^3) [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 2.3 mmol, O_2 flow = 10 cm^3/min, reaction temperature = 25 ºC and reaction period = 0.5 h].

Halide added to the reaction medium	Hydrazine sulfate conversion (%)	H_2O_2 formed per mol of hydrazine sulfate consumed (mol/mol)	H_2O_2 yield [c] (%)
Catalyst = Pd/Al_2O_3			
None [b]	100	0.0	0.0
KF [a]	100	0.0	0.0
KCl [b]	100	0.0	0.0
KBr [a]	100	1.17	58.7
KI [a]	10	0.0	0.0
Catalyst = Pd/C			
None	100	0.0	0.0
KF	100	0.0	0.0
KCl	100	0.03	1.5
KBr	100	0.75	35.0
KI	5.0	0.0	0.0

[a] *No Pd leaching in the reaction was detected.* [b] *Significant Pd leaching in the reaction was detected.* [c] *Based on the hydrogen from hydrazine.*

It may be noted that when hydrazine sulfate ($N_2H_4.H_2SO_4$) is employed instead of hydrazine hydrate ($N_2H_4.H_2O$), addition of mineral acid to the aqueous medium is not essential because of the release of associated acid molecules (H_2SO_4) from the hydrazine sulfate after its hydrolysis, making its aqueous solution acidic (pH < 2).

8.4.2 Influence of Cation Present in Bromide Compound Added to Reaction Medium

Results showing the influence of different bromide-compounds added to the aqueous medium on the performance of the reduced Pd/Al_2O_3 catalyst in the oxidation of hydrazine from hydrazine sulfate to H_2O_2 are presented in Table 8.5. The results obtained with the different bromide compounds are comparable emphasizing the importance of the Br^- ions over the associated cations. The cations (except H^+ ions) have only a little or no influence on the selective oxidation of hydrazine to H_2O_2. It may be noted that, like in the direct H_2-to-H_2O_2 oxidation, cations (except H^+ ions) play a very little or no role for the selective formation of H_2O_2 in the N_2H_4-to-H_2O_2 oxidation.

Table 8.5 Effect of bromide compound present in aqueous medium (pure water) on the formation of H_2O_2 in the oxidation of hydrazine sulfate by O_2 over the reduced Pd (5%)Al_2O_3 [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 2.3 mmol, concentration of Br^- = 4.7 $mmol.dm^{-3}$, O_2 flow rate = 10 $cm^3.min^{-1}$, reaction temperature = 25 ºC and reaction period = 0.5 h].

Bromide compound added to the reaction medium	Hydrazine sulfate conversion (%)	H_2O_2 formed per mol of hydrazine consumed (mol/mol)	H_2O_2 yield [a] (%)
HBr	100	1.22	60.9
NaBr	100	1.13	56.5
KBr	100	1.18	58.7
NH_4Br	100	1.22	60.9

[a] *Based on the consumption of hydrogen from hydrazine.*

8.4.3 Influence of Br^- Concentration in Reaction Medium

Results showing the influence of Br^- (introduced as KBr) concentration in the aqueous reaction medium on the activity/selectivity of the Pd/C and Pd/Al_2O_3 catalysts in the oxidation of hydrazine (from hydrazine sulfate) to H_2O_2 are presented in Figures 8.3 and 8.4, respectively. The results in Figure 8.3 show that, with increasing the Br^- concentration in the reaction medium, the H_2O_2 yield is increased and then passed through a maximum. At the higher Br^- concentrations both the hydrazine conversion and H_2O_2 yield are decreased.

