



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Review

A review of catalyst performance and novel reaction engineering concepts in direct synthesis of hydrogen peroxide

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ARTICLE INFO

Article history:

Received 20 December 2013

Received in revised form 20 March 2014

Accepted 21 March 2014

Available online xxx

Keywords:

Hydrogen peroxide

Microchannel process technology

Direct Synthesis

Palladium

Catalytic Membrane

ABSTRACT

The recent literature on direct synthesis of H₂O₂ is reviewed with respect to two important directions. The best catalysts to date are assessed with a view to their composition, e.g., alloys, and regarding the role of the support material and solvent used. Moreover, a number of novel reactor concepts that have been proposed in literature for direct synthesis of H₂O₂ are analyzed with a focus on their potential for practical implementation. These include: (i) microchannel process technology for safe mixing and conversion of the reactants in undiluted gaseous state, (ii) dense palladium-based membranes acting as a means to prevent gas-phase contact of the reactants while providing a catalytically active interface, (iii) asymmetrically porous catalytic membranes operated in wetted state as an interphase contactor where one reactant is introduced in a controlled way from the gas phase into the liquid reaction medium, (iv) microreactors for multiphase operation with improved mass transfer efficiency compared to conventional reactor technologies, and (v) electrocatalytic synthesis, both in electrolysis mode and in fuel cell mode, which also promise improved safety by avoiding gas-phase mixing of hydrogen and oxygen and increased selectivity due to improved reaction control.

Concerning the first aim, an acid-pretreated 5 wt.% Pd/C catalyst appears to be the best choice for methanol as solvent whereas a Pd-Au exchanged Cs-containing heteropolyacid catalyst is the current benchmark for water as solvent. With proper acid pre-treatment of the Pd/C catalyst or acid function incorporated into the support (heteropoly acids), no halides and no inorganic acids are needed in the solvent to prevent hydrogen peroxide decomposition. However, the H₂O₂ hydrogenation activity in pure water is still rather high which limits the selectivity. Among the different reactor concepts, microchannel process technology seems to offer key advantages in terms of high productivity, selectivity and process safety. The electrocatalytic approach also looks promising. However, major achievements are still needed, e.g., successful scale-up of these concepts to relevant throughputs confirming the good performance obtained in lab scale.

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1. Introduction

From chemical point of view and as outlined in many relevant papers, e.g., [1–3], H₂O₂ is the best single-oxygen donor next to molecular oxygen. The oxygen is cleanly transferred, and the only byproduct is water. In terms of reactivity and selectivity, H₂O₂ is better than molecular oxygen. On a commercial scale, at present, H₂O₂ is mainly used as a bleaching agent in the pulp and paper industry, as a disinfectant in the cosmetic and pharmaceutical industry, and as an oxidant in water treatment and in the synthesis of specialty chemicals [4,5]. In highly purified form, it is also used for etching and cleaning in the electronics industry. Recently, several large propylene oxide (PO) plants have come on stream in China (Evonik-Uhde), Belgium (BASF-DOW) and Thailand (SCG-DOW) with capacities ranging from 230,000 to 390,000 t/year utilizing H₂O₂ for catalytic oxidation of propene to PO (HPPO). Due to the economics of PO production, the capacity of the H₂O₂ plants for PO production is by a factor of 2 larger compared to the supply of the classical markets. Therefore, the start-up of a new HPPO-plant has a tremendous impact on the global size of the H₂O₂ market. However, the H₂O₂ used by these units is still manufactured by the AO-process via anthraquinone autoxidation [6]. This now over 70 years old process remains the only one used commercially to produce H₂O₂. Because of its complexity, economics of scale dictate the use of large production units on one hand and set a limit to the maximum scale per production train on the other hand. However, this makes it necessary to transport H₂O₂ in concentrated form over large distances to the consumers. The costs for transport and storage of concentrated H₂O₂ solutions add substantially to its price for the end user. Therefore, despite its advantages as a clean oxidant, H₂O₂ is still not economically competitive for the production of bulk chemicals or for more widespread use in wastewater treatment. For most applications, dilute solutions of H₂O₂ are adequate and an on-site production would be highly desirable as it would minimize handling and eliminate the need for transportation of concentrated H₂O₂ over long distances.

