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Direct Synthesis of Hydrogen Peroxide in Microreactors

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Abstract—Several studies concerning direct synthesis of hydrogen peroxide in microreactors are reviewed. Several types of microreactors have been applied. Their high surface area-to-volume ratio and small internal volume improve safety, which is required when operating with explosive gases. The tested microreactors represent capillary reactors and more sophisticated reactors with a special plate structure on which reaction channels have been machined. Both single- and multi-channel arrangements have been applied. The catalysts have been installed in the reactor in the form of powder or washcoat layer on the channel wall. Palladium and platinum on various support material, such as SiO_2, Al_2O_3 and C, have been tested. Water was the most common solvent, but also methanol, ethanol, and isopropanol have been used because of their better gas dissolving properties. In addition to solvents, chemicals, often called promoters, have been utilised to improve productivity. The most typical promoters were halide ions, such as Br^- and Cl^- and inorganic acids. Hydrogen peroxide has been produced successfully by several research groups. The highest reported mass fraction of hydrogen peroxide was 5 wt %.

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INTRODUCTION

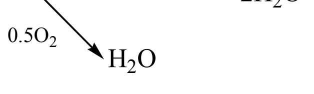
Hydrogen peroxide is used in many applications, e.g. oxidation reactions, bleaching, disinfection, wastewater treatment, and electronic industry. Production of hydrogen peroxide is carried out mainly by the anthraquinone process. When compared to direct synthesis of hydrogen peroxide, the process is relatively safe but more complex and requires larger volumes to be economic [1].

Direct synthesis is an alternative production method for hydrogen peroxide. Idea was presented first time by Henkel and Weber [2]. In the process, dilute solution of hydrogen peroxide is produced directly from hydrogen and oxygen gases. The method is especially suitable for on-site production and low production capacity. The main challenge is safety. The mixture of hydrogen and oxygen is very explosive. The explosion limits for H_2 in O_2 are 5–94 vol% and for H_2 in air 5–75 vol % [1]. The common way to design a direct synthesis process is to choose operation outside the explosion regime. Low hydrogen concentrations result in the need of high operating pressure in order to get sufficient hydrogen and oxygen concentration in the solvent. This feature sets challenges for production equipment. Microreactor technology is an alternative to cope with the above-mentioned challenges. It can be expected that their use will improve safety substantially. This paper reviews the direct synthesis technology for hydrogen peroxide production in microreactors from different viewpoints, such as reactor technology, catalysts, and process performance.

Process Description

Reaction Scheme

Several reactions are involved in the direct synthesis process. The whole reaction scheme consists of oxidation, reduction, and decomposition reactions [3]. Complete oxidation of hydrogen and reduction of hydrogen peroxide have to be avoided to prevent formation of water. The reaction scheme is shown below:



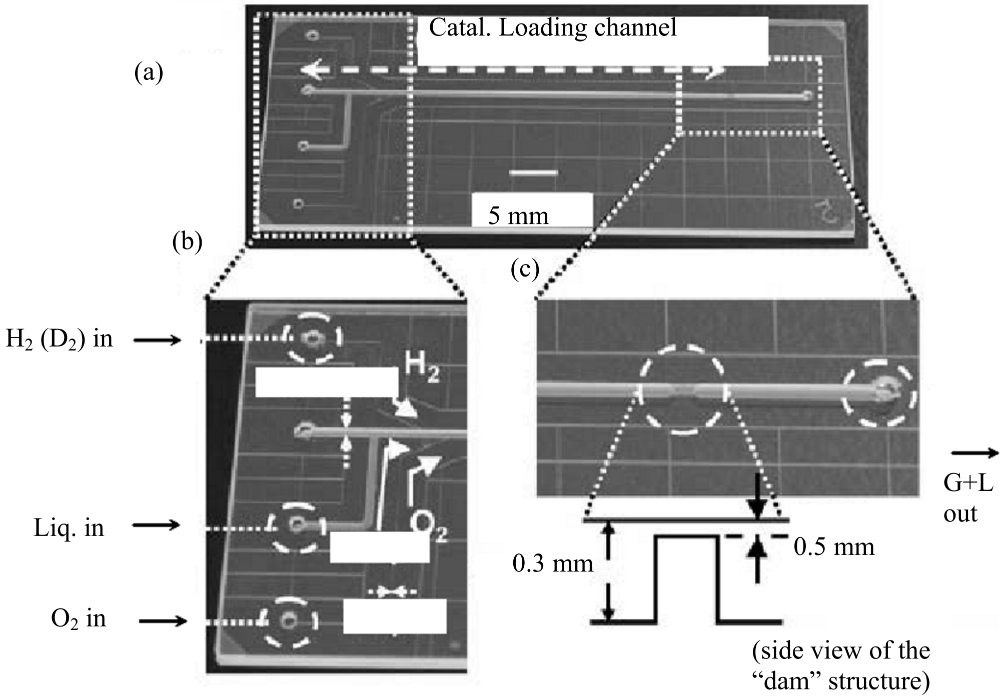


Fig. 1. Design of a single-channel microreactor for direct synthesis of hydrogen peroxide: (a) whole structure, (b) inlet section (magnified), (c) structure for retaining a powdered catalyst in the channel (magnified) [9].

Microreactors

There exist several studies where the direct synthesis of hydrogen peroxide has been carried out in laboratory-scale microreactors. Small channel dimensions in microreactors lead to a high surface area-to-volume ratio. This enhances heat and mass transfer rates. Low internal volumes together with efficient heat and mass transfer make microreactors an inherently safe technology. The simplest structure is a single-channel capillary reactor. It is a closed system which may limit to use of different catalyst-fixing techniques. Such structure was used by Voloshin et al. [3], Maehara et al. [4], Ng et al. [5], and Lawal et al. [6]. Ng et al. [5] used a capillary microreactor with different channel diameters. The diameters of the glass capillaries were 0.53, 1, and 2 mm. The total length of the reactor was 34.5 cm. Maehara et al. [4] used a silicon capillary with the inner diameter of 1 mm and length of 1–6 m. Voloshin et al. [3,7] tested the synthesis in a stainless-steel capillary with the inner diameter of 0.765 mm and length of 4 – 6 cm.

In addition to standard capillaries, hydrogen peroxide has been produced in various microreactors with more sophisticated constructions. Often these reactors consist of plates on which required channels have been machined. Both single-channel and multichannel devices have been used. Manufacturing of channels of the sub-millimeter range requires a high-precision machinery. In the case of parallel channels, the dimensions should be as uniform as possible to ensure even distribution of multiphase flow in the channels, as stated by Inoue et al. [8].

Inoue et al. [8, 9] fabricated a single-channel reactor of Tempax glass sheets. The width of the reaction channel was 0.6 mm, whereas the depths were either 0.3 mm or 0.9 mm. The channels were manufactured by means of chemical isotropic etching and mechanical machining. After manufacturing the inlet structures and reaction and catalyst loading channels, the glass sheets were thermally bonded together. The design of their reactor is shown in Fig. 1.

Wang et al. [10] constructed a single-channel reactor by the hot embossing method. The channel pattern was first developed on a brass plate mold. The mold was pressed into the polymethylmethacrylate chip with adjusted force and at 140°C. Finally, the polymethylmethacrylate chip was covered by another polymethylmethacrylate plate by means of thermal bonding. The achieved channel width, depth, and length were 1, 0.4, and 45 mm, respectively. Maehara et al.

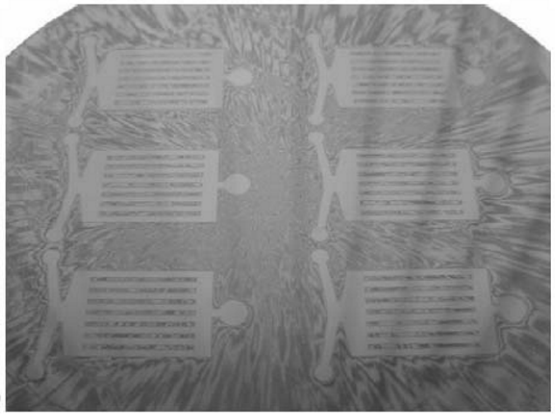


Fig. 2. A multichannel reactor for the synthesis of hydrogen peroxide. The channels are etched on a silicon wafer [10].