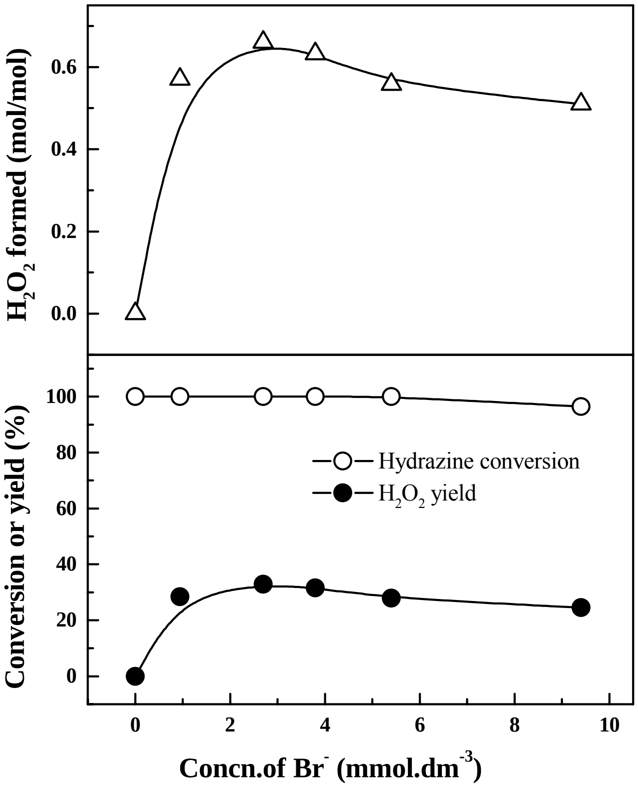


Figure 8.3 Effect of Br^- concentration in the aqueous medium on the hydrazine (from hydrazine sulfate) conversion, H_2O_2 formed per mol of hydrazine consumed and H_2O_2 yield in the oxidation of hydrazine by O_2 over reduced Pd (5%)/C catalyst [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 3.1 mmol, O_2 flow = 10 cm^3/min, reaction temperature = 25 ºC and reaction period = 0.5 h].

Results in Figure 8.4 show that the H_2O_2 yield in the hydrazine oxidation is increased and then leveled off with increasing the Br^- concentration in the reaction medium. In the absence of Br^- anions there is no formation of H_2O_2, hydrazine is oxidized with its 100% conversion to water.

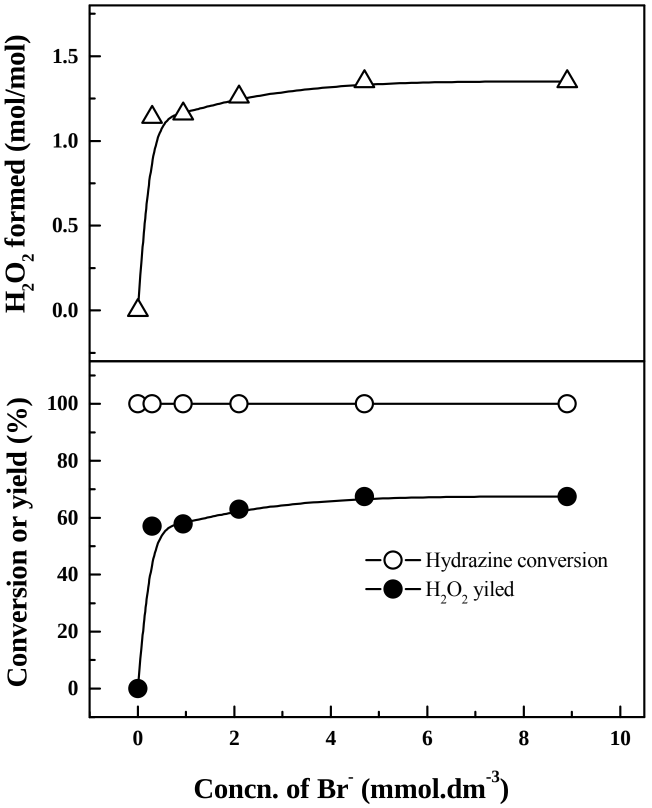


Figure 8.4 Effect of the concentration of Br⁻ in the reaction medium on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate consumed and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over reduced Pd (5%)/Al_2O_3 catalyst [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 2.3 mmol, O_2 flow = 10 $cm^3.min^{-1}$, reaction temperature = 25 ºC and reaction period = 0.5 h].

