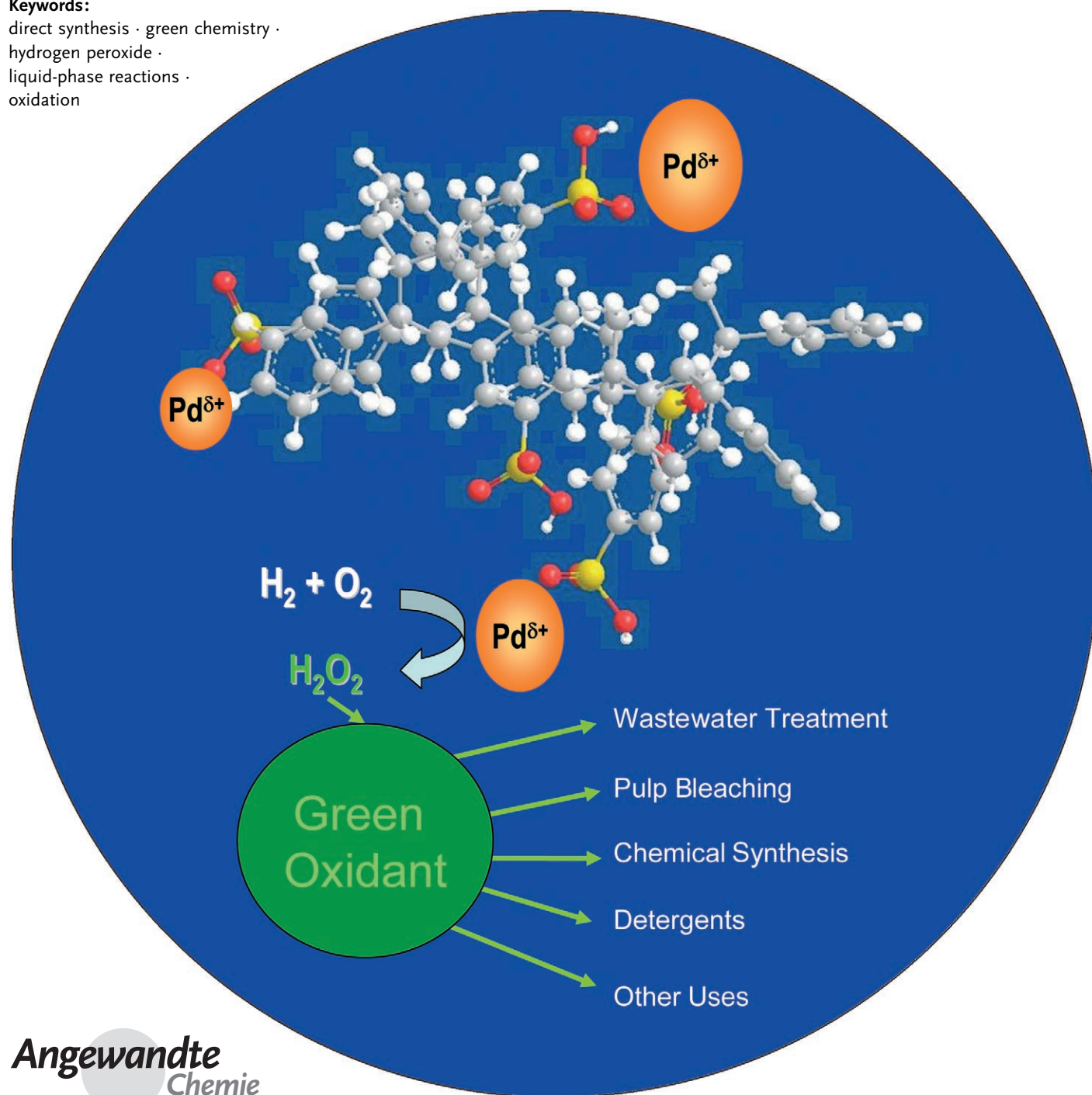


Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process

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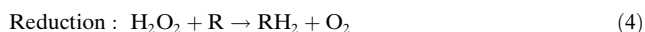
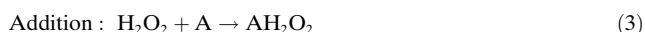
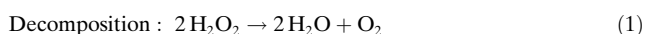
direct synthesis · green chemistry ·
hydrogen peroxide ·
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oxidation



Hydrogen peroxide (H_2O_2) is widely used in almost all industrial areas, particularly in the chemical industry and environmental protection. The only degradation product of its use is water, and thus it has played a large role in environmentally friendly methods in the chemical industry. Hydrogen peroxide is produced on an industrial scale by the anthraquinone oxidation (AO) process. However, this process can hardly be considered a green method. It involves the sequential hydrogenation and oxidation of an alkylanthraquinone precursor dissolved in a mixture of organic solvents followed by liquid–liquid extraction to recover H_2O_2 . The AO process is a multi-step method that requires significant energy input and generates waste, which has a negative effect on its sustainability and production costs. The transport, storage, and handling of bulk H_2O_2 involve hazards and escalating expenses. Thus, novel, cleaner methods for the production of H_2O_2 are being explored. The direct synthesis of H_2O_2 from O_2 and H_2 using a variety of catalysts, and the factors influencing the formation and decomposition of H_2O_2 are examined in detail in this Review.

1. General Aspects of the Chemistry of Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) was first recognized by Thenard in 1818 as the product of the reaction of barium peroxide with nitric acid. Hydrogen peroxide is a versatile oxidant that is effective over the whole pH range with high oxidation potential ($E_o = 1.763$ V at pH 0, $E_o = 0.878$ V at pH 14) and water as the only coproduct. Equations (1)–(5) summarize the reactions that hydrogen peroxide may undergo, depending on the type of substrate: decomposition, oxidation, molecular addition, reduction, and substitution.



The decomposition of hydrogen peroxide [Eq. (1)] must be controlled because the reaction produces gaseous oxygen and heat ($100.4 \text{ kJ mol}^{-1}$). The rate of decomposition depends on the temperature and concentration of the peroxide, as well as on the presence of impurities and stabilizers. Peroxide decomposes in the presence of many substances, for example most of the transition metals and their compounds, as well as certain organic compounds, which catalyze the decomposition. The decomposition reaction is also catalyzed by the enzyme catalase, whose main function in the body is to remove the toxic by-products of metabolism and to reduce oxidative stress. The rate of decomposition of a solution of H_2O_2 can be minimized by the removal of impurities and

From the Contents

1. General Aspects of the Chemistry of Hydrogen Peroxide	6963
2. Requirements in an Expanding Market	6963
3. Large-Scale Production	6965
4. Emerging Alternatives	6970
5. Other Methodologies	6977
6. Summary and Outlook	6979

addition of stabilizers. Sodium pyrophosphate is often employed as a chelating agent for catalytic impurities. Another option is the use of sodium stannate, which forms a protective colloid.

Hydrogen peroxide is a strong oxidant [Eq. (2)], which can oxidize a broad variety of inorganic and organic substrates in liquid-phase reactions under very mild reaction conditions. In the liquid phase, hydrogen peroxide binds molecularly to metal peroxides (M_2O_2 , $M = \text{alkali metal}$; or $M'O_2$, $M' = \text{alkaline-earth metal}$), oxoacid salts, zirconyl acetate, percarbonates, urea (to form urea–hydrogen peroxide adduct, UHP), and nitrogen compounds [Eq. (3)] to form crystalline peroxyhydrates. As a strong reducing agent, hydrogen peroxide reduces other stronger oxidizing compounds, such as $KMnO_4$, $Ce(SO_4)_2$, $NaClO$, and Cl_2 [Eq. (4)]; $KMnO_4$ and $Ce(SO_4)_2$ are used as standards for the volumetric determination of hydrogen peroxide. Substitution reactions of hydrogen peroxide with organic reagents produce a variety of peroxido compounds [Eq. (5)] that are widely used in organic synthesis and a number of applications.

2. Requirements in an Expanding Market

Hydrogen peroxide is currently produced almost exclusively with the anthraquinone oxidation (AO) process,^[1,2] in which hydrogen, atmospheric oxygen, and an anthraquinone derivative (typically 2-ethylantraquinone) are employed in the reaction cycle, the latter acting as a “reaction carrier”. The crude hydrogen peroxide obtained is then purified and concentrated and is usually marketed with an added stabilizer as aqueous solutions at concentrations of 35, 50, and 70 % by

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weight. For certain applications, such as in detergents, it is commonly delivered as a stable solid precursor such as sodium perborate or sodium percarbonate, which produce hydrogen peroxide in solution. Owing to its low molecular weight, hydrogen peroxide is a more efficient oxidizing agent than other oxidants, such as nitric acid and sodium hypochlorite (Table 1). It is a stable and safe chemical when

Table 1: Common industrially oxidants available.

Oxidant	Active oxygen (% w/w)	By-product
H ₂ O ₂	47.1	H ₂ O
<i>t</i> BuOOH	17.8	<i>t</i> BuOH
HNO ₃	25.0	NO _x , N ₂ O, N ₂
N ₂ O	36.4	N ₂
NaClO	21.6	NaCl
NaClO ₂	35.6	NaCl
NaBrO	13.4	NaBr
"KHSO ₅ " ^[a]	10.5	KHSO ₄
NaIO ₄	29.9 ^[b]	NaI
PhIO	7.3	PhI

[a] Stabilized and marketed as the "triple salt" 2KHSO₅·KHSO₄·K₂SO₄ (oxone). [b] Assuming that all four oxygen atoms are used.

handled correctly and offers the advantage of being soluble in water and many organic solvents or in the substrate itself. H₂O₂ has an environmentally benign profile since it decomposes to give only water and oxygen as the only reaction products, which makes it one of the cleanest, most versatile chemical oxidants available (Figure 1). These characteristics render hydrogen peroxide an environmentally safe oxidizing agent for many large-scale applications, such as pulp and paper bleaching, textile applications, detergent applications, wastewater treatment, and chemical oxidation processes.

One of the most important applications of hydrogen peroxide is currently its use in pulp and paper bleaching.^[3–6] Its use for this process replaces chlorine-based bleaches and avoids halogenated products in waste streams. Its use as a bleach relies on the hydrogenperoxide(1–) anion in alkaline media, which eliminates various chromophores in the lignin structures. In a similar manner to that described for the bleaching of tea stains, the carbonyl structures are prone to react with nucleophilic HO₂[–]. As well as for colored lignin residues in chemical and mechanical pulp, hydrogen peroxide

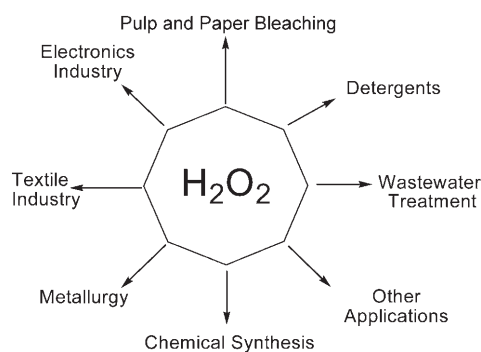


Figure 1. Principal uses of hydrogen peroxide.

is also used in the bleaching of recycled paper. For this process, a combination of H₂O₂ and reductive bleaching steps with sodium dithionite are employed to remove the printing dyes.

Hydrogen peroxide is widely used as a bleaching agent in the textile industry. It has advantages over other alternatives such as sodium hypochlorite and sodium hydrosulfite in that it is suitable for continuous processing, has no severe toxicity or effluent problems, and is noncorrosive.

Color-safe laundry bleaches containing hydrogen peroxide have increasingly replaced bleaches containing hypochlorite. In this case, the hydrogen peroxide is used with stable precursors such as sodium percarbonate and sodium perborate, which release hydrogen peroxide when dissolved in water. Sodium percarbonate is being increasingly used in preference to sodium perborate in detergent formulations because of its lower dissolution temperature in water. Detergent or bleach compositions formulated with sodium percarbonate/perborate have strong stain-removal capabilities, are color safe, brighten colors, and do not lead to yellowing or darkening of the fabric, which is a problem with bleaches containing hypochlorite. Sodium percarbonate/perborate is effective as a disinfectant against bacteria and viruses.

