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# Catalytic direct synthesis of hydrogen peroxide in a novel microstructured reactor

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### ABSTRACT

The direct synthesis of hydrogen peroxide was investigated in a bench-scale continuous process using a novel microstructured reactor. This plate-type reactor was developed to offer favorable hydrodynamic and mass transfer conditions. Supported Pd catalyst on activated carbon cloths was employed. The experiments were conducted with hydrogen and oxygen using methanol as a solvent. Effects of process conditions, e.g. gas composition, gas and liquid flow rates, pressure and amount and composition of catalyst were studied. The promising results and plans for further development of the reactor and process concept are discussed.

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## 1. Introduction

Hydrogen peroxide is a very powerful and green oxidant used in many industries. Currently, hydrogen peroxide is mainly produced by auto-oxidation in anthraquinone process. This process, however, has certain drawbacks. The chemistry is complicated with plenty of side reactions and byproducts. The investment costs are relatively high because of high number of equipment and large capacity is needed to achieve acceptable profitability. Moreover, using of a large amount of organic solvent makes the process less sustainable [1,2].

Direct synthesis of hydrogen peroxide has been studied as an attractive, green alternative over past decades [3]. The main benefits include:

- The chemistry is more straightforward than in the case of anthraquinone process.
- Lower investment and operating costs due to a substantially smaller number of equipment.
- The process is green when compared to anthraquinone process. This is clear if water is used as a solvent. The direct synthesis is greener even with methanol as a solvent because the total volume of organic liquid in the process would be substantially less.
- The process is favorable for on-site production.

However, there are a number of technical challenges in the direct synthesis. Hydrogen and oxygen generate an explosive mixture at wide range of concentrations (5–96 vol% H<sub>2</sub>) [4]. Moreover, several side reactions are involved, as shown in Fig. 1. Therefore, selectivity is a challenge.

The safety risk can be decreased by utilizing microreactor technology. Proceeding of explosion could be suppressed by small dimensions of the reaction space. Moreover, the small holdup in microreactor limits the damage to be small even in the case of explosion. Therefore microreactors can be considered as inherently safe tools for hydrogen peroxide synthesis. Microreactors might even be able to be operated at explosive regime of gas mixture [5–8] allowing then also higher gas concentrations in the solvent, leading to higher yield.

The selectivity problem (see Fig. 1) can be solved by catalyst development [9]. Catalyst is very crucial to obtain high yield and selectivity, which tend to be rather low. Supported Pd catalysts, such as Pd/C, Pd/SiO<sub>2</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub>, are traditionally used in the direct synthesis [3]. In recent years, bimetallic Au–Pd catalysts were found to exhibit high activity with high selectivity [10–12].

The direct synthesis has been studied in various types of reactors from conventional ones to microreactors. A number of investigations in batch reactors [9,13–17] and trickle bed reactors has been carried out [12,18,19]. Pd catalysts on various support materials including activated carbon [9,12–15,17], SiO<sub>2</sub>, CeS, and ZrO<sub>2</sub> [19] have been used. Many attempts to use single channel and multi-channel microreactors have been done [5–8,11,20,21]. Some of the experiments were done in the explosive regime [5–8] and sometimes small explosions were detected by Inoue et al. [7].

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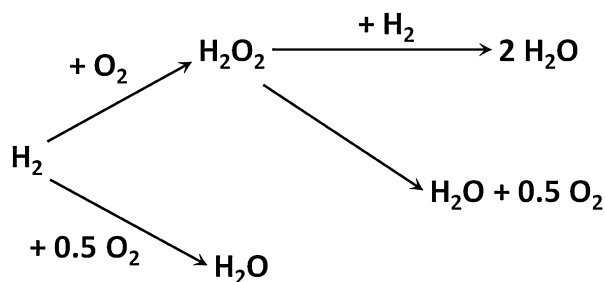


Fig. 1. Reactions in the direct synthesis of  $\text{H}_2\text{O}_2$ .

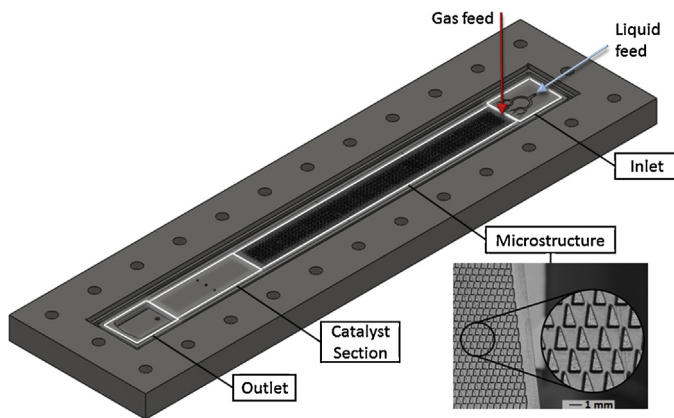


Fig. 2. Microreactor plate in this study.