8.4.4 Influence of Halide Added to Pd/Al_2O_3 (or Ga_2O_3) Catalyst

Results showing the influence of different halides (F^-, Cl^-, Br^- and I^-) incorporated in the Pd/Al_2O_3 and Ga_2O_3 catalysts on their performance in the hydrazine sulfate oxidation (by O_2) in aqueous reaction medium are presented in Table 8.6. The results reveal that after the bromination of the catalysts, the H_2O_2 yield in the hydrazine oxidation is dramatically increased from zero to 61.5 and 60.5% for the Pd/Al_2O_3 and Pd/Ga_2O_3 catalysts, respectively. The incorporation of iodide in the catalyst causes a marked decrease in its activity for hydrazine conversion. The incorporation of F^- or Cl^- anions in the catalyst leads to the formation of H_2O, without formation of any H_2O_2 in the oxidation of hydrazine sulfate over the catalyst. The highly improved performance of the Pd/Al_2O_3 (or Ga_2O_3) in the hydrazize-to-H_2O_2 oxidation, after its bromination is attributed mostly to the poisoning and/or modification of the catalytic active sites, responsible for the dissociation of dioxygen and H_2O_2 decomposition and thereby inhibiting the non-selective hydrazine to water oxidation.

Table 8.6 Formation of H_2O_2 in the oxidation hydrazine sulfate by O_2 over halogenated Pd/Al_2O_3 (or Ga_2O_3) catalysts (halide loading 1.0 wt %) in aqueous reaction medium (pure water) [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 2.3 mmol, O_2 flow = 10 cm^3/min, temperature = 25 ºC and reaction period = 0.5 h].

Halide incorporated in the catalyst [a]	Hydrazine sulfate conversion (%)	H_2O_2 formed per mol of hydrazine sulfate consumed (mol/mol)	H_2O_2 yield [b] (%)
Catalyst = Pd/Al_2O_3			
None	100	0.0	0.0
F	100	0.0	0.0
Cl	100	0.0	0.0
Br	100	1.23	61.5
I	10	0.0	0.0
Catalyst = Pd/Ga_2O_3			
None	100	0.0	0.0
F	100	0.0	0.0
Cl	100	0.0	0.0
Br	100	1.01	50.5
I	5.0	0.0	0.0

[a] *The halide addition was accomplished by depositing corresponding ammonium halide on the catalyst, followed by its calcination under flowing* N_2 *at 400 ºC for 1h .* [b] *Based on the hydrogen from hydrazine.*

8.4.5 Influence of Br^- Concentration in Pd/Al_2O_3 Catalyst

The results in Figure 8.5 reveal that there is an optimum concentration of Br^- in the brominated Pd/Al_2O_3 (≅1.25 wt %) for achieving highest H_2O_2 yield in the hydrazine sulfate-to H_2O_2 oxidation. With the increase in the amount of Br^- incorporated in the catalyst, the H_2O_2 yield is passed through a maximum. The hydrazine conversion is reduced but to a small extent at the higher Br^- concentrations in the catalyst.