Hydrogen peroxide is used in municipal wastewater treatment for the removal of hydrogen sulfide (H₂S), which forms in sewer pipes. The most significant environmental application of hydrogen peroxide is the treatment of a broad variety of industrial wastes. Cyanide, thiocyanate, nitrite, chloride, hypochlorite, and organic matter can be efficiently



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removed by H_2O_2 treatment.^[7] Hydrogen peroxide is also used as a source of hydroxyl radicals in more complex advanced oxidation processes.^[8] Hydroxyl radicals are, after fluorine, the second most powerful oxidant available. After absorption in an aqueous scrubbing liquor, oxides of nitrogen and sulfur, mercaptans, and several other toxic odorous components of waste gases can be removed by oxidation with hydrogen peroxide. Examples include the removal of NO_x during pickling processes, the deodorization of gaseous effluents from animal carcasses, and the oxidation of sulfur dioxide. Hydrogen peroxide can be used as a source of oxygen, in the biological treatment of bulking sludges, and for the prevention of denitrification in settling tanks. The in situ bioremediation of contaminated soils has recently been developed. This process consists of the injection into the ground of microorganisms and nutrients together with hydrogen peroxide as a source of oxygen.

Hydrogen peroxide currently finds many applications in the chemical industry. It is employed, either directly or following transformation into a peroxocarboxylic acid, in the manufacture of many organic and inorganic chemicals, for example, hydrazine, cyanogen, cyanogen chloride, bromine, iodic acid, high-purity ferric sulfate, perborates, and percarbonates. Typical applications of hydrogen peroxide in organic syntheses include oxidation,^[9–26] epoxidation, hydroxylation,^[27–29] and oxohalogenation reactions (flame retardants),^[30] as well as for the initiation of emulsion polymerization reactions (benzyl peroxide, lauryl peroxide).^[31]

A number of applications in mining and metal processing involve the hydrogen peroxide.^[32] Typical applications in this field include the extraction and purification of uranium, gold recovery, the extraction and separation of chromium, copper, cobalt, tungsten, molybdenum, and other metals, and metal finishing (etching, stainless steel pickling, non-ferrous metal finishing). High-purity hydrogen peroxide is used in the electronics industry for cleaning of germanium and silicon semiconductor wafers and etching printed circuit boards. For various electronic and semiconductor applications, high-purity hydrogen peroxide is available with total cationic impurity levels below 10 ppb (parts per billion), 1 ppb, 0.1 ppb, and 0.01 ppb. Hydrogen sulfide, S-containing hydrocarbons, nitrogen oxides, and sulfur dioxide can be removed by hydrogen peroxide from exhaust gases generated in chemical and pharmaceutical syntheses, the production of

graphite, titanium dioxide, and sulfuric acid, as well as in the combustion of sulfur-containing fuels.

The annual world production of hydrogen peroxide is approximately 2.2 million metric tons.^[6] About 50 % is used for pulp and paper bleaching and 10 % for textile bleaching. However, its use depends on the market region. The two major areas of demand in Europe are chemical synthesis, mainly in detergent applications (43 %), and pulp and paper bleaching (41 %; Figure 2). The demand for hydrogen perox-

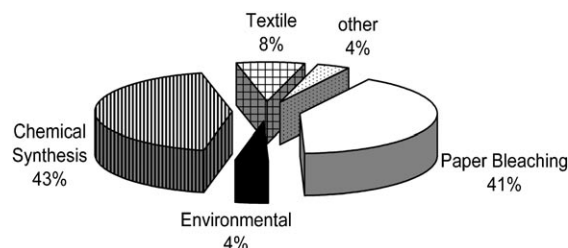


Figure 2. Distribution of hydrogen peroxide consumption in Europe.

ide in pulp bleaching is expected to grow slowly in the near future, but the commercialization of the integrated HPPO (hydrogen peroxide–propylene oxide) process, in which the hydrogen peroxide required for the epoxidation of propylene is produced on site, should lead to a large growth in the proportion of hydrogen peroxide used in chemical syntheses. BASF and Dow Chemical announced a new HPPO plant expected to begin production in 2008 with a yearly capacity of about 2×10^5 metric tons.^[33] Most segments of the Japanese hydrogen peroxide market are mature, and, as in Europe, the major areas of demand are pulp and paper production and chemical synthesis. Growth in the demand for chemical synthesis in Japan stems from the commercialization of Sumitomo's route to caprolactam. The circumstances in the USA are slightly different. The demand for hydrogen peroxide is dominated by the pulp and paper bleaching markets (about 59 %), whereas both organic and inorganic synthesis together represent only 13 % and electronics etching accounts for approximately 5 %.

3. Large-Scale Production

3.1. Anthraquinone Autoxidation

The first commercial anthraquinone autoxidation process (1 metric ton H_2O_2 per day) was introduced by IG Farbenindustrie in Germany in the 1940s. All subsequent anthraquinone-based production plants built worldwide in the following five decades maintained the original concept. However, important improvements were made in each of the four major steps: hydrogenation, oxidation, hydrogen peroxide extraction, and treatment of the working solution. A simplified flow diagram of the process steps is given in Figure 3. The main reactions involved the Riedl–Pfleiderer process,^[34] which currently accounts for the largest part of hydrogen peroxide production, are shown in Scheme 1. A 2-alkylanthraquinone



Jose Luis G. Fierro studied chemistry at the University of Oviedo (1973) and received his PhD at the Complutense University of Madrid (1976). In 1978 he took up tenure in the Institute of Catalysis and Petrochemistry in Madrid, where he was promoted to a Research Scientist in 1985 and to Professor in 1988. Over many postdoctoral stays he worked on NMR studies of micro- and mesoporous systems, oxygen isotopic exchange on metal oxide semiconductors, and the development of heterogeneous catalysts for oil refining. His current research focuses on heterogeneous catalysis, chemical technology, environmental catalysis, and the chemistry of materials.

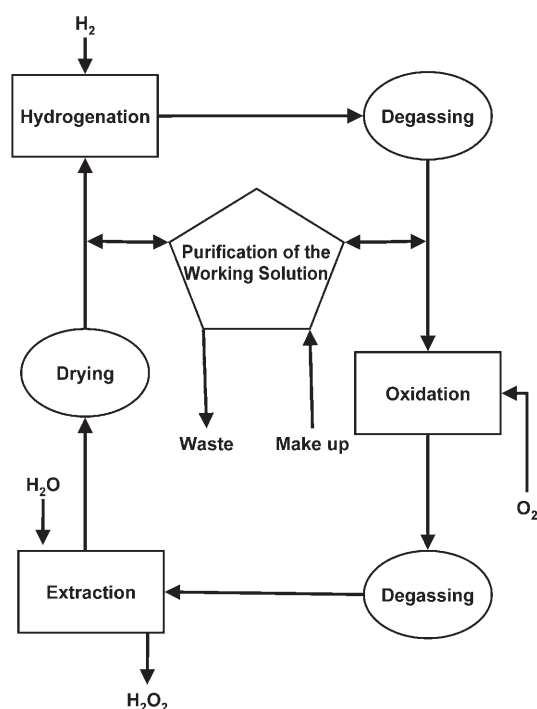
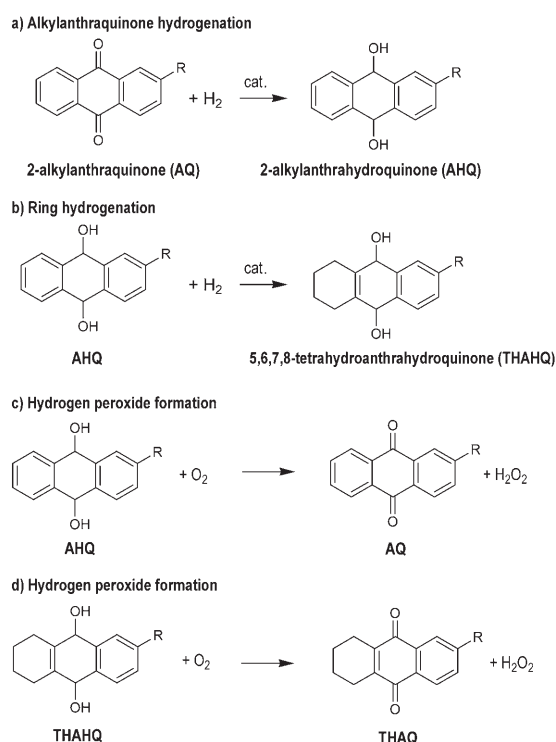


Figure 3. Block diagram of the steps involved in the anthraquinone method for the synthesis of hydrogen peroxide.

(AQ; usually 2-ethylantraquinone) in an appropriate solvent or mixture of solvents is hydrogenated catalytically to the corresponding anthraquinol or anthrahydroquinone (AHQ; Scheme 1 a). However, a side reaction is the hydrogenation of the unsubstituted aromatic ring to yield 5,6,7,8-tetrahydroan-



Scheme 1. Anthraquinone autoxidation reactions.

thrahydroquinone (Scheme 1 b). The solution containing the AHQ is separated from the hydrogenation catalyst and then oxidized with air to re-form the original anthraquinone (Scheme 1 c,d) and simultaneously produce equimolecular amounts of hydrogen peroxide.^[1,2] The hydrogen peroxide is stripped from the organic working solution by demineralized water in a countercurrent column to produce a solution that is usually 30% by weight H₂O₂. The aqueous H₂O₂ is then distilled to remove impurities and increase the concentration to as high as 70%, and the solvent/anthraquinone mixture is recycled. The reactions a–d in Scheme 1 represent only an oversimplification of the reactions involved in this process. A series of side reactions can occur in this process, which leads to a net consumption of anthraquinone.

The advantage of the AO process is the very high yield of hydrogen peroxide per cycle. However, its major disadvantages come not only from the side reactions, which require regeneration of the solution and the hydrogenation catalyst, but also from the separation steps involved in the removal of organic impurities from the hydrogen peroxide product. Despite the high yield of hydrogen peroxide per cycle, improvements have been proposed in the literature for each process step.

3.1.1. Hydrogenation

The working solution is hydrogenated over a catalyst at temperatures of 40–50 °C under a hydrogen partial pressure up to 4 bar. The extent of hydrogenation (conversion of AQ to AHQ) is carefully controlled and kept under 60% to minimize secondary hydrogenation reactions. Nickel and supported Pd catalysts have been used in the hydrogenation step.^[35,36]

Raney nickel catalysts were used in the original process for the reduction of AQ, but this process has two serious drawbacks: excessive hydrogenation and rapid deactivation. The second generation of catalysts, based on palladium, is more selective, but hydrogenation by-products can not be completely avoided (extra consumption of hydrogen and anthraquinone). Thus, a highly selective catalyst that hydrogenates only the carbonyl group and leaves the aromatic ring intact would be highly desirable. These requirements are fulfilled by a new generation of catalysts based on chemically reduced nanosized amorphous Ni/B^[37,38] and Ni/Cr/B^[39] alloys.

Amorphous Ni/B alloys show good performance in AQ hydrogenation.^[37] The hydrogenation activity of the amorphous Ni/B alloy increases upon La incorporation up to an atomic ratio of La/Ni = 0.034; the more efficient hydrogenation step leads to an improvement in the overall process. The better performance of these Ni/B catalysts can essentially be attributed to their amorphous structure, which was shown to be favorable for the hydrogenation reactions.^[40,41] The increase in activity can be ascribed to the better dispersion of Ni in the presence of La, which leads to a greater number of active hydrogenation centers.

The incorporation of chromium increases the stability of Ni/B catalysts, as is shown by the relatively constant gradients of AQ and THAHQ concentrations in Figure 4. A stable

reaction system minimizes the formation of side products and leads to increased yields of H_2O_2 .^[36] The yield of H_2O_2 increases sharply up to 100% over a reaction time of 60 min and then drops very slowly. The Cr^{III} species acts as a Lewis

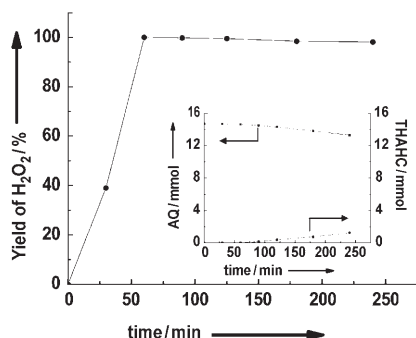
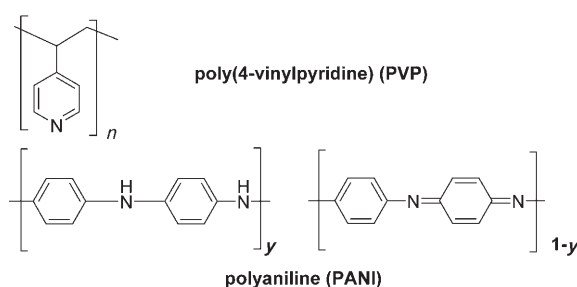


Figure 4. Yield of H_2O_2 and amounts of AQ and THAHQ in the working solution after oxidation as a function of time.^[43]

acid to activate the carbonyl group by accepting the lone electron pair on the oxygen atom.^[41] This activation favors the nucleophilic attack of the carbon atom by hydrogen dissociatively adsorbed on the nickel, thus leading to enhanced hydrogenation activity of the carbonyl group and hence greater selectivity in the hydrogenation of AQ to AHQ.