[4] developed a stacked microreactor which consisted of polymethylmethacrylate and silicon sheets. The reaction channel pattern was cut out in a polymethylmethacrylate sheet which was then covered by silicon sheets. The silicon and polymethylmethacrylate sheets alternated in the structure. The stacked system contained a 1.36 m long rectangular channel. The width of the channel was 1 mm and depth 0.1 mm.

Inoue et al. [11] utilized a multichannel microreactor. Their reactor contained 10 parallel reaction channels. The width of each channel was 0.625, depth 0.350 and length 20 mm. The unit consisted of three wafers. Top wafer of Pyrex glass was 0.5 mm, middle silicon wafer 0.5 mm and bottom silicon wafer 1 mm thick. The inlets and outlet were fabricated through the bottom wafer and the reaction channels were manufactured on the middle wafer. Several fabrication technologies were applied in this unit, such as photolithographic method, etching and bonding techniques. Wang et al. [10] developed a multichannel device with eight parallel channels. Also they used silicon as structural material. The channels were etched on the silicon surface with dimensions of 15 mm (length), 1 mm (width) and 0.3 mm (depth). The design of the reactor plates is shown in Fig. 2. Dada et al. [12] reported about a multichannel and multilayer microreactor which comprised approximately 450 channels. The channel cross section was a square with dimensions of 0.8 mm. Tonkovich et al. [13] patented a reactor system which consisted of feed, reaction, and outlet units. They presented several alternatives to arrange flows. The reaction unit included the catalyst which was fixed on the wall of the reaction channels. Alternatively, a porous catalyst support can be used. Towler and Vanden Bussche [14] developed a mixer-sparger to mix first hydrogen and oxygen gases and after to mix gas mixture with liquid. The mixer-sparger consisted of stacked plates with thin channels which produced fine gas bubbles in the liquid.

In the set-up of Maehara et al. [4], hydrogen and oxygen were generated electrochemically in an electrolyser before introducing them into the reactor. Trimmer and Sears [15] presented also an electrochemically operated reactor to produce hydrogen peroxide batchwise. In their design, electrodes and reaction channels were machined on a silicon chip. In the operation, the reactor was first filled with water and an electrolyte. Oxygen was then generated at the anode and hydrogen at the cathode. From the electrodes, the gases diffused towards reaction channel, where the formation of hydrogen peroxide took place in the presence of a catalyst.

Flow Patterns and Hydrodynamics

Because of the small dimensions, slug flow is the most typical flow pattern in microchannel. Flow patterns play important role in multiphase reactors because of their influence on mixing, mass and heat transfer. Gas-liquid slug flow was often observed in microchannels [4,5]. In many cases they did not represent regular Taylor flow because capillaries were filled with small catalyst particles. However, separated gas and liquid slugs could be observed [3]. Inoue et al. [8] observed trickling flow patterns in their device. Voloshin et al. [7] determined also gas-liquid mass transfer coefficients which are shown in Fig. 3. They carried out reduction reaction of hydrogen peroxide in the mass transfer controlled area and determined the effect of total flow rate on the volumetric gas-liquid mass transfer coefficient. Very high volumetric gas-liquid mass transfer coefficient could be achieved.

Wang et al. [10] and Ng et al. [5] have estimated the gas–liquid mass transfer efficiency in their reactor, using a correlation of Bercic and Pintar [16]. They concluded that decreasing of the lengths of liquid and gas slugs resulted in higher productivity of hydrogen peroxide indicating improved mass transfer.