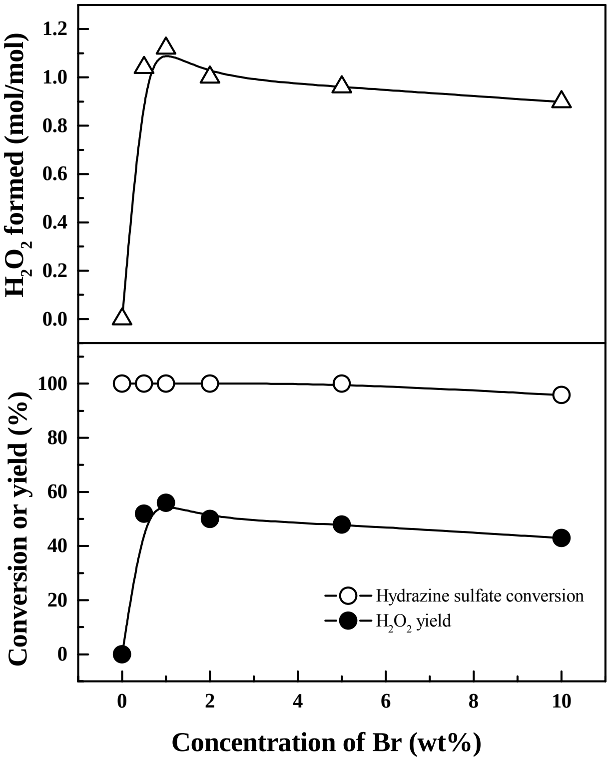


Figure 8.5 Effect of the concentration of Br^- in the brominated Pd (5%)/Al_2O_3 catalyst on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate consumed and H_2O_2 yield in the oxidation of hydrazine sulfate [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, amount of hydrazine sulfate = 2.3 mmol, O_2 flow = 10 cm^3/min, temperature = 25 ºC and reaction period = 1.0 h].

8.5 OXIDATION OF HYDRAZINE SULFATE TO H_2O_2 OVER BROMINATED Pd/Al_2O_3 CATALYST IN AQUEOUS REACTION MEDIUM

8.5.1 Influence of Reaction Temperature

Results in Figure 8.6 show a strong influence of the reaction temperature on the H_2O_2 yield in the hydrazine sulfate oxidation over the catalyst in aqueous medium. The H_2O_2 yield in the reaction is drastically reduced at the higher reaction temperature (65 ºC). The observed very low H_2O_2 yield at the higher reaction temperature is because of a large increase in the rate of decomposition of H_2O_2 formed over the Pd catalyst. At the lower reaction temperature (5 ºC), the hydrazine conversion is reduced but to a small extent.

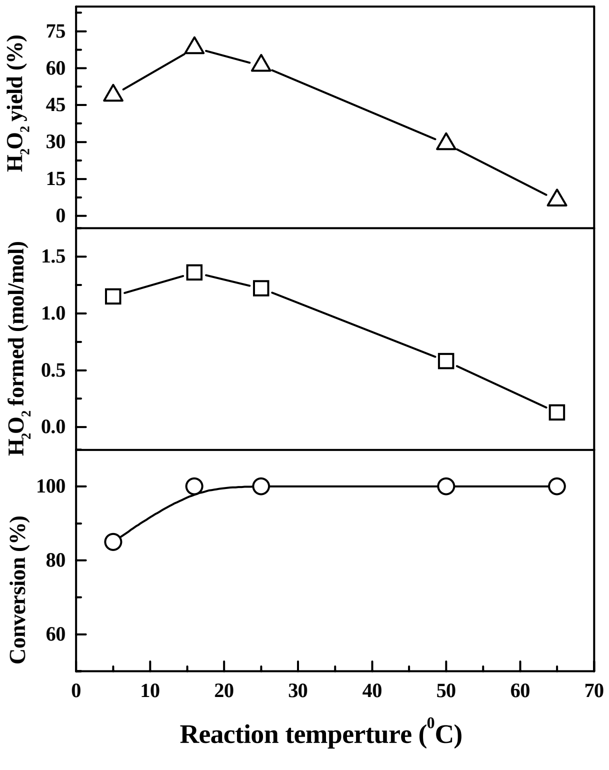


Figure 8.6 Effect of reaction temperature on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate consumed and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over the brominated Pd (5%)/Al_2O_3 catalyst (1 wt% Br) in aqueous medium [reaction conditions: amount of catalyst = 0.1 g, reaction medium = pure water (50 cm^3), hydrazine sulfate = 2.3 mmol, O_2 flow rate = 10 cm^3.min^{-1} and reaction period = 0.5 h].

8.5.2 Influence of Reaction Period

Results in Figure 8.7 reveal that, with increasing the reaction time, both the hydrazine conversion and H_2O_2 yield are increased. At the higher reaction period (after the complete conversion of hydrazine) the H_2O_2 yield is reduced because of the decomposition of H_2O_2 formed over the catalyst.