The most common catalysts for the hydrogenation stage of the anthraquinone process are based on palladium supported on Al_2O_3 , SiO_2 , and $\text{SiO}_2/\text{Al}_2\text{O}_3$.^[36] The selectivity of supported Pd catalysts can be improved by adding promoters or by changing the nature of the support. A new generation of hydrogenation catalysts for both slurry and fixed-bed operation are based on palladium catalysts supported on functionalized resins.^[42,43] In the patent literature,^[44] a Pd^{2+} -polyethyleneimine system is described that has recently been applied with success. Substrates such as poly(4-vinylpyridine) (PVP) and polyaniline (PANI) (Scheme 2) containing 1–10% Pd were shown to be efficient for AQ hydrogenation.^[45,46] Very small Pd^0 particles produced by reduction of palladium hydroxide (or oxide) precipitated on polymer grains show the highest activity and also the lowest tendency towards AHQ degradation.

Another substantial improvement of the hydrogenation step is based on the concept of the foam regime developed by Solvay.^[47] The hydrogenation reaction is conducted at moderate temperature (50–70°C) with a surface velocity of the hydrogenating gas in the range from 3 to 10 cm s^{-1} and a liquid surface velocity in the range of 0.5 to 1.0 cm s^{-1} , while the liquid/gas ratio is kept at below 0.15. Under these conditions, no degradation of the working solution by overhydrogenation is observed despite the high hydrogenation rates achieved. The hydrogenation reaction can also be enhanced by microwave radiation. An example is the approach of Kemira,^[48] which uses a 5%

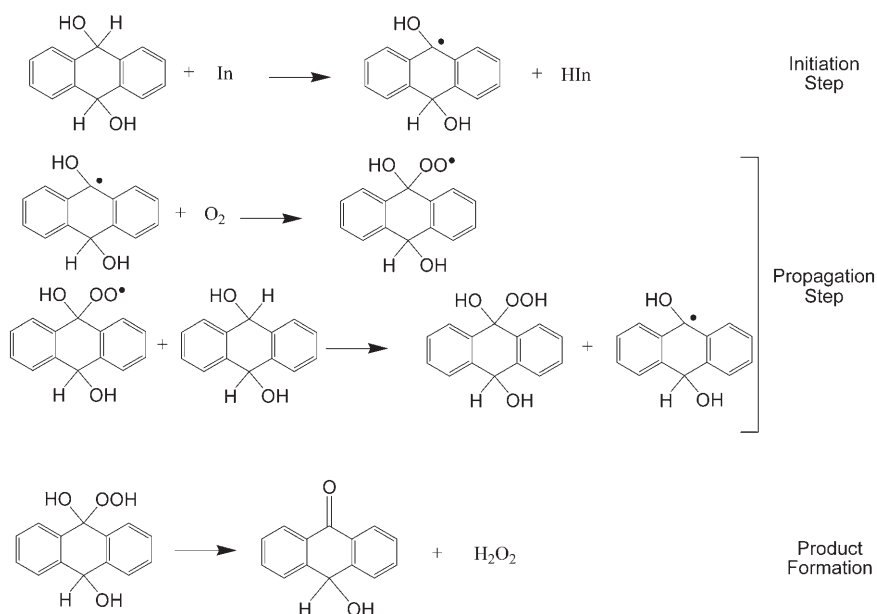


Scheme 2. Polymeric support for hydrogenation catalysts.

Pd/C catalyst and a working solution containing AQ/THAHQ in a mixture containing 70% aromatic hydrocarbon solvent as well as trioctylphosphate and tetrabutyl urea.

3.1.2. Oxidation

The hydroquinone is oxidized—usually by air—to produce hydrogen peroxide and to regenerate the quinone. The oxidation is carried out noncatalytically by bubbling air through the solution at 30–60°C and near atmospheric pressure. This reaction occurs by means of a well-documented free-radical chain mechanism (Scheme 3).^[49] In the first step, a tertiary hydrogen atom of AHQ is abstracted by an initiator, which can be an impurity in the hydrogen peroxide. The radical produced reacts with oxygen to form a hydroperoxy radical, which reacts with a second AHQ molecule to give an unstable alcohol hydroperoxide and an AHQ radical. The former product decomposes to a ketone and hydrogen peroxide, and the latter starts another propagation cycle. An improved method proposed by Degussa involves a secondary amine as catalyst for the oxidation of the a THAHQ-containing working solution.^[50] The oxidation reaction can be accelerated by addition of 0.1% w/w of a slightly water-soluble secondary amine such as di-*n*-octylamine to the



Scheme 3. H_2O_2 synthesis by the anthrahydroquinone oxidation reaction.

working solution. The hydrogen peroxide is extracted with water, and the yield is about 95 % of the theoretical amount of hydrogen peroxide.

The oxidation of THAHQ is another key reaction in the industrial production of hydrogen peroxide. This reaction occurs with molecular oxygen at the gas–liquid interface, and its rate is strongly affected by the mass transfer of oxygen across the liquid film.^[51,52] Therefore, both the interfacial area and the liquid containment volume in industrial reactors should be maximized. A second-order kinetic equation satisfactorily describes the reaction rates. It is possible that oxygen might form a complex with the hydroquinone, followed by the formation of two radicals that rapidly react to yield the corresponding hydroperoxide, as depicted in Scheme 3. The formation of radicals would be the rate-determining step, and consequently the reaction rates can be expressed by Equation (6), in which K_e is the equilibrium constant for the formation of the complex, k is the true kinetic constant, and $[C_R]$ is the concentration of the THAHQ radical.

$$r = k [\text{complex}] = k K_e [C_R] [O_2] \quad (6)$$

An activation energy of 62.7 kJ mol^{−1} was calculated from experiments performed under batch conditions^[54] at different temperatures. This result confirms that the radical mechanism [Eq. (6)] is more reliable than the classic autoxidation mechanism.

3.1.3. Extraction

Hydrogen peroxide can be separated from the working solution by different methods, but those most generally used involve extraction with water. The hydrogen peroxide in the working solution has a concentration between 0.8 and 1.9 % w/w and efficient extractors can recover more than 95 %. The concentration of hydrogen peroxide in this crude product is between 25 and 45 %, and further steps are required to meet commercial grades for purity and concentration.

An extremely useful concept for combining the oxidation of AHQ and the separation of hydrogen peroxide in a single step is the recently developed reactive separation process.^[54–59] This approach improves the yield of H₂O₂, because immediate separation of by-products avoids their participation in the reaction equilibrium. Reactive separation technology thus leads to substantial savings in capital and operation costs. When the oxidation of AHQ with oxygen and the extraction of hydrogen peroxide from the anthraquinone working solution are carried out in a sieve plate column, both the conversion of AHQ and the extraction efficiency increase with the superficial velocity of the gaseous phase.^[60] This increase may be caused by an increase in the contact time of oxygen (reactive gas) and the dispersed phase (reactive liquid phase) owing to their oscillatory motion and/or an increase in the containment volumes of dispersed and gaseous phases.^[61] Alternatively, the mass-transfer coefficient at the gas–liquid interface increases with increasing flow rate of the

reactive gas,^[62,63] and thus the rate of oxidation increases and the conversion of AHQ is improved.

3.2. Oxidation of Alcohols

3.2.1. 2-Propanol

Another alternative for producing hydrogen peroxide is the partial oxidation of primary or secondary alcohols, which produces an aldehyde or ketone as a coproduct.^[64,65] This liquid-phase process is based on the autoxidation of 2-propanol (Scheme 4). In this process, which was used by

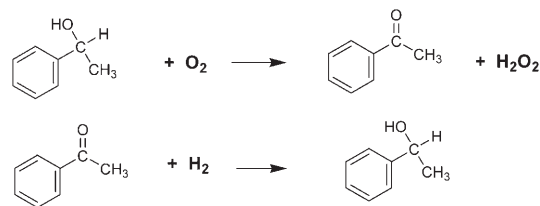


Scheme 4. H₂O₂ synthesis by the oxidation of a secondary alcohol.

Shell Chemical from 1957 to 1980, the 2-propanol/water azeotrope containing hydrogen peroxide is oxidized by an oxygen-enriched gas stream (80–90 % O₂) at moderate temperatures (90–140 °C) under pressure (10–20 bar). To reduce the formation of acetic acid and other by-products, the isopropyl conversion per cycle is kept below 15 %, and the oxidation reaction is conducted in several consecutive steps at decreasing temperatures. The reaction vessel must be constructed with enamel-lined steel or passivated steel to avoid the decomposition of hydrogen peroxide formed. The product mixture containing unconverted 2-propanol, acetone, and hydrogen peroxide is separated by evaporation. Water and organic compounds are then further distilled to recover acetone and 2-propanol. The hydrogen peroxide, which concentrates at the base of evaporator, is diluted with water to maintain its concentration below 50 % and further purified in a countercurrent solvent-extraction column. The quality of the hydrogen peroxide produced by alcohol oxidation is worse than that from the AO process owing to the solubility of the alcohol in peroxide phase, which makes it difficult to obtain a high purity of H₂O₂.

3.2.2. Methylbenzylalcohol

Lyondell Chemical (formerly Arco Chemical) and Repsol Química developed in parallel a process for the production of hydrogen peroxide based on the oxidation of a methylbenzylalcohol (MBA; Scheme 5). MBA is a coproduct of their propylene/oxide/styrene process.



Scheme 5. H₂O₂ synthesis by oxidation of MBA.

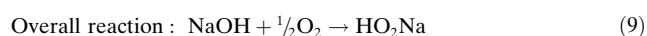
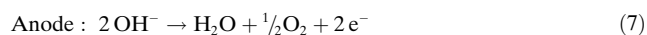
The oxidation of MBA in the liquid phase is usually conducted in the absence of catalyst at temperatures from 120 to 180 °C and pressures between 3 and 10 bar.^[66] The patent claims a conversion of MBA of 32 % and a selectivity for H₂O₂ of 97 %.^[66] The hydrogen peroxide content attained in the liquid phase of about 7.5 % is much higher than that achieved with the conventional anthraquinone-based process. The liquid hydrogen peroxide stream is fed to the extraction and distillation units to recover the hydrogen peroxide product at the desired concentration. The distillate is hydrogenated to recycle acetophenone back into methylbenzylalcohol.

Although in the original concept involves noncatalytic oxidation of the methylbenzylalcohol^[53] to give hydrogen peroxide and acetophenone, the oxidation can also be performed in the presence of a catalyst. Several nickel(II) β-diketone complex were employed as homogenous catalysts, as these complexes do not catalyze the decomposition of hydrogen peroxide.^[67] As a general rule, the addition of nickel increases the alcohol conversion, but the yield of hydrogen peroxide depends on the nature of the ligand employed. Cyclic β-diketones, such as 2-acetylcyclopentanoate or 2-acetylcyclohexanoate, increase the yield and selectivity for H₂O₂, but nickel complexes with basic ligands inhibit the oxidation reaction.

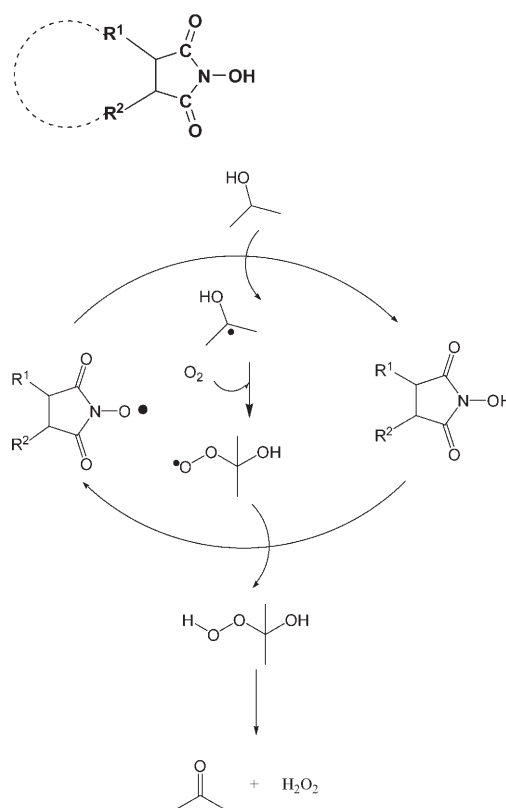
A recent patent^[68] claims that the oxidation of primary and secondary alcohols with molecular oxygen can efficiently yield hydrogen peroxide in the presence of an *N*-hydroxyimide (Scheme 6). The *N*-hydroxyimide in this process favors the formation of radicals from the secondary alcohol.^[69] A promoter can also be used in combination with the imide catalyst to enhance both the reaction rate and selectivity. Many compounds have been found to promote the target reaction, including carbonyl-containing organic compounds, transition-metal salts, and organic salts of Group 15 and 16 elements. A significant improvement of this process was achieved by adding a reactive solvent that allows cooxidation of the MBA.^[67,70,71] The cooxidation of hydrocarbons has been known for a long time,^[72–75] but this methodology has not been applied to the oxidation of secondary alcohols. This method affords high concentrations of H₂O₂ and very high selectivity for H₂O₂ with respect to consumed MBA (> 99 %).^[70,71]

3.3. Electrochemical Synthesis

Hydrogen peroxide can be synthesized by electrolysis of a dilute solution of NaOH in an electrochemical cell (Dow process). The anodic and cathodic reactions are given in Equations (7)–(9).



