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Carbon dioxide as an alternative solvent for the direct synthesis of hydrogen peroxide: A review of recent activities

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ABSTRACT

The importance of the direct synthesis process for the production of hydrogen peroxide from hydrogen and oxygen is apparent from the numerous publications and patents on the subject since the beginning of the 20th century. The prospects it would open up for various hydrogen peroxide applications are undeniable. However, the challenges with which the process has to cope are not to be underestimated. Besides the development of different reactor concepts, one attempt to address the issues concerning safety, activity, selectivity and cost, is the search of alternative solvents. Deploying dense carbon dioxide as solvent is a possibility investigated in recent years. Carbon dioxide would be an environmentally friendly alternative and would also offer benefits in terms of enhanced solubility for the reactants as well as diffusivity. This review summarizes the proposed concepts for CO₂ as medium for the direct synthesis process of hydrogen peroxide and the challenges going along with it. Relevant properties of CO₂ for this particular process together with some economic aspects will be discussed as well.

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1. Introduction

Decomposing to yield only oxygen and water, hydrogen peroxide is one of the cleanest, most versatile oxidants available. Therefore, it finds various applications in a number of industrial branches such as pulp, paper and textile industries, metallurgy, electronic industries, waste water and exhaust air treatment, etc. It has great potential for the chemical industry as a very active and selective reagent used in processes such as oxidations, epoxidations, hydroxylations etc. and for the production of many organic and inorganic chemicals (specialty chemicals) [1,2].

A limiting factor for the applications of hydrogen peroxide, however, is its relatively high price, resulting from the complex industrial production route. The dominating multi step anthraquinone (AQ) autoxidation process, although safe (prevents the contact of oxygen and hydrogen during the reaction), is highly energy consuming with an expensive and complex organic solvent system, making it economically viable only for large-scale hydrogen peroxide production (>40 kt yr⁻¹) [1,2]. As an environmentally friendly and energetically more efficient alternative, the process of

direct formation of hydrogen peroxide from hydrogen and oxygen has been investigated for decades already in patent literature [3–8] and scientific reviews [2,9–11]. This synthesis route would open up alternatives for small-scale, decentralized, on-site, on-demand hydrogen peroxide production for various applications, avoiding additional costs for transportation, storage and safety measures. However, currently the direct synthesis route has been developed only up to pilot scale. One of the earliest examples is the process developed by Du Pont in the late 80s based on bimetallic Pd/Pt catalyst supported on carbon, alumina or silica in an aqueous reaction medium [12–14]. The work was developed up to pilot scale, but then shut down due to safety concerns. Evonik/Degussa started a demonstration plant in 2006 at its site in Hanau-Wolfgang, Germany, using a supported Pd/C catalyst in a fixed bed reactor with methanol as solvent [15]. No further reports concerning the industrialization of the process have been found in literature since, although all of the global players on the H₂O₂ market have their own research activities on the direct synthesis process.

The factors preventing the implementation of the direct synthesis process on large scale are well known:

- *Process safety:* H₂/O₂ mixtures are explosive over a wide range of hydrogen concentrations making the task of designing a safe process a challenge and bringing about the need to operate under high dilution, thus negatively affecting productivity. Therefore,

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Table 1
Solubility of hydrogen and oxygen in water and methanol at 298 K and 0.1 MPa expressed as Henry constant ($k_H : p_{\text{H}_2/\text{O}_2} = k_H \times x$) or gas mole fraction in the liquid phase (x). Smaller k_H means larger x at the same pressure—higher solubility.

	Henry constant (k_H) [Pa molfr ⁻¹]		Gas mole fraction in the liquid phase (x) [mol mol ⁻¹]	
	Water	Methanol	Water	Methanol
H ₂	6.82×10^9	5.34×10^8	1.43×10^{-5}	1.59×10^{-4}
O ₂	4.70×10^9	2.66×10^8	2.25×10^{-5}	4.15×10^{-4}

operation at higher pressure is pursued which, however, raises again safety and economic issues.

- **Selectivity:** low selectivity to hydrogen peroxide is caused by the fact that materials catalyzing the formation of hydrogen peroxide in general are also active for its decomposition and for the parallel formation of water, which is thermodynamically more stable.
- **Yield and productivity:** the goal is to maximize productivity and yield. However, this is usually connected to a compromise in selectivity with advancing contact time due to formation of water. Catalyst stability is also an issue with possibility of deactivation or active metal leaching.
- **Costs:** in order to be economically viable the direct synthesis process should offer lower costs for the product compared to the anthraquinone process. This might be a challenge for process designs relying on high pressure (which is normally the case) or involving expensive membrane modules with complicated geometry or compact layers of precious metals as catalysts.