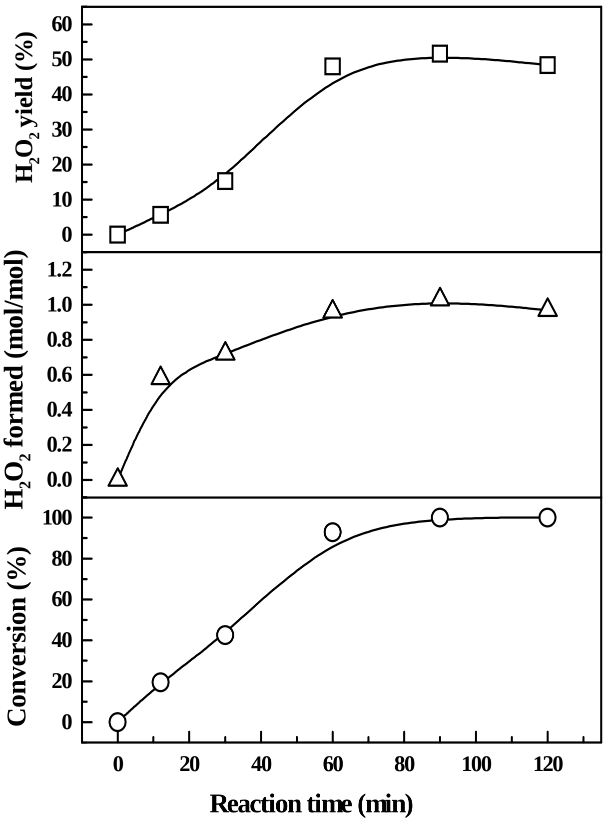


Figure 8.7 Effect of reaction time on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over the brominated Pd (5%)/Al_2O_3 catalyst (1 wt% Br) [reaction conditions: reaction medium = pure water (50 cm^3), amount of catalyst = 0.1 g, hydrazine sulfate = 6.2 mmol and reaction temperature = 25 ºC].

8.5.3 Influence of Hydrazine Sulfate Concentration

Results showing the influence of the initial concentration of hydrazine sulfate in aqueous reaction medium on the conversion hydrazine and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over the brominated Pd/Al_2O_3 catalyst is presented in Figure 8.8.

Both the hydrazine conversion and yield of H_2O_2 formed in the reaction are reduced at the higher hydrazine sulfate concentrations in the reaction medium. It may be noted that hydrazine sulfate has a limited solubility (3 g per 100 g water) in cold water. At the initial high concentration of hydrazine sulfate in the reaction medium, the partial conversion of hydrazine only takes place. The unconverted hydrazine and H_2O_2 formed in the reaction medium react further leading to the destruction of H_2O_2 formed.