The alkaline peroxide is synthesized at an H₂O₂/NaOH weight ratio of 1:1.7 by cathodic reduction of oxygen on a



Scheme 6. Activation of *N*-hydroxyimide and proposed catalytic cycle for oxidation of secondary alcohols.

trickle-bed cathode. This cathode consists of graphite chips coated with carbon black and a fluorocarbon binder to facilitate O₂ transfer at atmospheric pressure.^[76,77] A cell operating at 2.3 V and 62 mA cm⁻² yields an NaOH/HO₂⁻ weight ratio of 1.6–1.8:1 at a current efficiency of 90 %. Combining the trickle-bed cathode with an ion-exchange membrane affords a 2.1 % w/w HO₂⁻ solution in 5.0 % w/w NaOH with 95 % current efficiency.^[78] The anolyte, which consists of a solution of NaOH in demineralized water, is fed into the anode compartment of the cell. A solution of Na₄edta (edta = ethylenediamine-*N,N,N',N'*-tetraacetate) is added to the anolyte as a trace-metal scavenger at a rate sufficient to maintain a solution concentration above 0.002 % in the electrolyte. This alkali peroxide technology is best suited to applications for which it is not necessary to separate the peroxide from the caustic soda in the product, for example, pulp bleaching. An integrated electrochemical synthetic process for pulp bleaching has been patented.^[79]

A new membrane-type electrochemical cell with a sulfuric acid solution as electrolyte has also been reported.^[80] The addition of poly(4-vinylpyridinium-*p*-toluenesulfonate) (PVPPTS) enhances the cell performance, and higher current density, lower cell voltage, and higher peroxide concentrations are obtained.

3.4. Comparison of Large-Scale Production Methods

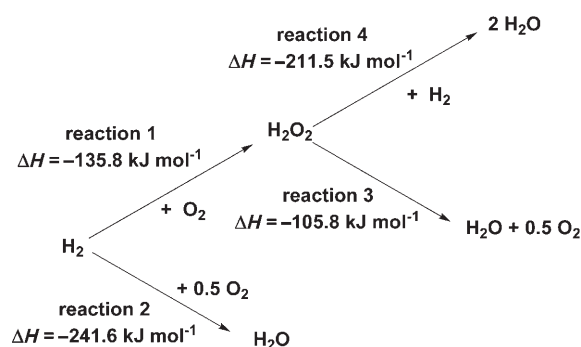
The AO process has supplanted all its competitors (primary and secondary alcohol oxidation, electrochemical) and accounts for more than 95 % of the world's production of H_2O_2 . One reason for this is that H_2O_2 is produced continuously at mild temperatures and direct contact of O_2 and H_2 is avoided. However, the AO process suffers from inefficiencies caused by mass-transport limitations in the hydrogenation and oxidation reactors, as well as organic contamination of H_2O_2 during its recovery by liquid–liquid extraction. As a consequence, heavier equipment and higher temperatures than those for kinetically controlled reactions are required. The difficulty in controlling the H_2 /AQ ratio and the AQ residence time during the hydrogenation step leads to the formation of by-products (overhydrogenated AQ and solvent), which must be continually removed. A further problem is cross-contamination of the phases as a result of contact between the working solution and water within the stripping column. Furthermore, the partition coefficient of H_2O_2 between water and the organic phase is not optimal, and thus distillation of both the concentrated and purified H_2O_2 is required, which is associated with considerable consumption of energy.^[1,2]

4. Emerging Alternatives

To take advantage of the full potential of hydrogen peroxide, a simple production process that can be implemented at the point of use is needed. This is the goal of recent approaches based on a clean technology that generates hydrogen peroxide directly from H_2 and O_2 .

4.1. Direct Synthesis

One alternative route to H_2O_2 that avoids the use of AQ is the direct synthesis from hydrogen and oxygen in the presence of a catalyst. A real breakthrough in H_2O_2 chemistry would be a one-pot process involving the direct synthesis of H_2O_2 from its elements^[81] and its direct application in an oxidation reaction.^[28,82] The reaction $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$ is in principle the simplest method to form hydrogen peroxide and should lead to a reduction in the capital investment and operating costs. Notwithstanding, the reaction scheme is more complex because of the occurrence of simultaneous or consecutive reactions, all of which are thermodynamically favored and highly exothermic (Scheme 7). Among these unwanted reactions are: a) the formation of water (reaction 2), b) the decomposition of hydrogen peroxide (reaction 3), and c) the reduction of H_2O_2 (reaction 4). Each of these reactions can be favored depending on the catalyst used, the promoters or additives in the reaction medium, and the reaction conditions. Although the catalytic liquid-phase oxidation of hydrogen for the production of hydrogen peroxide has been known since 1914^[83] and several patents have been issued since,^[84–118] this process has not yet been put into practice.



Scheme 7. Reactions involved in the direct production of H_2O_2 .

There are two major drawbacks to the direct synthesis of hydrogen peroxide. First, hydrogen/oxygen mixtures are explosive over a wide range of concentrations,^[88] so either the ratio of hydrogen to oxygen needs to be carefully controlled or a diluent such as nitrogen, carbon dioxide, or argon must be added. As the stoichiometry that corresponds to the best selectivity for H_2O_2 lies the explosive regime for O_2/H_2 mixtures (5:1 to 20:1), large quantities of nitrogen must be added for safety reasons, which naturally greatly reduces productivity.^[84] A strategy to avoid direct contact between O_2 and H_2 reagents is the use of catalytic membrane reactors, in which pure gases can be used. The other major problem in obtaining good selectivity for hydrogen peroxide over water is that catalysts for the production of hydrogen peroxide are also active for the combustion of hydrogen to water and the decomposition of hydrogen peroxide.^[119–122] As pure hydrogen peroxide is highly unstable and decomposes into water and oxygen, the reaction between H_2 and O_2 to yield hydrogen peroxide must be conducted in the presence of an appropriate solvent. Thus, three phases, namely gases (H_2 and O_2), a liquid (solvent), and a solid (catalyst) are required, which makes the process exceedingly complicated. Therefore, in many works attempts were made to minimize the mass-transport barrier between the gas phase and the solvent. For example, one innovative idea to deal with the inherent transport limitations of the process is the proposal to employ microbubbles of H_2 and O_2 .^[109]

These drawbacks, however, appear to be controllable, as Degussa-Headwaters have announced the construction in 2007 of a new production plant for the direct synthesis of hydrogen peroxide coupled with propylene oxide production.^[123] The patents of these companies reveal that an industrial method is possible involving an active catalyst based on palladium nanoparticles deposited on carbon and an appropriate solvent (in general an alcohol), as well as the use of concentrations of hydrogen outside the flammability limits.

4.1.1. Catalysts

The catalysts described in the literature are based on noble metals or combinations thereof supported on a great variety of substrates such as alumina, silica, and carbon.^[96,119–124] Palladium is the most suitable active metal in most catalyst formulations. Acids are often incorporated into the reaction medium in addition to the heterogeneous

catalyst to delay or prevent the decomposition of hydrogen peroxide, which occurs in the presence of base.^[119] Another approach involves the addition of catalyst poisons (i.e., halides) to delay the water production and increase the hydrogen peroxide selectivity.^[126] Although halides show good selectivity for H_2O_2 formation, they also delay the hydrogen conversion.^[119,121] This suggests that the halide ions are adsorbed on the metal centers that participate in the surface reaction between hydrogen and oxygen.^[125] Chlorides^[101] and bromides^[111] are the most commonly employed halides.^[125] An obvious choice as promoters are the hydrogen halides, as these combine the function of the acidic proton with the effect of the anion on the catalyst centers.^[90,91,125] Phosphoric acid is also often used as stabilizer of hydrogen peroxide because it has not only a stabilization effect but also the function of an acid.^[114] Special equipment is required for operation with highly concentrated acid solutions to avoid corrosion. The presence of acid solutions and halogen ions also favors the dissolution of the active metal,^[127,128] which results in deactivation of the catalyst. Colloidal Pd is believed to be involved in the catalytic cycle of palladium catalysts, which may, in part, be homogeneous. Although such a system is very interesting at a fundamental level, the management of a colloid would be difficult in a commercial process, because its recovery is not viable at the very low concentration of dissolved metal involved.

For these reasons, acidic supports are often used to reduce the required concentration of inorganic acid and hence minimize its impact on corrosion. Among the solid acids, regularly cited examples include a superacid consisting of tungsten oxide on a zirconia substrate,^[99] acidic supports such as molybdenum oxide on zirconia, vanadium oxide on zirconia, supported sulfuric acid catalysts,^[97,118,129] and fluorinated alumina.^[119] However, only very low yields of hydrogen peroxide are obtained with this methods. In contrast, excellent yields have been reported recently with neutral solutions and heterogeneous catalysts consisting of functionalized carbons with sulfonic acid groups,^[123] or sulfonic acid functionalized polystyrene resins ($\text{PS-SO}_3\text{H}$).^[130–133] These $\text{PS-SO}_3\text{H}$ resins exhibit moderate specific surface areas of approximately $40\text{ m}^2\text{ g}^{-1}$ and a high degree of cross-linking. Neither property seems to be detrimental to the liquid-phase reaction because the resins swell in the presence of solvent, and access of the reagents (H_2 and O_2) to the active sites is thus facilitated.^[134]

Catalysts prepared by anchoring Pd^{II} ions onto $\text{PS-SO}_3\text{H}$ ion-exchange resins (1.34–1.49% w/w Pd) are highly effective for the direct synthesis of hydrogen peroxide with methanol as solvent at 40°C . The consumption of hydrogen is in all cases fairly high ($>90\%$), and the H_2O_2 concentration profiles depend linearly on reaction time, which indicates that the reaction proceeds at a constant rate (Figure 5). The hydrogen peroxide production rates are very high (close to $1100\text{ mmol H}_2\text{O}_2\text{ h}^{-1}\text{ g(Pd)}^{-1}$) and are almost two orders of magnitude higher than the value for methods with acid-free solvents.^[135] The high performance of these catalytic systems results from the ability of the sulfonic acid groups of the resin to interact with and stabilize the Pd^{II} ions without further reduction to metallic palladium, as revealed by photoelectron

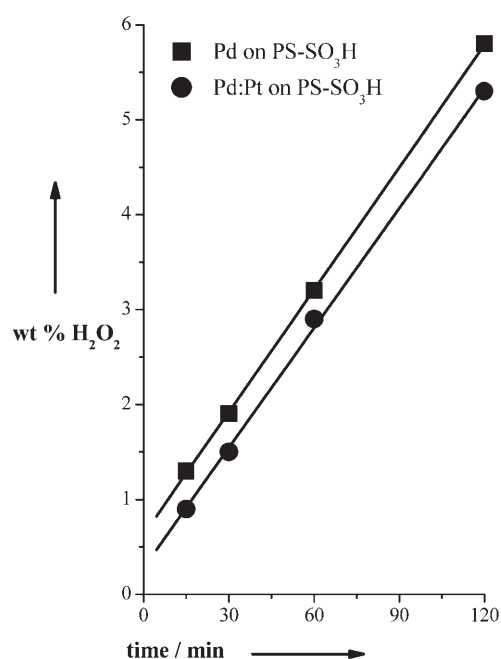


Figure 5. Hydrogen peroxide concentration profile versus time for the direct reaction of hydrogen and oxygen at 313 K .^[132]

spectroscopy. The $\text{Pd } 3d_{5/2}$ peak shows a component at 336.5 eV , which is assigned to PdO clusters, and a second component at 338.2 eV associated with Pd^{II} ions interacting with the SO_3H groups of the resins (Figure 6). The ratio of these species depends on the type of resin employed in the

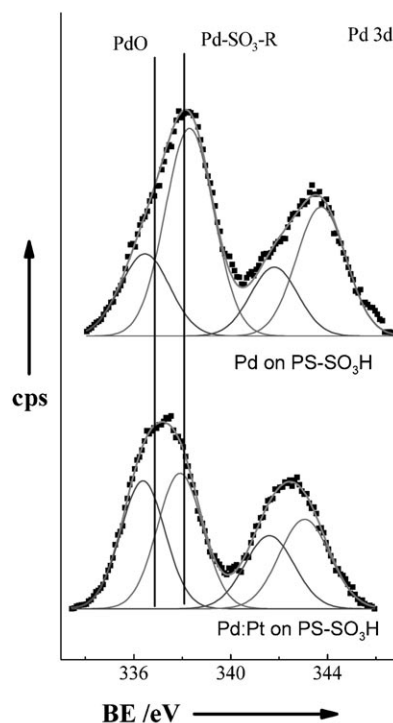


Figure 6. Photoelectron spectra of the $\text{Pd } 3d$ region of catalysts supported on $\text{PS-SO}_3\text{H}$ exchange resins.^[132] cps = counts per second, BE = binding energy.

preparation; resins with high surface densities of sulfonic acid groups lead to higher amounts of Pd^{II} ions interacting with the SO₃H groups. Thus, photoelectron spectroscopy provides direct evidence of the interaction between small palladium particles and the sulfonic acid groups of the resin.^[132] This interaction creates a positive charge on the Pd particles which enhances the selectivity for hydrogen peroxide.