In many studies, the reaction channels were filled by catalyst particles, glass beads or other obstacles. They inevitably affect the flow patterns, but they also have a beneficial effect on safety. Small void fractions, thus small distances, in the channel can suppress explosions [7]. Due to this feature, it has been claimed

Process conditions used in the direct syntheses of hydrogen peroxide

Temperature,°C	Pressure, MPa	Typical residence times, s	Solvents	Promoters	Reference
5–20		93	Water	HCl	[4]
20–30	0.1 (ambient pressure)		Water, methanol, ethanol, isopropanol	HCl, KBr	[10]
30–50	0.3–2.2	0.8–1.1	Water	H_2SO_4, NaBr	[3, 7]
20	1–2.5	23	Water	H_2SO_4, H_3PO_4, NaBr	[8, 11]
20	0.1 (ambient pressure)		Methanol, water	HCl, KBr	[5]
			Water	NaBr	[12]
50	3				[19]

that operation in the explosive regime is possible with microreactors. Higher temperature and pressure are needed to initiate explosion in microscale than in macroscale [17,18]. However, explosions were observed by Inoue et al. [8, 11]. Explosions occurred in dry conditions without water. They added inert silica particles in the channels which created small void spaces and therefore, eliminated the explosions. Water also can reduce the risk of explosion.

Process Conditions and Chemicals

Safety margins restrict operation conditions. Operations have been often performed outside the explosion regime. High pressure is, therefore, needed to dissolve hydrogen enough in liquid in order to increase the productivity. The main operating conditions, solvents and additional chemicals used in the systems are listed in the table. Water has been used as a solvent in most cases. The use of methanol, ethanol and propanol is promoted by the fact that solubility of hydrogen and oxygen in these alcohols is clearly higher than in water [10]. However, alcohol as a solvent may require a process to separate it from hydrogen peroxide and water. Many research groups have used acids and bromide compounds as promoters. It has been demonstrated that Br^-, Cl^- ions and H^+ ions inhibit the direct formation of water and reduction of hydrogen peroxide, thus, improving the yield [3].

Catalysts

Direct synthesis of hydrogen peroxide is a catalytic process. The most commonly used metal in the catalyst is palladium (Pd) [3–5, 7–9, 11]. Wang et al. [10] used platinum (Pt) and Pd-Pt mixture in their studies. Bimetallic Pd-Pt catalyst was tested also by Inoue et al. [11]. Although, gold (Au) seems to promote the formation of hydrogen peroxide [20], it has not been applied yet in microreactors.

The support material of the catalyst plays an important role in the selectivity of the reaction. Different support materials and fixing techniques have been tested. Installing the catalyst and support material in a microreactor often requires a specific technique due to the small channel sizes.

Voloshin et al. [3, 7] used SiO_2 as a catalyst support. They prepared a 2-wt % Pd on a SiO_2 catalyst by the sol–gel method. The palladium was obtained from $PdCl_2$. In addition, tetraethoxysilane, ethanol and water were needed in the preparation of the gel. After calcination, the catalyst was ground and sieved resulting in the particle diameters of 75–150 μm. The specific area of the catalyst was 603 m^2/g. The catalyst particles were packed in the capillary of the microreactor, and a filter was installed at the end of the capillary to retain the particles in the reactor.

Inoue et al. [11] used a SiO_2 support for bimetallic Pd-Pt catalyst. $PdCl_2$ and $PtCl_4$ were first dissolved in HCl and after that silica gel was added in the solution. The slurry was then filtered, dried and calcined. The catalyst was sieved to separate particles with diameters of 50–70 μm. Fine catalyst particles were suspended in deionised water and pumped in the reactor channels. Also here, a filter was used to retain catalyst particles in the reaction channels. The reactor was dried in the oven after which the catalytic packed bed was formed in the channels. Similar technique has been used to install commercial Pd/C and Pd/Al_2O_3 catalysts in the reaction channels [8, 11].

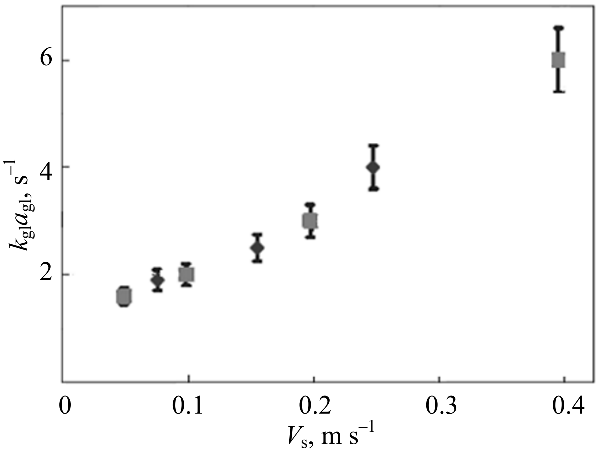


Fig. 3. Effect of total superficial velocity on the volumetric gas–liquid mass transfer coefficient in a capillary microreactor [7].