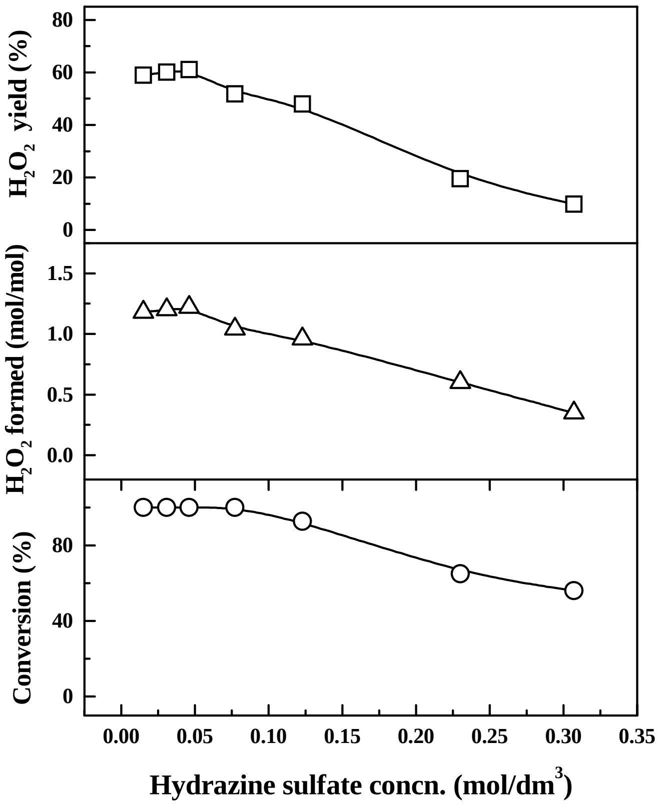


Figure 8.8 Effect of the initial hydrazine sulfate concentration in the reaction medium on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate consumed and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over the brominated Pd (5%)/Al_2O_3 catalyst (1 wt % Br) in aqueous medium [reaction conditions: amount of catalyst = 0.1 g, reaction medium = pure water (50 cm^3), O_2 flow rate = 10 $cm^3.min^{-1}$, reaction temperature = 25 °C and reaction time = 1h].

8.5.4 Influence of Acid (H_3PO_4) Added to Reaction Medium

Results in Fig. 8.9 show that the addition of acid (H_3PO_4) in the aqueous medium leads to an increase of the H_2O_2 yield in the hydrazine sulfate oxidation. In absence of acid, there is also significant formation of H_2O_2 in the hydrazine (from hydrazine sulfate) oxidation because of the release of the associated acid (H_2SO_4) molecules in the aqueous medium.

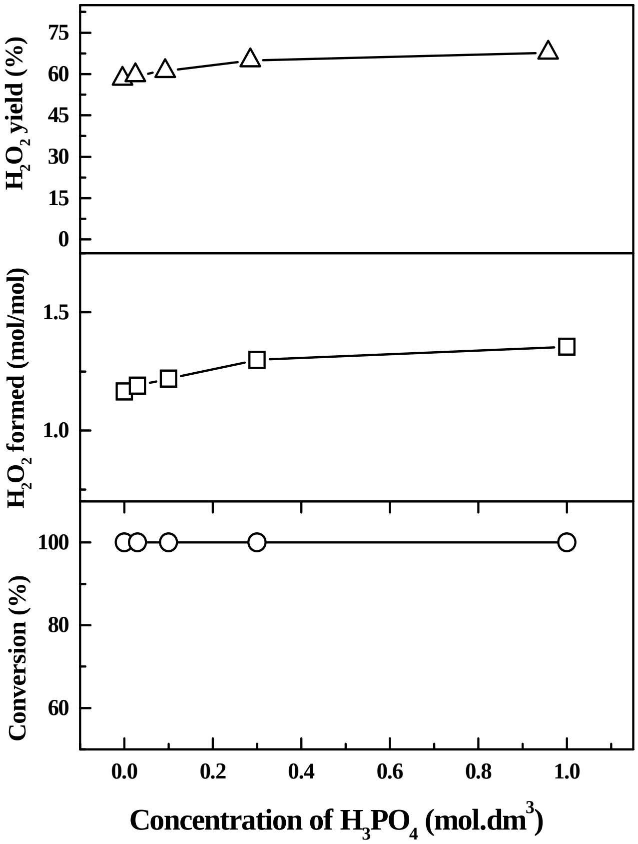


Figure 8.9 Effect of H_3PO_4 concentration in the aqueous medium on the hydrazine sulfate conversion, H_2O_2 formed per mol of hydrazine sulfate and H_2O_2 yield in the oxidation of hydrazine sulfate by O_2 over the brominated Pd (5%)/Al_2O_3 catalyst (1 wt% Br) in aqueous medium [reaction conditions: amount of catalyst = 0.1 g, reaction medium = pure water (50 cm^3), amount of hydrazine sulfate = 2.3 mmol, O_2 flow rate = 15 cm^3.min^{-1} and reaction period = 0.5 h]

8.6 GENERAL REMARKS

Although the hydrazine oxidation to H_2O_2 is not commercially feasible for the H_2O_2 production, it may be useful for the in situ H_2O_2 production in the synthesis of fine/speciality chemicals in aqueous medium. The work on the in situ generation of H_2O_2 for fine chemical synthesis in our group is in progress.