Appropriate modification of the support substrate also appears to be of great importance for the optimization of catalyst performance. For example, hydrophobic substrates are especially well suited for this purpose as mass transport is facilitated after the formation of hydrogen peroxide. Thus, the extent of secondary reactions of hydrogen peroxide, such as hydrogenation or decomposition into water, is minimized. Supports modified with this objective include carbon treated with fluorine,^[101] inorganic supports such as alumina, silica/alumina, zeolites, etc. coated with a thin layer of hydrophobic polymer,^[137] as well as sulfonic acid functionalized carbon.^[138]

Most catalysts employed in the direct synthesis of H₂O₂ are based on palladium. These catalysts are activated by mild, carefully controlled reduction to form small metallic Pd clusters on the support surface. Recent studies propose that palladium nanoparticles with a high number of Pd atoms with a low degree of coordination are active and selective catalysts for hydrogen peroxide (Figure 7).^[118,139] Owing to their

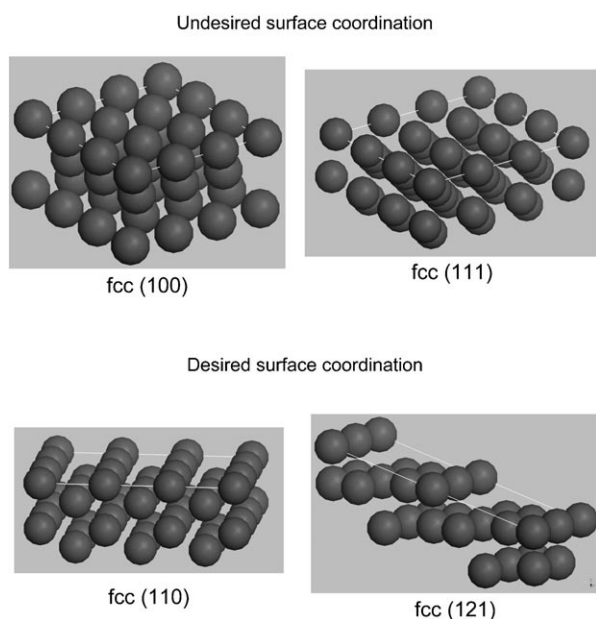


Figure 7. Desired and undesired surface coordinations of metal particles for the synthesis of H₂O₂ from H₂ and O₂.

electrodeficiency, these locations appear particularly well suited for interacting with promoters present in the reaction medium. This particular structure of Pd particles may be related to the promoter effect observed upon adding small amounts of a second metal to palladium.^[91,118,140] It can also be inferred that the improvement in performance is not associated with alloy formation between Pd and the second metal, as the proportion of promoter is very low.

It has recently been demonstrated that high selectivity for H₂O₂ can be achieved in the presence of cationic palladium species. No prior reduction of the catalyst is required in this case,^[123–132] and the selectivity for H₂O₂ is improved upon oxidation of the catalyst by oxygen^[136] or treatment with acid following impregnation.^[117,138] This observation may be understood by assuming that the reduced Pd species readily form H₂O₂ but are also able to oxidize the formed H₂O₂ to give H₂O at a high rate, whereas a mild oxidation treatment of the catalyst to some extent inhibits the metallic character of the metal particles, which results in a net higher rate of H₂O₂ production.^[142]

The in situ production of H₂O₂ from O₂/H₂ mixtures over supported Au catalysts was investigated with a view to a possible combination with the oxidation of propene to propene oxide.^[143,144] The presumed oxidant in this reaction is a surface hydroperoxide species formed on the metal surface. Studies of the energetics of the elementary reactions involved in the synthesis of hydrogen peroxide over noble-metal catalysts (Pd, Pt, Ag, and Au) by the bond order conservation Morse potential (BOC-MP) approach showed that the formation of hydrogen peroxide is most selective on gold catalysts.^[145] This observation supports the notion that gold is an active metal for the direct synthesis of hydrogen peroxide. Such an early prediction was then confirmed experimentally by using alumina,^[146] silica,^[147] titania,^[148] and iron oxide^[135] as substrates for gold particles. The catalytic behavior was also studied by theoretical calculations, which revealed that small gold clusters can act as viable sites for the direct synthesis of hydrogen peroxide.^[149–153] It was found that the rate of H₂O₂ formation decreased with an increase in the mean diameter of the Au nanoparticles.^[147] This tendency was also corroborated with an Au/SiO₂ catalyst, prepared by impregnation methodology and with a mean diameter of the Au particles of about 30 nm. Only H₂O but in no H₂O₂ was produced.^[147]

Substantial improvements in the yield of H₂O₂ can be obtained with Au catalysts containing a second metal. The best suited combination is gold and palladium,^[135,146,148,154,155] for which the rate of H₂O₂ production is higher than the sum of the rates provided by the individual monometallic systems.^[133,135,146,148,154,155] A atomic ratio of the two metals of 1:1 gives the best results.^[135,146,154] This effect in Pd/Au alloys was recently attributed to the isolation of Pd atoms within the gold matrix, whereby these isolated atoms are the most active catalytic centers.^[156] However, it should be emphasized that both the selectivity and production rate of H₂O₂ are far below the levels required for industrial application.

4.1.2. Solvents

Water is the most suitable solvent because it offers the greatest safety of the process, is nontoxic, nonflammable, and highly miscible with hydrogen peroxide. A major drawback is the very low solubility of reagent gases (both H₂ and O₂) in water, which strongly limits the rate of hydrogen peroxide production. Solvents other than water have been used with a view to overcoming this limitation, for example, a biphasic mixture of water and a fluorinated solvent, which leads to a

high solubility of oxygen and hydrogen.^[157,158] Mitsubishi has also reported a process for the direct generation of H_2O_2 in an organic solvent.^[159] However, contamination of the aqueous phase by the organic solvent is still an unsolved problem.

CO_2 is a more suitable as a solvent under both liquid and supercritical operating conditions. H_2 and O_2 are miscible with CO_2 in all proportions, and, even under subcritical conditions, the solubility of H_2 and O_2 in CO_2 is much higher than in organic solvents or water. However, supercritical conditions are preferred to avoid mass transport limitations between the gas and liquid phase.^[160] Furthermore, CO_2/H_2 mixtures do not react to form CO over a Pd catalyst at temperatures below 100°C .^[161–162] Also, the solubility of hydrogen peroxide in CO_2 is low, which means that H_2O_2 is expelled from the solvent once formed and a biphasic system is formed. The direct synthesis of H_2O_2 has been achieved following these principles with either CO_2 -soluble Pd^{II} or Pd^0 catalysts.^[163–165]

Mixtures of hydrogen peroxide and organic solvents are of practical importance, as they can be used in oxidation reactions in which H_2O_2 is the source of oxygen.^[9–32] Organic solvents, especially alcohols, are potentially better suited than water for the synthesis because of the greater solubility of H_2 and O_2 .^[166–168] The performance of a palladium-supported catalyst on a hafnium phosphate/viologen phosphonate material was studied in several different organic solvents (methanol, ethanol, 2-propanol, dioxane, and acetone), as well as in water, as the liquid phase.^[169] Even though the system appears to be limited by mass transfer at the liquid–gas interface, differences in the rate of H_2O_2 formation are observed among the organic solvents. Methanol gave the highest rate of reaction. The results obtained with water depend greatly on the acid added to the reaction medium (an acid is always required for the direct formation of H_2O_2). The rate of H_2O_2 formation in water with HCl, at least initially, was comparable to that observed in organic solvents. However, solvents such as methanol,^[170] acetone,^[114] and acetonitrile^[171] enhance both H_2 conversion and H_2O_2 selectivity. Solvents such as toluene and hexane increase the solubility of hydrogen and oxygen in the liquid phase,^[119] and hence enhance the reaction rate, although they impair the selectivity for H_2O_2 . These results underscore the fact that the solubility of the reagent gases O_2 and H_2 in the solvent is indeed an important condition for the production of hydrogen peroxide,^[172] but the catalytically active phase within the reaction medium also plays a deciding role. Thus, if the concentration of H_2 gas in the liquid phase is too high, the palladium component is reduced to Pd^0 metal, which in turn favors the decomposition/hydrogenation of hydrogen peroxide.^[142] A low concentration of dissolved hydrogen would result in a low reaction rate.

The principal role of the solvent is to increase the solubility of hydrogen in the liquid phase, although it can also act in different ways. Solvents such as ethanol (or oxidized species derived from it) and acetonitrile are prone to coordinate palladium and hence may act as inhibitors of the water-forming reaction.^[173,174] Another interesting observation is the almost complete suppression of Pd colloids in the bulk liquid when organic solvents are used.^[173,174] This

observation confirms that the supported Pd is the primary form of the active catalyst, and explains why catalysts become more stable in industrial reactors when through the use of solvents.

4.1.3. Membranes

A recent, elegant approach to direct hydrogen peroxide synthesis involves the use of membrane catalysts to keep the two reactants separate and thus avoid the major safety concerns of hydrogen/oxygen mixtures.^[136,137,141,175–179] In particular, dense palladium membranes display good performance for the liquid-phase synthesis of hydrogen peroxide from H_2 and O_2 .^[136] Another important role of these membranes is to supply atomic hydrogen to a catalyst deposited on the pores of the surface, which is in contact with an oxygen-containing liquid phase.

A significant increase in the selectivity for H_2O_2 was observed in a Pd membrane consisting of a thin film of Pd metal deposited on the stable surface of a Pd/Ag alloy on α - or γ - Al_2O_3 .^[136] The marked increase results from the bulk oxidation of the Pd film. The selectivity can be increased slightly further by covering the oxidized Pd film with a hydrophobic polymer membrane. This membrane is only permeable to H atoms, but inhibits the transport of molecular H_2 to the other side of the membrane, where O_2 gas is bubbled in the liquid phase ($0.02\text{ M H}_2\text{SO}_4$).^[136] As H atoms are more reactive than molecular H_2 , the permeated H atoms react with molecular oxygen to yield H_2O_2 at the catalyst surface. The H_2O_2 produced remains in the aqueous phase. The hydrophobic nature of the polymeric layer prevents further contact of the produced H_2O_2 with the catalyst surface. This design leads to complete consumption of H_2 , which indicates that the transport of H_2 through the membrane is rate-limiting. This situation allows the production of H_2O_2 to be modulated by controlling, for example, the pressure of H_2 . Besides conversion and selectivity, the H_2O_2 concentration attained in the liquid phase is essential for potential applications. Although the use of membranes avoids the formation of explosive mixtures, the reaction rate of H_2O_2 formation, which is essentially controlled by mass transport, is too low for industrial applications.