Maehara et al. [4] utilised a commercial 5 wt % Pd/C catalyst in their reactor. The inner surface of the reaction capillary was coated by pumping the Pd/C catalyst slurry through it. As a result, the catalyst adhered strongly on the surface of the capillary resulting the loading of 94 mg catalyst/m of silicon capillary, corresponding 30 g catalyst/m^2. In the case of the stacked microreactor, the loading of 84 mg was achieved. Zeolite was used as a catalyst support by Wang et al. [10]. Pd catalyst was impregnated on the zeolite support. Aqueous solution of $PdCl_2$ was mixed with NH_4OH to form $Pd(NH_3)_4Cl_2$ solution. This solution was then mixed with selected zeolites, e.g. H-ZMS-5, H-beta or H-ferrierite. After mixing, water was removed by evaporation. Finally, the impregnated zeolite was calcined. The same group also prepared also a Pd–silicalite catalyst. In the preparation, Pd $(NH_3)_4Cl_2$ was first mixed with silicalite gel to give a 0.3–5 wt % metal loading. Crystallisation of the catalyst material was performed in an autoclave. The catalyst powder was slurried and deposited in the reaction channel, where a 100 μm thick layer was formed on the surface. Wang et al. [10] applied also another method to install the catalyst in the reactor. They first deposited zeolite on the surfaces of the multichannel silicon reactor and after that impregnated Pd and Pt metal on the zeolite support. In this seeding technique, they first deposited seed zeolites on the surfaces. After that the zeolite layer was grown from the solution on the channel surface.

Ng et al. [5] fixed catalyst in the reactor by using a polymeric binder. Polystyrene, tetrakis(trisphenylphosphine)palladium, THF, and cyclohexane were mixed to form polymer micelles. This mixture was used to fill the small reaction tubes. Polymer micelles precipitated on the glass surface, and the solvent evaporated during the preparation process. After solvent evaporation, a thin and uniform film of a yellow precipitate formed on the surface of the tubes. Finally, after washing with hexane, drying and heating tetrakis(trisphenylphosphine)palladium decomposed and formed a palladium nanoparticle layer on the glass surface.

Factors Affecting Conversion and Yield

Catalyst System

Only Pd and Pd–Pt have been reported as catalysts in direct microreactor synthesis of hydrogen peroxide. Research groups have also studied the effect of support material and catalyst loading.

Wang et al. [10] made experiments with Pd catalysts and Pd-Pt catalysts. In their experiments, the total catalyst loading on the silicalite support was 2.0 wt %. When Pt loading was increased from 0 to 0.3 wt % and correspondingly Pd decreased from 2 to 1.7 wt %, hydrogen peroxide concentration, hydrogen conversion and selectivity increased and reached the maximum values. Further increasing of Pt and decreasing of Pd resulted in lower performance. By using 1.7 wt % of Pd and 0.3 wt % Pt on silicalite support, 70% selectivity, 5.4% conversion and 0.3 mol/l hydrogen peroxide concentration were achieved. Inoue et al. [11] tested also Pd-Pt catalyst but the real effect of Pt could not be concluded because they used different support for Pd catalysts. In the case of bimetallic catalyst, they had silica support and for Pd catalyst they used both Al_2O_3 and C support. However, selectivity of the Pd–Pt catalyst was clearly lower than that of Pd/C catalyst.