The goal of this study is to investigate the direct synthesis in a novel microstructured reactor which was developed in previous studies [22]. Pd supported catalysts on activated carbon cloths [9] were used. Effects of gas composition, pressure, catalyst, and hydrodynamic conditions were studied.

## 2. Experimental setup

### 2.1. Microreactor

The development of the plate type microstructured reactor used in this study has been reported by Ratchananusorn et al. [22] and Semyonov et al. [23]. This structure was chosen because of several benefits. Firstly, gas–liquid mass transfer might be faster than in the reactor with parallel microchannels. The reason is that the gas slugs in the channels are surrounded by thin liquid films which easily become saturated with gas. In that case, mass transfer can only take place through the ends of the slugs [24], i.e. through reduced interfacial area. Moreover, the reactor can be easily opened for cleaning and catalyst replacement or regeneration. The plugging problem is also expected to be less severe when compared to conventional microreactors with several microchannels. The safety is enhanced by small dimensions and holdup. Moreover, the scale up of this type of microreactor is straightforward. Several parallel plates can be installed (numbering up).

The configuration of the reactor is shown in Fig. 2. It is made of stainless steel and consists of several sections. The reactor plate is installed in vertical position. The inlets for gas and liquid feeds are located at the top section. Bifurcation configuration was used for the liquid feed to improve the distribution and prevent channeling problem. The gas feed takes place through the cover plate which is installed against the microreactor plate. The microstructure section is located below the inlet section. The width of this section is 32 mm, height 300 mm and depth 300  $\mu\text{m}$ . The microstructure consists of number of triangular elements (see Fig. 2). The size

of each element is 1 mm  $\times$  2 mm  $\times$  300  $\mu\text{m}$  (base  $\times$  height  $\times$  depth). The elements are arranged in staggered arrays providing void fraction of 75% for reaction space. The holdup for gas/liquid mixture was 3.84  $\text{cm}^3$ . The microstructure was designed to improve the mixing of the two phases and to generate high interfacial area. Below the microstructure section is the catalyst bed. Pd catalyst was supported on active carbon cloth. A single layer of the cloth was installed in the catalyst bed between the plates.

### 2.2. Catalyst

#### 2.2.1. Catalyst support

Carbon supported Pd catalysts have been extensively used in many studies for the direct synthesis with high performance [9,12–15,17]. Acidic pretreatment of the support and oxidized state of the catalyst usually give better performance [9]. Activated carbon has been found in many studies to give better performance than other supports.

In this study, activated carbon cloth (ACC) was used as a catalyst support. Because ACC is a fabric-type support, it can be placed directly between the reaction plate and the cover plate. Thus the replacement and regeneration of the catalyst can be done easily by opening the reactor and taking the ACC out. The packing problems are less difficult than with conventional granulated or powder catalysts.

Activated carbon cloth is flexible and easily applicable, it can be cut to proper size, bent, and rolled to fit into any reactor geometry. A large specific surface area is available (over 2000  $\text{m}^2/\text{g}$ ). The diameter of fibers is small and uniform. Therefore, a good contact between the flowing fluid and the catalyst surface can be obtained and excellent mass transfer characteristics achieved [25].

The catalysts used in this study were developed and tested extensively in an autoclave batch reactor by Gudarzi et al. [9].

ACC is available from many manufacturers with different properties. In this study, ACC was purchased from Kynol GmbH, Germany, and the model number was ACC507-15. The specific surface area (BET) is as high as 1500  $\text{m}^2/\text{g}$  and the fiber size 9.2  $\mu\text{m}$ . The microstructure of the fiber is uniform with straight pores rather than branched ones in granulated activated carbon.

#### 2.2.2. Catalyst preparation

Series of Pd/ACC catalysts were prepared by precipitation of Pd on ACC. The pretreatment of the support was done with 20% nitric acid for overnight. Acidic solution of  $\text{PdCl}_2$  was used to prepare the catalysts. The procedure has been described by Gudarzi et al. [9].

SEM images of catalysts with different Pd loading are shown in Fig. 3. The white spots represent metal particles which are well distributed throughout the ACC fibers. According to the images, Pd loading up to 1 wt.% mainly occurred inside the micropores of the ACC, because no particles can be detected on the outer surface of ACC. Increasing the amount of Pd led to development of large Pd particles on the outer surface [9].

### 2.3. Experimental bench-scale process

A continuous bench scale process for the direct synthesis is shown in Fig. 4. The stainless steel equipment was initially passivated with 20% citric acid at 333.15 K for 12 h to minimize the decomposition of hydrogen peroxide. Methanol was used as a solvent allowing higher solubility of gases. Solvent was saturated with oxygen in a saturation vessel at 20 bar. Excess of oxygen gas was used in order to also strip away dissolved carbon dioxide and hydrogen left in the recycled solvent. The vessel was cooled to maintain solvent temperature at 273.15 K. From the saturation vessel, solvent with dissolved oxygen was fed into the microreactor together

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