4.2. Photocatalysis

Photocatalytic reactions over semiconductor oxides have been investigated in some detail in recent years.^[175] Reactive O-containing species, namely OH^\bullet , O_2^- , and H_2O_2 , are usually formed at the surface of semiconductor oxides under UV irradiation.^[180–184] Illumination of an aqueous suspension of TiO_2 particles at an energy above 3.23 eV ($\lambda > 385\text{ nm}$ for anatase) excites an electron from the valence band (VB) to the conduction band (CB) of the semiconductor, while a positively charged hole is formed in the VB. The positive hole (h^+) oxidizes H_2O to form an OH^\bullet radical, and the electron reduces O_2 to O_2^- . Thus, the edges of the VB and CB represent the oxidation and reduction sites, respectively, on a TiO_2 particle. Hydrogen peroxide is produced through

dismutation of superoxide of a radical and also by recombination of hydroxyl radicals at the liquid interface or in the bulk solution.^[185,186] Both anatase and rutile crystalline forms of TiO₂ are photoactive but their reactivities are different. As the anatase phase is produced at lower temperatures than the rutile one, a higher density of surface defects is expected in the anatase phase. This may be the reason for the high catalytic activity observed for the production of hydrogen peroxide on anatase powder.

The concentrations of H₂O₂ formed on these UV-irradiated TiO₂ surfaces are in the micromolar range. The production of H₂O₂ can be increased by up to 20 times by the addition of small amounts of Cu^{II} solution to the suspension of TiO₂ particles. The concentration of H₂O₂ increases progressively with 0–50 μM added Cu^{II} and then levels off. Cu²⁺ ions are released from the surface of the Cu/TiO₂ particles upon illumination of an O₂-purged suspension and are redeposited on the surface upon purging with nitrogen.^[187] It is assumed that dissolved oxygen reacts with the photogenerated electron to form O₂^{•−} species.

Two alternative mechanisms have been proposed for the formation of H₂O₂.^[188,189] The first involves oxidation of H₂O by the photogenerated hole according to Equation (10). The second considers the reduction of dissolved O₂ by the photogenerated electron as shown in Equation (11), in which h_{VB}⁺ and e_{CB}[−] are the photogenerated hole in the VB and the electron in the CB, respectively.



Comparison of the amount of hydrogen peroxide produced in the presence and absence of O₂ over Cu^{II} ions allows the mechanism involved to be resolved. H₂O₂ is only formed when O₂ is bubbled through the TiO₂–Cu²⁺ suspension but not under O₂-free conditions.^[183] These results are conclusive that the mechanism of H₂O₂ formation involves the reduction of O₂ by the photogenerated e_{CB}[−] (Figure 8).

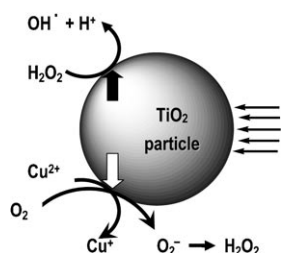


Figure 8. Photocatalytic formation of H₂O₂ and OH[•] in the presence of copper(II) ions.

The principal species involved in photocatalytic reactions on TiO₂ surfaces are OH[•], H₂O₂, and O₂^{•−}. The OH[•] radical is the most reactive of these species, and is also formed from H₂O₂ in the Fenton reaction in the presence of Fe²⁺ [Eq. (12)].^[190]



The tandem reactions of H₂O₂ production by the TiO₂–Cu²⁺ system and the decomposition of H₂O₂ into OH[•] radicals through the Fenton reaction can be exploited for the oxidation of organic substrates in the liquid phase. Similarly, the quantum yield of the photocatalytic oxidation of aromatic compounds by TiO₂ increases by about 16-fold in the presence of Cu^{II}.^[190] However, addition of H₂O₂ to the reaction system inhibits the photooxidation ability of TiO₂ owing to the formation of a peroxido complex on the TiO₂ surface.

As stated above, the most plausible mechanism of H₂O₂ formation involves O₂ reduction by an electron in the CB.^[182,183] However, little is known about the influence of the presence of anions or the nature and concentration of the hole scavenger. If H₂O₂ were formed mainly through dismutation of superoxide radicals then the rate of formation would be pH-dependent. F[−] ions adsorbed on the surface of TiO₂ particles have a strong influence on the photocatalytic oxidation mechanism of organic substrates.^[191,192] The photodegradation of phenol in the TiO₂/F system proceeds almost entirely through oxidation mediated by free OH radicals, whereas on pure TiO₂ about 10% if the reaction results from direct hole oxidation and 90% from adsorbed OH. It was reported recently that UV irradiation of fluorinated TiO₂ suspensions in water in the presence of oxygen and a hole scavenger leads to the production of H₂O₂ with a steady-state concentration of up to 1.3 mM when the TiO₂ surface is completely covered by fluoride ions.^[193] A possible role of the inert ligand is the inhibition of the formation of surface peroxido/superoxido species.

4.3. Fuel Cells

Large-scale production of hydrogen peroxide by electrolysis can be traced back to 1895.^[194] The Consortium für Elektrochemische Industrie investigated the electrolysis of sulfuric acid and successfully obtained peroxomono- and peroxodisulfuric acid, further hydrolysis of which yielded hydrogen peroxide. This proved to be an economically viable process for the production of highly concentrated solutions of hydrogen peroxide of high purity and stability. Electrogenerated hydrogen peroxide is currently employed as a bleach in the pulp and paper industry. The production of H₂O₂ relies on the electrolysis of O₂ in alkaline solutions in an electrochemical cell containing a carbon cathode.^[76,77] On-site electrochemical production of H₂O₂ for industrial applications requires a production method with high reaction rates, high efficiency, and low costs.

Hydrogen peroxide can be electrosynthesized through two-electron reduction of O₂ in acidic and alkaline media by using a large variety of three-dimensional electrodes (e.g., carbon-particle bed, reticulated vitreous carbon (RVC), and gas-diffusion electrodes. As described in Equations (7) and (8) in Section 3.3, the hydroperoxide ion HO₂[−] (the conjugate base of hydrogen peroxide) is produced in alkaline media through anodic oxidation of OH[−] as well as cathodic reduction of O₂. The overall four-electron reaction for this electrolytic process is depicted in Equation (13).



The electrochemical production of HO_2^- according to Equation (13) on an industrial scale in alkaline solution has been developed.^[34,35,195] The yield for a small cell with a carbon-felt cathode at a cell voltage of 1.6 V and 100 mA cm^{-2} at 60°C was 2 % w/w HO_2^- with a current efficiency of 75 %.^[195]

A promising alternative is the production of hydrogen peroxide with inexpensive fuel cells, which, unlike electrolytic devices, do not require electrical energy. Several methods have been proposed for the direct and continuous production of hydrogen peroxide in fuel cells. The simplest design consists of a fuel cell divided by an electrolyte membrane (nafion 117). The anodic face of this membrane (where H_2 is oxidized) is deposited with Pt, and the cathode face (where O_2 is reduced to hydrogen peroxide) is covered with graphite or an Au mesh.^[196] A current density of $10\text{--}30 \text{ mA cm}^{-2}$ was obtained for a 0.1M HCl solution in contact with the cathode. The current efficiency sharply dropped from 100 to 70 % during 3 h of operation. Another design of divided fuel cells comprises a membrane of polyfluorosulfonic acid monomer sandwiched between an H_2 -diffusion anode and an O_2 -diffusion cathode with different catalysts, and a water flow with O_2 is directly injected into the cathode. This system yields current efficiencies below 70 %.^[197]

The limiting factor in these designs is the O_2 concentration in the cathode compartment. This problem has been solved recently in a new fuel-cell setup for the synthesis of H_2O_2 .^[198] The underlying concept of this fuel cell is the application of a three-phase boundary (solid cathode/aqueous electrolyte/gaseous O_2) for the formation of hydrogen peroxide. The use of a porous membrane electrode prepared from carbon powder (vapor-grown carbon fiber, VGCF) allows an O_2 pressure as high as 1 bar at the active site at the three-phase boundary.^[199] In this way, the reduction of O_2 to H_2O_2 is enhanced and the consecutive degradation of H_2O_2 into H_2O is minimized. By feeding pure O_2 (1 bar) into the cathode, a concentration of H_2O_2 as high as 6 % w/w can be reached after 2 h at a high current efficiency of about 90 %. Both the formation rate of H_2O_2 and current density are slightly decreased when air is used instead pure O_2 , but the performance of the cell is not altered. For the industrial production of H_2O_2 by this method, the replacement of O_2 with air has a considerable cost advantage.

Another design for on-site production of HO_2^- is an undivided alkaline fuel cell (AFC) containing an H_2 -diffusion anode and a commercial O_2 -diffusion electrode.^[200] H_2 gas is oxidized to water in a two-electron reaction at the anode [Eq. (14)], and O_2 gas is reduced to HO_2^- at the cathode. The overall two-electron process of the AFC is given in Equation (15).



As for an electrolytic system, 1 mol of OH^- is also consumed per mol of HO_2^- generated. Quasi-steady-state behavior is observed when a fresh KOH solution is continuously injected into the cell at rates of 20 mL min^{-1} , and

current densities of about 100 mA cm^{-2} and current efficiencies close to 100 % are obtained for 1.0M KOH at 20°C .^[201] However, lower electrolyte flow rates lead to diminished electrogeneration of HO_2^- . A drop in the liquid flow rate from 20 to 2.1 mL min^{-1} diminishes the average current density by 11 % and the current efficiency by 27 %. This loss of cell performance may be related to the adsorption of HO_2^- on the anode surface, followed by its decomposition to O_2 catalyzed by the Pt anode.

Another important parameter for the production of HO_2^- is the external resistance between the electrodes, as this regulates the cell voltage and current density supplied by the flow AFC. For external resistances above 100Ω , the experimental conditions exert only a slight influence on the voltage–current density curves. Cell voltages over 0.650 V always lead to current densities lower than 10 mA cm^{-2} , which suggests that the cell process is limited mainly by the charge-transfer reactions.^[201] When the external resistance decreases from 100 to 0.10Ω , the activation can also be influenced by mass transfer and ohmic losses.

Another innovative approach for the production of hydrogen peroxide from H_2 and air with the simultaneous generation of electricity in a fuel cell relies on the chemical attachment of quinones to a carbon electrode.^[202] In the classical anthraquinone process (Section 3.1), the quinone is hydrogenated catalytically in an appropriate solvent to give the corresponding hydroanthraquinone (AHQ), which is then oxidized with air to re-form the original anthraquinone and simultaneously produce hydrogen peroxide (see Scheme 1). In this new approach, the quinone moiety is attached on the surface of a glassy-carbon electrode (Figure 9). Anthraquinone, and especially phenanthrenequinone (PQ), reduce oxygen in alkaline media to the superoxide radical. This reaction is mediated by the semiquinone anion of AQ or PQ ($\text{AQ}^{\cdot-}$, $\text{PQ}^{\cdot-}$), formed by the electrochemical reduction of the quinone. It has been proposed that these semiquinones provide the adsorption sites for oxygen; thus, the first step

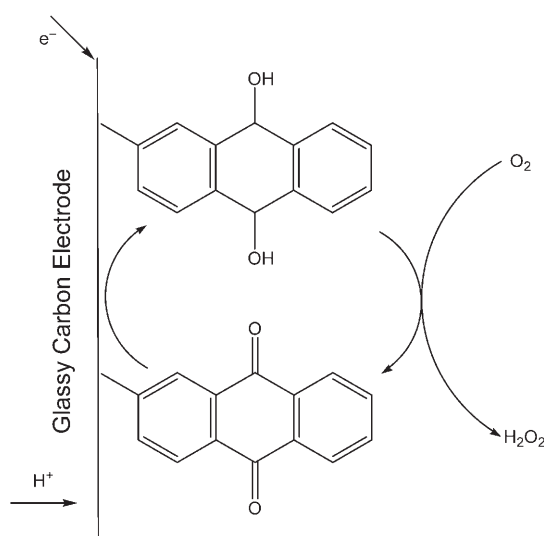


Figure 9. Attachment of a quinone on the surface of a glassy-carbon electrode for the electrochemical synthesis of H_2O_2 .

in the reduction of O_2 in alkaline solutions is the formation of superoxide. The adsorbed superoxide is then further reduced to peroxide.^[203] The reaction mechanism most probably involves partially reduced C=O surface groups, and it has been speculated that the very active native surface groups on glassy carbon interact with the *o*-quinone functionalities.^[204]

H_2O_2 generated in situ from O_2 and H_2 in a polymer electrolyte membrane fuel cell can be used for the direct hydroxylation of benzene to phenol with the simultaneous generation of electricity in both the liquid^[205] and gas phase.^[206] The essence of this process is the electrochemical production of hydrogen peroxide at the cathode through reduction of O_2 and subsequent chemical reaction with an organic substrate.^[207] Figure 10 illustrates the experimental setup of the membrane-electrode assembly. The electrochemical reduction of O_2 proceeds through two pathways, which are mainly determined by the electrocatalyst and electrode potential: direct four-electron reduction of O_2 into

H_2O [Eq. (16)] and two-electron reduction of O_2 into H_2O_2 [Eq. (17)].^[208]



The rate of phenol formation depends on the current and increases to a maximum value of $0.17 \text{ mmol min}^{-1}$ at 600 mA and 60°C (or $0.25 \text{ } \mu\text{mol min}^{-1}$ at 900 mA and 80°C) and then decreases at higher currents (Figure 10, bottom).^[209] From an electrochemical point of view, the current—as a kinetic parameter—accounts for the reaction rate of the electrochemical reaction, whereas the voltage—as a thermodynamic parameter—determines which reaction occurs. The observed dependence of phenol formation is assumed to be closely related to the in situ formation of H_2O_2 . At higher voltages, O_2 reduction may occur through the peroxide pathway. The amount of in situ generated H_2O_2 increases with the current, which leads to an increased rate of phenol formation.