Recently Ng et al. [5] demonstrated the effect of catalyst loading on the synthesis reaction. They used Pd catalyst on a polymer support. Catalyst loadings of 1, 2 and 4 wt % were studied and improved production of hydrogen peroxide was observed when catalyst loading was increased. Hydrogen peroxide concentration of 0.29 mol/l was achieved. When considering the productivity in the form of molar amount of hydrogen peroxide/time and mass of catalyst, the 2 wt % loading resulted in the highest productivity. A minor loss of activity with increased catalyst loading from 2 to 4 wt % may originate from a slight increase of Pd particle size. The effect of Pd loading was also studied by

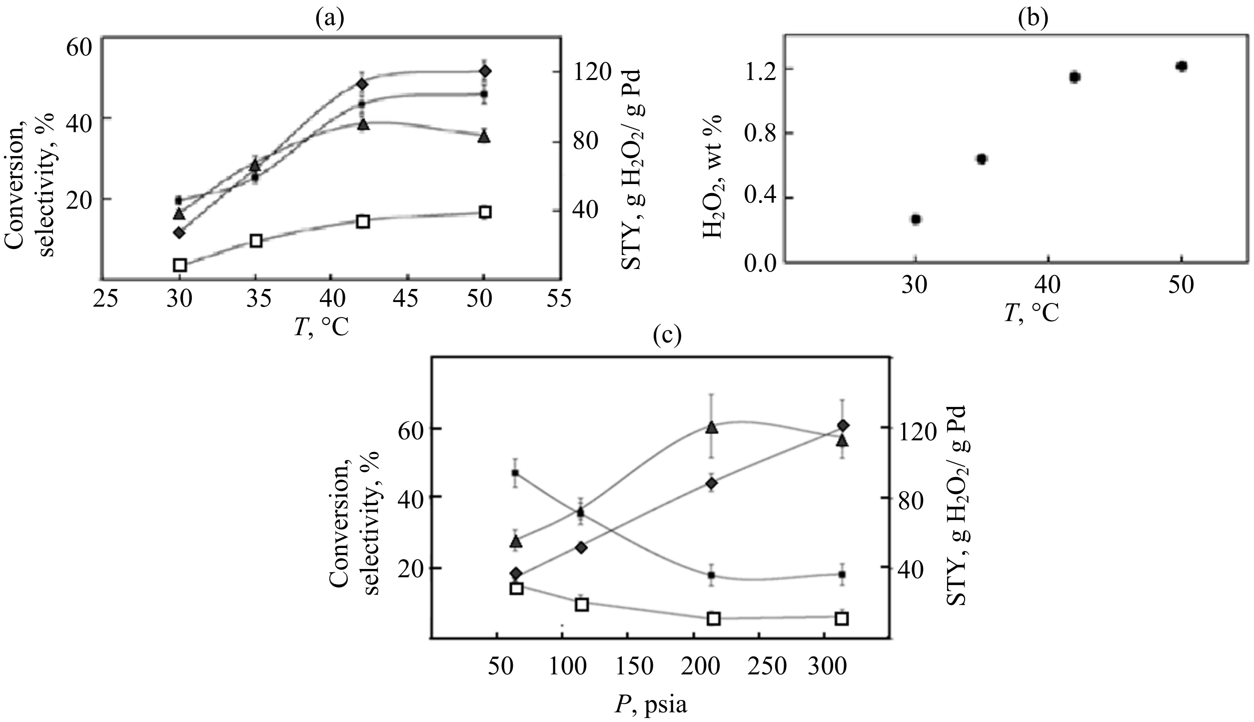


Fig. 4. Effect of temperature and total pressure on the formation of hydrogen peroxide: (a) hydrogen conversion, oxygen conversion, hydrogen peroxide selectivity, and space-time yield (STY) and (b) outlet concentration of hydrogen peroxide. Reaction conditions: gas composition 9.1% H_2 in air, total pressure 2.2 MPa, gas flow rate 22 nml/min, liquid flow rate 0.05 ml/min, and catalyst amount 15 mg (2% Pd/SiO_2) [3]. (c) Reaction conditions: gas composition 9.1% H_2 in air, temperature 42°C. 50 psia = 0.34 MPa, 100 psia = 0.69 MPa, 150 psia = 1.03 MPa, 200 psia = 1.38 MPa, 250 psia = 1.72 MPa, 300 psia = 2.07 MPa, and 350 psia = 2.41 MPa [3].