Among the various alternative approaches to produce H₂O₂, the direct reaction of hydrogen and oxygen to H₂O₂ is conceptually the most straightforward and therefore most attractive one. However, despite significant R&D efforts by several academic groups and major industrial companies, the process has not yet been demonstrated on commercial scale. Poor economics caused by lower selectivity combined with only modest savings on the investment compared to the AO-process as well as challenges for the scale-up and the safety of the process due to the wide explosive range of H₂/O₂ mixtures (e.g., 4–75 mol% in air, 4–94 mol% in oxygen at 1 atm pressure) are the main reasons.

As H₂O₂ is highly unstable under reaction conditions, the reaction is carried out in an appropriate solvent. Water, short-chain alcohols, or mixtures thereof are most often used as solvents. Water is generally preferred from an environmental and safety standpoint for most applications in bleaching, wastewater treatment

and non-chemical processes, whereas for the use in chemical syntheses alcohols, e.g., methanol or the like, are often more suitable. Inorganic acids are added to lower the pH value, because the decomposition of H₂O₂ is favored in a basic environment. Due to the low solubility of hydrogen and oxygen in conventional solvents, high pressures up to more than 100 bar are applied in order to raise the productivity. But high pressure, as a downside, also increases the hazard potential. The reaction temperature is generally kept low, i.e., below 50 °C, again with a view to limit the decomposition of the peroxide.

The selectivity issue arises from the fact that water is the thermodynamically preferred product which can be formed directly in a parallel reaction path from hydrogen and oxygen as well as in two consecutive reactions from H₂O₂ with and without involvement of hydrogen, as indicated in Fig. 1.

High selectivity in the direct synthesis reaction requires a catalyst which, on one hand, can provide appropriate oxygen species that favor H₂O₂ as the primary product and, on the other hand, does promote as little as possible the decomposition and overhydrogenation of the peroxide. The lower the activity for the consecutive decomposition of H₂O₂ the higher the maximum peroxide concentration that can be obtained. Low decomposition activity therefore is imperative for obtaining H₂O₂ concentrations of practical relevance. In addition, good control of the reaction conditions in the whole reactor is essential, as the state of the catalyst surface is affected by the reaction conditions. For example, the oxygen to hydrogen ratio in the reaction medium is known to have a strong impact on activity and selectivity as it influences the oxidation state of the catalyst. The same holds for the pH value and with reservations also for the temperature. Furthermore, from a practical point of view, the inside surface of the reactor vessel, all pipes and downstream installations made from steel in contact with the

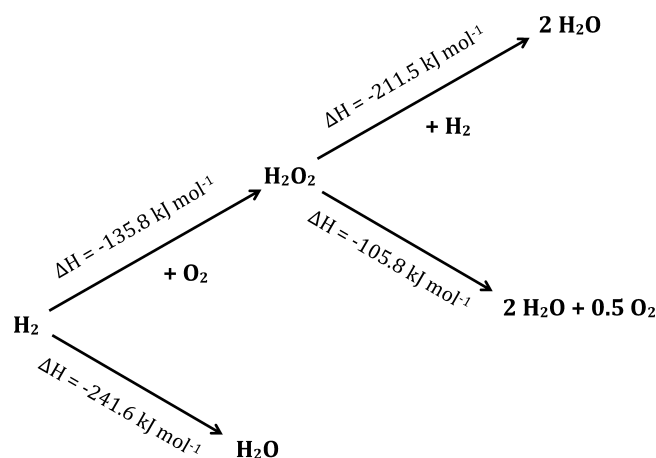


Fig. 1. Reactions involved in direct synthesis of H₂O₂. Adapted from Ref. [2].

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