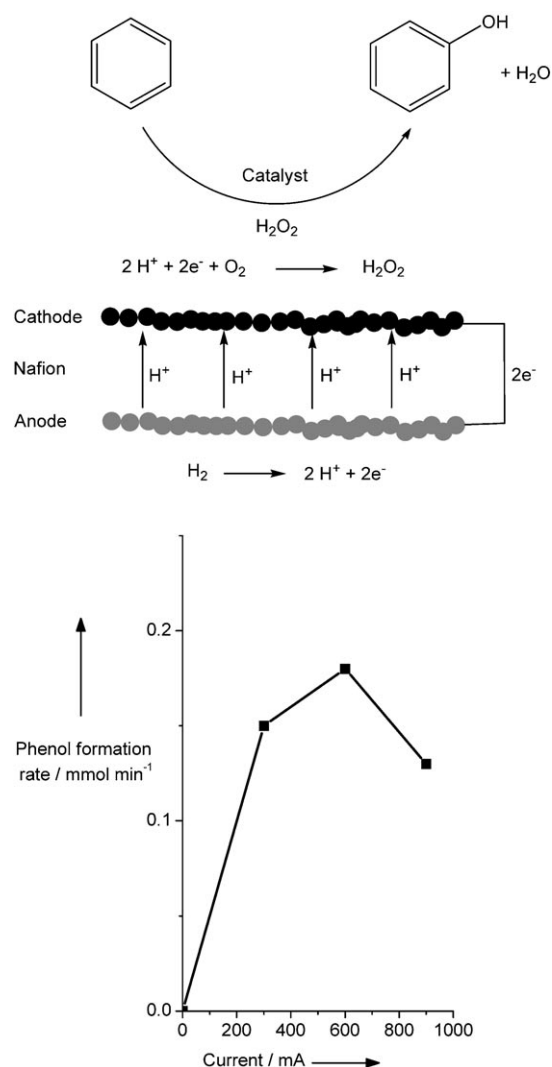
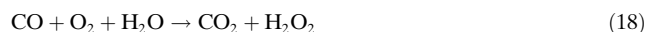


Figure 10. Top: Reaction scheme for phenol synthesis with in situ generated H_2O_2 in a proton-exchange membrane fuel cell (PEMFC). Bottom: Influence of current on the rate of formation of phenol at 60°C . Cathode: Pd black; anode: Pt black.^[209]

4.4. Synthesis from $CO/O_2/H_2O$ Mixtures

The production of H_2O_2 is possible not only by direct synthesis from H_2/O_2 mixtures, but also from mixtures of CO , O_2 , and H_2O [Eq. (18)], as first demonstrated in the presence of metal complexes.^[210]

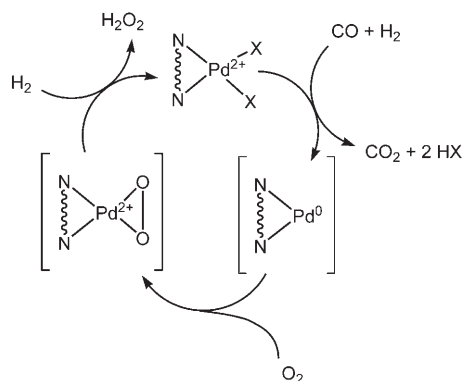


The reaction is thermodynamically favorable, as the standard free energy is highly negative ($\Delta G^\circ = -134.2 \text{ kJ mol}^{-1}$). The feasibility of the concept was first demonstrated by using homogeneous palladium triphenylphosphate complexes. The turnover (TON) values (moles of H_2O_2 produced per mol of Pd), however, were no higher than 5, thus the catalyst seem to be unsuitable for technical application. Furthermore, the system is rapidly deactivated as a result of oxidation of phosphate ligands and subsequent formation of colloidal palladium nanoparticles within the liquid phase. The efficiency of this reaction can be significantly improved (TON = 87) by using the more-stable ligand triphenylarsane,^[211] although not sufficient for practical application.

Ligand oxidation can be minimized by carrying out the reaction in a biphasic medium in the presence of palladium complexes with bidentate phenanthroline ligands.^[212–214] The formation of H_2O_2 depends strongly on the type of the substituent at the 2,9-positions of the phenanthroline ligand. Ligands bearing bulky substituents such as 2,9-di-*n*-butyl-1,10-phenanthroline or 2,9-diphenyl-1,10-phenanthroline do not form binuclear species as a result of steric hindrance close to the N donor atom, but instead give soluble Pd^0 complexes that dissociate rapidly to form colloidal Pd nanoparticles. In contrast, the highest rate of H_2O_2 production is obtained with the ligands 2,9-dimethyl-1,10-phenanthroline and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. The electron-

withdrawing Cl substituents in 2,9-dichloro-1,10-phenanthroline lead to lower reaction rates.

The palladium phenanthroline complexes are most stable when halogen-free solvents are used and HCl is added to the reaction mixture (Cl/Pd equimolar) to prevent the formation of colloidal Pd⁰ particles. Under these reaction conditions, H₂O₂ concentrations in the aqueous phase as high as 8% w/w can be achieved.^[212] Moreover, the catalyst can easily be recovered from the organic phase and used in consecutive reaction cycles with no significant loss in activity. However, only a little is known about the reaction mechanism. It is assumed that the Pd^{II} complex is reduced by CO to form a Pd⁰ complex (Scheme 8) via a palladium–hydride intermedi-



Scheme 8. Reaction mechanism for hydrogen peroxide synthesis from CO/O₂/H₂O mixtures with palladium N,N catalysts (NN is a bidentate N ligand).

ate.^[215] The subsequent oxidation of the Pd⁰ species to afford a Pd^{II} peroxido species and finally, in acidic media, hydrogen peroxide is already known.^[216] Although similar complexes, stabilized by phosphane ligands, have long been known,^[216] analogous nitrogen-donor complexes have not yet been reported.^[216,217] Carbon monoxide^[218] and carbon dioxide^[219] are inserted in the O–O bond of the [(PPh₃)₂Pd(η²-O₂)] complex, each yielding [(PPh₃)₂Pd(η²-CO₃)]. CO₂ likely first forms the percarbonate complex [(PPh₃)₂Pd(η²-CO₄)], which undergoes further transformation into [(PPh₃)₂Pd(η²-CO₃)] through oxidation of a PPh₃ ligand. Although both insertion reactions are feasible, the corresponding N,N-chelate complexes of palladium did not produce any H₂O₂, but only consumed CO and O₂ (2 CO + O₂ → 2 CO₂).^[217] Key issues for the development of this approach to the synthesis of H₂O₂ are a detailed knowledge of this mechanism as well as optimization of the ligands.

Comparatively little effort has been directed towards the development of heterogeneous catalysts for the production of H₂O₂ from CO/O₂/H₂O mixtures. Palladium supported on calcite and ruthenium on graphite display reasonable activity in this reaction, but selectivity for H₂O₂ is still far from satisfactory.^[220] Non-noble metal catalysts, such as rare-earth-modified alumina-supported nickel^[221] and alumina-supported copper^[222] systems also exhibit good performance, although only the performance of the latter surpasses that of noble-metal-based catalysts. The rate of H₂O₂ formation with

a Ni/La/B/Al₂O₃ catalyst with La/Ni atomic ratio of 1:15^[221] is comparable (0.07 mmol g⁻¹ h) to the value (0.100 mmol g⁻¹ h) achieved with the Pd/CaCO₃ catalyst. However, the catalyst becomes deactivated after a few hours under reaction conditions through poisoning by water and loss of surface-active nickel species, the active NiO species reacts with H₂O in the medium to form the catalytically inactive Ni(OH)₂ species. This species undergoes further reaction by phosphoric acid, added as a stabilizing agent for H₂O₂, to yield nickel phosphate, which is slowly solubilized. In contrast, the Cu/Al₂O₃ catalyst catalyzes the formation of H₂O₂ more than three times faster (0.326 mmol g⁻¹ h) than the Pd/CaCO₃ catalyst (0.100 mmol g⁻¹ h). Although supported noble metals such as Pd and Au are the best candidates for the direct synthesis of H₂O₂ from H₂/O₂ mixtures,^[223] this is not the case for CO/O₂/H₂O mixtures. In the limited known studies, the superior performance of these Cu/Al₂O₃ systems for the production of H₂O₂ from CO/O₂/H₂O mixtures is associated with a two-step reaction mechanism. This mechanism involves the water-gas-shift reaction (WGS) [Eq. (19)], followed by the reaction between O₂ and the H₂ produced by the WGS reaction.



Thus, it is plausible why the copper catalyst widely used in industrial-scale WGS reactions exhibits better performance than other supported metals for the synthesis of H₂O₂.^[224]

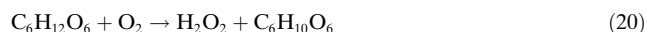
The catalytic activity of the Cu/Al₂O₃ system for the target reaction depends, among other reasons, on the type of solvent employed. Acetone appears to be the most appropriate solvent in that it affords a high H₂O₂ production rate (0.326 mmol g⁻¹ h), although this solvent may result in safety concerns because of the possibility of the formation of explosive peroxides. It has been shown for the related Pd/Al₂O₃ system that the reaction rate for H₂O₂ synthesis from H₂/O₂ mixtures is affected by the reaction medium. The transport of the reagent from the gas to the liquid phase appears to be the rate-limiting process.^[225] Furthermore, the particle size of the copper crystallites also influences catalyst performance. The highest reaction rate is observed for copper particles with an average diameter of 12 nm. These are generated by wet reduction of the Cu²⁺ precursor with an aqueous solution of KBH₄ in presence of KOH.^[222]

5. Other Methodologies

5.1. Bioinspired Approach

Hydrogen peroxide is formed in living organisms either through one-electron reduction of dioxygen or as a by-product of autoxidation reactions. The synthesis is enzymatic, and organic substrates are often oxidized by dioxygen. The reduction step of oxygen is often overshadowed by two major parasitic reactions which result in the loss of product. H₂O₂ is oxidized above pH 7 to O₂, but reduced to OH⁻ below pH 7. H₂O₂ can also be lost by dismutation into OH⁻ and O₂. The enzyme galactose oxidase is a versatile biocatalyst that not

only oxidizes the primary OH groups of galactose to form the corresponding aldehyde but also allows the conversion of simple primary alcohols.^[226,227] The enzymatic oxidation of organic substrates is a conceptually simple and safe approach to the production of hydrogen peroxide under very mild conditions [Eq. (20)]. This is illustrated by the flavoenzyme glucose oxidase, which catalyzes the oxidation of β -D-glucose by molecular oxygen to δ -D-gluconolactone with simultaneous production of equimolecular amounts of hydrogen peroxide.



Few of the many oxidoreductase enzymes are able to yield significant concentrations ($\geq 1\%$) of H_2O_2 .^[228] H_2O_2 is often generated in living organisms through dioxygen reduction by oxygenases, but catalase enzymes are invariably produced as well and these destroy H_2O_2 at a high rate without release of other active oxidants. Peroxidase enzymes catalyze many organic oxidations, among which the removal of phenolic pollutants^[229,230] and the recovery of industrially important azo dyes^[231–233] from aqueous solutions are prominent. However, peroxidases work naturally with small concentrations of peroxide and are not very stable to oxidation (immobilized enzymes have a strictly limited lifetime). Interestingly, Novo Nordisk has developed peroxidases that can survive high concentrations of H_2O_2 (ARP enzymes). These make it possible to use peroxidases under conditions more suitable to practical applications. The instability of peroxidases is alleviated in part by co-immobilization of glucose oxidase and peroxidases.^[234] The immobilization of glucose oxidase on inorganic substrates is an attractive option for the reaction and the possible recovery and recycling of the enzyme. The methods for immobilization of glucose oxidase explored to date include sol–gel^[235,236] and chemical bonding to a silica surface.^[237] In the sol–gel approach, the enzyme is physically dispersed in the matrix, which allows good accessibility of the substrate to the enzyme locations in the aqueous phase. This method affords a very high rate of epoxidation for 4-styrenesulfonic acid (Figure 11). However, recycling the sol–

gel leads to loss of enzyme activity. A much more effective methodology is the covalent attachment of enzymes to a silica substrate.^[238] In other cases, as with ligninases, self-destruction is a normal part of the mode of action. It is conceivable that this drawback could be overcome by using cells rather than isolated enzymes. This practice is not widespread in the chemical industry at present. Furthermore, the low concentration limit and high molecular weight of the enzyme mean that the space yield is low and recovery/recycling of the enzyme is difficult. Therefore, peroxidases as such are not particularly attractive as catalysts in industrial oxidation. This conclusion applies particularly to heme-based systems. Vanadium and molybdenum enzymes are more robust, but also less active towards substrates of industrial interest.