8.7 CONCLUSIONS

From the present studies on the hydrazine (from hydrazine hydrate or hydrazine sulfate) to H_2O_2 oxidation over the supported Pd catalysts, the following important conclusions can be made:

1. Very appreciable amount of H_2O_2 is formed in the interaction of O_2 with the hydrazine-reduced boron containing Pd catalysts in the presence of a mineral acid and bromide anions in the aqueous reaction medium. In the absence of boron (in the catalyst), acid and bromide anions, there is no formation of H_2O_2. The source for hydrogen for the H_2O_2 formation is the chemisorbed hydrazine during the catalyst reduction, as confirmed by the further studies.

2. Unlike in the direct H_2-to-H_2O_2 oxidation, the formation of H_2O_2 in the oxidation of hydrazine (by O_2) is non-hazardous; there is no involvement of explosive gas mixture. Moreover, in this process only environmentally benign by-product (N_2) and side product (water) are formed.

3. The formation of H_2O_2 in the oxidation of hydrazine takes place only when both the acid and Br^- ions are present in the reaction medium. In the absence of one of them, water is formed, without any formation of H_2O_2. The Br^- ions may be added to the reaction medium or incorporated in the catalyst. The presence of I^- in the acidic reaction medium or in the catalyst drastically reduces the hydrazine conversion over the catalyst, indicating a strong poisoning of the catalyst due to the presence of I^- ions.

4. The cations (except H^+ ions) have only a little or no influence on the H_2O_2 formation in the oxidation of hydrazine. The H^+ ions present in the reaction medium reduce the Pd catalyzed decomposition of H_2O_2 and also the reaction between the unconverted hydrazine and H_2O_2 formed in the reaction.

5. When hydrazine sulfate is employed as the source of hydrazine, addition of mineral acid in the aqueous medium is not essential because of the release of associated acid molecules (H_2SO_4) from the hydrazine sulfate after its dissolution in water, making its aqueous solution acidic ($pH < 2$).

6. Like in the H_2-to-H_2O_2 oxidation, both the H_2O_2 and H_2O forming reactions occur simultaneously over the catalyst and, in both the cases Br^- ions (present in the reaction medium or in the catalyst) promote the selective formation of H_2O_2, in the direct oxidation of hydrazine to H_2O_2,

7. The H_2O_2 formation in the hydrazine oxidation is strongly influenced by the other process conditions (viz. temperature, initial concentration of or salt and time).

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Suggestion For Futher Work

Because of the limited facilities and funds, the catalysts used in the investigations reported in this thesis could not be throughly characterized. Also, the reactions were carried out only at atmospheric pressure. Following further work on the topic in this thesis may be carried out :

- Characterization of the supported Pd catalysts for their Pd dispersion, Pd particle size and also for a change in their electronic properties due to the addition of different promoters.
- Improvement in the Pd catalyst performance (both the H_2O_2 selectivity and yield) in the H_2-to-H_2O_2 oxidation by studying synergetic effects of various metal and/or halide additives in the catalyst and optimizing the catalyst parameters.
- Influence of the total pressure and concentration of H_2 on the H_2-to-H_2O_2 oxidation and H_2O_2 hydrogenation reactions.
- Detailed studies of the influence of gas-liquid, liquid-solid and intra-partcle mass transfer on the H_2-to-H_2O_2 oxidation and H_2O_2 hydrogenation reactions.
- Detailed kinetics of the reactions over promising catalyst under wide range of the reaction conditions and optimization of the process conditions for the H_2-to-H_2O_2 oxidation.
- Development of supported Pd catalyst with the incorporation of both the acid function and bromide promoter in the catalyst itself, which is of great practical importance.
- Explotation of hydrazine-to-H_2O_2 oxidation for in situ H_2O_2 generation in the synthesis of fine chemicals.

PUBLICATION AND PATENTS

PUBLICATIONS BASED ON THESIS WORK

1. Drastic increase of selectivity for H_2O_2 formation in direct oxidation of H_2 to H_2O_2 over supported Pd catalysts due to their bromination.