The “classical” approach for the direct synthesis process in the lab deploys powdered supported precious metal catalysts dispersed in a solvent, with the gaseous reactants saturated in the liquid phase at high pressure. Normally, a batch or semi-batch process (with continuous feed of the gas phase) is used. Active metals mostly used include monometallic Pd or Au or bimetallic combinations Pd-X (X=Au, Ag, Pt) on a variety of inorganic supports (alumina, zirconia, silica, titania, carbon etc.) [2,9–11,15–39].

A few other concepts for the direct synthesis of hydrogen peroxide have been proposed over the years addressing the issues pointed out above. Different types of catalytic membrane reactors based on the distributor [40–43] or contactor, [41,44,45] principle in both batch and continuous types of processes have been investigated mainly to cope with the safety issues by physically dividing the reactants hydrogen and oxygen. Another trend in recent research is the use of microstructured reactors and continuous flow process devices [10,46–50] with the aim of enhancing selectivity and productivity by exploring the benefits of improved safety and reduced transport limitations the micro dimensions have to offer. The use of microreactors and other advanced reaction engineering concepts for hydrogen peroxide direct synthesis is reported in a separate publication in this issue as well (Dittmeyer et al.).

It is not within the scopes of this article to go into the details of these concepts. For the aims of this review instead the focus is placed on the aspect of the reaction medium for the direct synthesis process and namely the use of alternative solvents such as carbon dioxide—either liquid or supercritical or in combination with water and standard organic solvents (so called CO₂-expanded solvents). An overview of the properties of CO₂ relevant for this reaction, as well as the state of the art of different concepts using CO₂ as medium will be presented. Last but not least some economical concerns will be addressed as well.

2. Direct synthesis of H₂O₂: Requirements for a reaction medium

When it comes to the solvent for the direct synthesis process a few prerequisites should be fulfilled. Because of the highly

explosive nature of the H₂/O₂ mixtures and the formation of a metastable liquid product, it is advantageous to perform the reaction in the liquid phase where both H₂ and O₂ are dissolved, potential explosions are prevented, and further conversion as well as decomposition of the hydrogen peroxide is retarded compared to the gas phase. Obviously the most convenient solvent for the reaction would be water, being non toxic, non flammable and completely miscible with the product. Furthermore, from the point of view of on-demand on-site production, aqueous hydrogen peroxide solutions are advantageous for most of its applications as a bleaching agent. However, at normal pressure solubility of H₂ and O₂ in water is rather low, thus limiting the productivity of the process, as summarized in Table 1 [51–56]. Therefore, higher pressures are usually applied. Using an organic solvent (ethanol [57,58], methanol [29,32], acetonitrile, toluene [9]) or mixtures of it with water would increase solubility of the reactants and, respectively, productivity.

For some H₂O₂ applications organic solvents would offer an advantage. For example, for the propylene oxide synthesis (HPPO process) a methanol solution of H₂O₂ is used. From a scientific point of view, organic solvents are preferred for process development, in order to be able to estimate the amount of water synthesized from the reaction (normally by Karl Fischer Titration). However, the use of organic solvents, especially under pressure, brings up a number of safety concerns.

Another important aspect concerning the solvent for the direct synthesis of H₂O₂ is the need to use additives such as halide ions (Br⁻, Cl⁻) and acids (H₂SO₄, H₃PO₃) to boost catalyst performance. Normally, Br⁻ ions are used to diminish catalyst activity for water formation and increase selectivity [9]. They act rather by suppressing the hydrogenation of H₂O₂ than its decomposition [19]. In addition, Cl⁻ ions are reported to inhibit the dissolution of Pd into the acidic medium [58]. Generally, halide–Pd interactions have been found to modify the electronic properties of Pd in the catalyst, resulting in the inhibition of the cleavage of O–O bonds in both H₂O₂ and O₂ during their adsorption on the catalytic sites, thus avoiding decomposition/hydrogenation of hydrogen peroxide [28,58]. There is an optimal Br⁻ to Pd ratio depending on catalyst type. However, the values suggested vary significantly between different studies, i.e., from 0.4–0.8 [9] up to 8.2–8.5 [32]. An excess of halide ions results in complete catalyst poisoning with the consequent decrease in activity. The presence of acid is needed to enhance the adsorption of the halides on the catalyst active sites [28].

Important work in recent years explicitly addressed the performance of the direct synthesis process in the absence of promoters. Promising results were reported for bimetallic PdAu/TiO₂ catalysts [59] and PdAu or PdPt catalysts supported on an ion exchange resin [60]. The addition of the second metal seems to enhance the performance of the catalyst compared to monometallic Pd. Even in the absence of additives selectivities up to 80% depending on the reaction conditions have been obtained [59]. These results clearly indicate the potential of bimetallic catalysis for “promoter-free” solvents, and may play an important role for the future development of the H₂O₂ direct synthesis technology.

However, at present in most cases the hydrogen peroxide direct synthesis reaction is performed in the presence of promoters. This might as well be a “bottleneck” towards the practical

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