5.2. Plasma

H_2O_2 can be synthesized from hydrogen and oxygen mixtures by plasma and other physical methods. The activation of H_2 and O_2 molecules in a nonequilibrium plasma by silent electric discharge yields H_2O_2 and H_2O at atmospheric pressure.^[239,240] This method has some advantages in that it does not involve any reagents other than H_2 and O_2 and the stoichiometry of the H_2/O_2 mixtures for optimum selectivity for H_2O_2 is far from the explosive regime of H_2/O_2 mixtures.^[239] The plasma method also avoids the mass-transfer limitations associated with heterogeneously catalyzed three-phase reactions.

Dielectric barrier discharge (DBD) at atmospheric pressure allows quite high yields of H_2O_2 to be obtained from the gas reaction of H_2/O_2 plasma, although this is depends strongly on the reactor configuration.^[241] With a suitable reactor configuration, H_2O_2 can be obtained in the product solution from an H_2/O_2 mixture containing 3.6% O_2 (the lower explosive limit for mixture is 6%) fed at a rate of 10 L h^{-1} . The concentration of H_2O_2 increases almost linearly with time, with concentrations of 1.5, 4.1, and 14.3% w/w obtained for discharge times of 1, 3, and 11 h, respectively.

5.3. Oxygen Reduction

Transition-metal complexes with catechol and semiquinone ligands display facile electron transfer between the metal and chelate ligand and are thus redox-active.^[242] It has long been known that these redox characteristics play a role in several enzyme-catalyzed reactions, for example, in ribonucleotide reductase^[243] and galactose oxidase.^[244] The redox nature of the catecholate complex arises from the relative ease with which catechol ligands can be oxidized to semiquinones and *o*-quinones (Scheme 9).

High-valent manganese complexes have been studied in detail because they play a key role in the formation of photosynthetic oxygen.^[245] Valence tautomerism has been observed between Mn^{IV} -catecholate and Mn^{II} -semiquinone structures, and interconversion may occur with only small changes in temperature. The synthesis of these Mn-catechol complexes is complicated because catechols are prone to

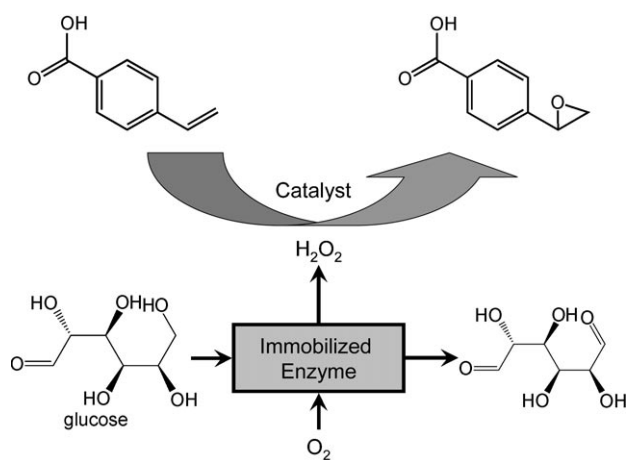
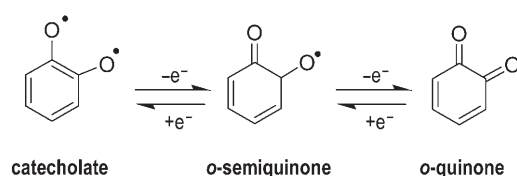


Figure 11. Reactions with immobilized glucose oxidase.



Scheme 9. Cathecol oxidation to semiquinone and *o*-quinone.

polymerization and oxidation by air, and only a few examples are known.^[246,247]

The complexes $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ (**1**) and $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ (**2**) facilitate the production of hydrogen peroxide from the substrates dioxygen and hydroxylamine in acetonitrile/water mixtures under ambient conditions. The rate of H_2O_2 production increases with increasing amounts of complex, but a rapid decomposition of H_2O_2 occurs at concentrations of the complexes above $10\ \mu\text{M}$, which suggests a slower manganese-catalyzed decomposition of H_2O_2 . The similarity of the rates of H_2O_2 production with **1** and **2** suggests that neither the oxidation state of the manganese nor the labile coordination sites around the Mn metal are important for catalysis. The turnover numbers of approximately $10\,000\ \text{h}^{-1}$ (mol H_2O_2 per mol Mn) compare very favorably with those for the commercial AO process.

The complexes **1** and **2** contain Mn^{III} and Mn^{IV} ions, which are reduced in the presence of hydroxylamine. The corresponding Mn^{II} complexes act as the active catalysts.^[248] There is evidence that hydroxylamine is highly effective at reducing the $\text{Mn}^{\text{III/IV}}$ centers in Mn-containing catalase enzymes to Mn^{II} centers.^[249] This may explain the equal rates of H_2O_2 production for Mn^{III} or Mn^{IV} complexes. Further insights into the reaction mechanism come from the observation that labile ligands around the central Mn ion have little influence on the reactivity. It appears that H_2O_2 formation takes place through an outer-sphere mechanism in which O_2 and NH_2OH are not coordinated to the central Mn^{II} ion.^[250] A reaction mechanism has been proposed for the production of hydrogen peroxide through reduction of bound O_2 by coordinated catechol in which NH_2OH acts as a sacrificial reducing agent to regenerate the catalyst from the oxidized quinone.^[242] This mechanism can be reconciled with the kinetic results for **1** and **2** if it is assumed that the reduction of O_2 by hydroxylamine proceeds via a key hydrogen-bonded intermediate.

The possible two-electron oxidation of catechol ligands to semiquinone and quinone species, the electronic properties of substituents on the catechol ring, and the nature of the manganese center with stable oxidation states Mn^{II} , Mn^{III} , and Mn^{IV} provide these complexes with enzymelike character. These properties allow the complexes to activate O_2 molecules for reduction to hydrogen peroxide by low-molecular-weight amines such as hydroxylamine and hydrazine.

6. Summary and Outlook

Hydrogen peroxide is often considered a key reagent of green chemistry, as water is the only reaction by-product in

oxidation reactions. The AO process for the production of H_2O_2 is commercially successful because it produces H_2O_2 continuously at moderate temperatures while avoiding direct contact between O_2 and H_2 . In comparison with its competitors (oxidation of primary and secondary alcohols, electrochemical methods), the AO method has many advantages, but also disadvantages. For example, the hydrogenation and oxidation steps are subject to mass-transport limitations, the H_2O_2 recovered by liquid–liquid extraction is contaminated by organic compounds, which requires substantial investment in purification equipment in industrial plants. The newer methods for H_2O_2 production outlined herein avoid these drawbacks.

A promising new method is the synthesis of H_2O_2 from $\text{CO}/\text{O}_2/\text{H}_2\text{O}$ mixtures ($\text{CO} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O}_2$). This process is an interesting option for cases in which a source of carbon monoxide is available. However, it can not be considered a green process, as carbon dioxide is produced along with the hydrogen peroxide. Critical issues for technological development of liquid-phase reactions in the presence of palladium complexes are ligand optimization and in-depth mechanistic investigations of the reaction. Comparatively little attention has been paid to the development of heterogeneous catalysts for $\text{CO}/\text{O}_2/\text{H}_2\text{O}$ mixtures. The systems employed for this purpose are reasonably active, but their selectivity for H_2O_2 is still far from satisfactory. A major problem to be overcome is deactivation of the catalysts by water. A substantial improvement in performance, specifically for copper catalysts, is obtained with a modification of the liquid-phase. The two-step reaction mechanism involves first the water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) and then further reaction of the generated H_2 with solubilized O_2 . Mass-transfer limitations are unavoidable,^[225] but a suitable choice of solvent helps to increase the transfer rate of oxygen to the catalytic site.

An undoubtedly greater challenge in the long term is the production of H_2O_2 over semiconductor surfaces in the presence of water under irradiation with UV or visible light. As H_2O_2 formation involves reduction of O_2 by a photo-generated electron in the conduction band, precise design of the semiconductor is a key issue for further improvements in efficiency. A high concentration of charge carriers must be attained at the conduction band and the recombination of electron–hole pairs within the solid must be largely avoided. This can be realized with new semiconductors or through appropriate doping of conventional materials.

The bioinspired production of hydrogen peroxide under very mild conditions is a conceptually simple and safe approach. However, immobilized peroxidases have limited lifetimes at high concentrations of hydrogen peroxide, which limits the practical application of enzymes. Nevertheless, Novo Nordisk has developed peroxidases that can survive high concentrations of H_2O_2 (ARP enzymes). The broad range of substrates susceptible to oxidation by certain enzymes allows the conversion of OH groups of monosaccharide or primary alcohols into the corresponding aldehydes with release of equimolecular amounts of H_2O_2 and selectivity close to 100%. However, as these reactions are stoichiometric, a tremendous amount of waste is produced, and thus this

method would only be justifiable if this waste could be completely recycled. An important advantage of biomimetic reactions is their selectivity, which may lead to some industrial applications, such as coupling of the in situ generation of H_2O_2 with reactions of certain substrates (e.g., epoxidation of olefins). Precise design and optimization of ligands could lead to improved stability. Notwithstanding, the use of oxidoreductase enzymes is difficult because they seldom yield significant concentrations ($\geq 1\%$) of H_2O_2 . H_2O_2 is often generated through dioxygen reduction by oxygenases, but a catalase enzyme is invariably also produced which quickly destroys H_2O_2 without producing other active oxidants. Peroxidase enzymes catalyze many organic oxidations with H_2O_2 . However, they likewise involve small peroxide concentrations and are not very stable against oxidation and hence have severely limited lifetimes.

The direct reaction of $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$ is conceptually the most straightforward method for producing hydrogen peroxide and is the method of choice in the medium term. As extraction of H_2O_2 is not required and the purification steps are simplified, the capital investment and operating costs are expected to be lower than for the AO process. This alternative appears of great relevance to the basic chemical industry, as shown by the integrated HPPO process. The direct synthesis of H_2O_2 on site allows the costs and hazards associated with the transport and handling of concentrated hydrogen peroxide to be significantly minimized. Several chemical companies have investigated the direct synthetic route over the past 25 years, and the number of patents in this field continues to grow. However, none of the processes available has been able to deliver both productivity and safety. A possible solution to the safety problem is the use of catalytic membranes. Following this approach, pure O_2 and H_2 can be used without a diluting agent since contact between the two streams is avoided. However, owing to the low permeation rates, the product yields are too low to be competitive with those attained in flow systems.

Most catalyst formulations employ palladium as the active metal. As well as the heterogeneous catalyst, acids are often incorporated into the reaction medium to delay or prevent the decomposition of hydrogen peroxide. Under these conditions, palladium is partly dissolved and forms a colloidal suspension that deactivates the catalyst. Although such a system is very interesting fundamentally, a colloid would be difficult to manage in a commercial process and its recovery would not be viable at the very low concentrations of dissolved metal employed. Notwithstanding, excellent yields of hydrogen peroxide have been recently reported with neutral solutions and heterogeneous catalysts consisting of functionalized carbons with sulfonic acid groups,^[123] or polystyrene resins functionalized with sulfonic acid.^[130–132] It has been demonstrated for a system with palladium loaded on a sulfonic acid modified divinylbenzene-cross-linked polystyrene resin that interactions occur between small palladium particles and the sulfonic acid groups of the resin.^[132] This interaction creates a positive charge on the Pd particles which enhances the selectivity for hydrogen peroxide.

Industry is expected to increase its focus the development of inorganic catalysts for hydrogen peroxide synthesis,

particularly for the production of fine chemicals. Complexes and enzymes will have little large-scale impact, even though these should improve further in robustness. The future will show whether the predicted developments actually occur.

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