   Vasant R. Choudhary, **Chanchal Samanta** and A. G. Gaikwad, Chem. Comm., (2004) 2054-2055.

2. Hydrogen peroxide formation in the interaction of oxygen with boron-containing Pd catalysts prereduced by hydrazine in aqueous acidic medium containing bromide anions.

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3. A novel green route for hydrogen peroxide : Non-hazardous/environ-friendly selective oxidation of hydrazine hydrate or salt to H_2O_2 over supported Pd catalyts at room temperature.

   Vasant R. Choudhary, **Chanchal Samanta** and P. Jana, J. Am. Chem. Soc., (communicated).

5. Large inhibition for the decomposition and hydrogenation of H_2O_2 leading to drastic enhancement in the H_2O_2 formation in direct oxidation of H_2 to H_2O_2 over Pd catalyts due to the presence of chloride or bromide anions in aqueous acidic reaction medium.

   Vasant R. Choudhary and **Chanchal Samanta**, J. Catal., (communicated).

5. Factors influencing H_2O_2 decomposition over Pd/Carbon catalyst in aqueous reaction medium.

   Vasant R. Choudhary and **Chanchal Samanta**, J. Catal., (to be communicated shortly).

6. Hydrogenation of H_2O_2 over Pd/Al_2O_3 in aqueous medium : Factors influencing H_2O_2 conversion under static and flowing H_2.

   Vasant R. Choudhary and **Chanchal Samanta**, Catal. Lett., (to be communicated shortly).

7. Direct H_2-to-H_2O_2 oxidation over Pd/Carbon catalyst in aqueous reaction medium containing different halides.

   Vasant R. Choudhary and **Chanchal Samanta**, J. Catal., (to be communicated shortly).

8. Direct H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions over Pd/Al_2O_3 catalyst : Influence of acid and halide present in the aqueous reaction medium.

   Vasant R. Choudhary and **Chanchal Samanta**, (to be communicated : J. Catal).

9. Direct oxidation of H_2 to H_2O_2 and H_2O_2 decomposition/hydrogenation over halogenated Pd/Al_2O_3 and Pd/C catalysts : Influence of halogen and its concentration in the catalyst.

   Vasant R. Choudhary and **Chanchal Samanta**, (to be communicated : App. Catal A).

10. Direct H_2-to-H_2O_2 oxidation and H_2O_2 decomposition over different supported Pd catalysts in presence of halide promoters added to aqueous acidic reaction medium or directly incorported in the catalysts.

    Vasant R. Choudhary and **Chanchal Samanta**, (to be communicated : J. Catal).

US AND INDIAN PATENT APPLICATIONS FILED

1. Method for drastically improving both the selectivity and yield of hydrogen peroxide in the direct oxidation of hydrogen to hydrogen peroxide over a sloid catalyst comprising palladium
   Vasant R. Choudhary, **Chanchal Samanta** and P. Jana, (date of file 05.04.2004).
2. A novel process for the production of hydrogen peroxide from hydrazine or hydrazine salt
   Vasant R. Choudhary, **Chanchal Samanta** and P. Jana, (date of file 20.04.2004).

PAPERS PRESENTED IN SYMPOSIUM/SEMINARS

1. Direct oxidation of H_2 to H_2O_2 over Pd/Carbon : Influence of halide promoters present in acidic reaction medium.

   Chanchal Samanta and Vasant R. Choudhary, Symposium : Catalysis-Concept to Practice, 26-27 June, 2002, NCL, Pune.
2. Direct oxidation of H_2 to H_2O_2 over Pd/Al_2O_3 : Influence of halide promoters present in acidic reaction medium.

   Chanchal Samanta and Vasant R. Choudhary, National Workshop on Catalysis. Loyala College, Chennai 6-7 Jan 2004.
3. Direct oxidation of H_2 to H_2O_2 over Pd/SiO_2 catalyst : Influence of halide promoters added to the reaction medium or incorporated in the catalyst.

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