Wang et al. [10]. They increased Pd loading on zeolite from 0.3 to 5 wt % and measured increased conversions but decreased selectivity. The highest hydrogen peroxide concentration was achieved at the loading of 1.2 wt %. Higher Pd loadings resulted in poorer metal dispersion that has negative impact on hydrogen peroxide formation.

Several catalyst supports were evaluated by Wang et al. [10]. In all cases they used 2 wt % Pd loading. According to their studies, the use of silicalite support resulted in higher conversion (5%), selectivity of hydrogen (43%), and concentration of hydrogen peroxide (0.20 M) than different zeolite supports. Inoue et al. [8, 11] compared the C and Al_2O_3 supports for Pd catalyst. In the earlier study they found out that a C-supported catalyst gave better selectivity and yield than an Al_2O_3-supported catalyst. However, they observed differences in wetting of the supports. In the case of the C-supported catalyst, voids between particles were filled almost totally by liquid. Between the Al_2O_3-supported catalyst, voids were partly dry. This feature could affect the catalyst activity. In the latest study they concluded that with an Al_2O_3-supported Pd catalyst, higher hydrogen peroxide production was achieved than in the case of the C support. The maximum reported yield and mass fraction were 9.9 and 3.2 wt %, respectively. On the other hand, they reported that the Pd/Al_2O_3 catalyst used in the latest study was not identical to that in the earlier study. There was a difference in the reduction treatment of the catalyst during preparation. Gas phase reduction was used in the earlier study and liquid phase reduction in the latest study.

Solvents and Promoters

Solvent selection plays an important role in the direct synthesis of hydrogen peroxide. In addition, some additional chemicals, often called promoters, improve the productivity of hydrogen peroxide by preventing undesired side reactions. Water has used mainly as the solvent, although the use of methanol, ethanol and isopropanol enable higher productivity of hydrogen peroxide due to the higher solubility of hydrogen and oxygen. This was concluded by Wang et al. [10] and Ng et al. [5]. The use of methanol which was acidified to 0.1 M by hydrochloric acid resulted in higher hydrogen peroxide concentration than that of ethanol and isopropanol [10]. Ng et al. [5] showed that using of Br^- and Cl^- ions in the system increases the yield of hydrogen peroxide. Hydrogen ions from acids and halide ions inhibit direct water formation, hydrogenation, and decomposition reactions. The highest concentration 0.33 M was achieved with the solvent system of methanol, hydrochloric acid, and potassium bromide, but conversion and selectivity were not determined. The system which consisted of methanol, sulfuric acid, and potassium bromide resulted in the concentration of 0.28 M. The hydrogen conversion and selectivity were 3.9 and 77%, respectively. When pure methanol was used, only 0.03 mol/l of hydrogen peroxide was produced. In this system, selectivity remained very low, only 0.65%.

Reaction Conditions

The effect of process conditions, such as temperature and pressure, on reaction has been studied. Maehara et al. [4] reported that hydrogen peroxide concentration decreased from 8 mM to 6 mM, when temperature was increased from 5 to 20°C. Voloshin et al. [3] observed that selectivity increased first, when temperature was increased from 30 to 40°C. Above 40°C, selectivity started to decrease slightly, indicating increased formation of side products (Figs. 4a, 4b). They also studied the effect of pressure (Fig. 4c). Also in this study selectivity first increased with pressure up to 1.4 MPa, after which it decreased slightly. Space–time yield increased linearly with pressure, while the conversions of hydrogen and oxygen decreased. It was thus concluded that the rate of the formation reaction of hydrogen peroxide is more strongly dependent on the partial pressures of hydrogen and oxygen than the rate of side reactions.

Gas Ratio

The whole hydrogen peroxide reaction scheme consists of oxidation and reduction reactions as shown in Fig. 1. The main reaction is oxidation of hydrogen. However, the complete oxidation of hydrogen should be avoided. In addition, reduction of hydrogen peroxide is also an undesired side reaction. Therefore, oxygen and hydrogen ratio is an important factor in the reaction system. Wang et al. [10] and Ng et al. [5] concluded that excess of hydrogen favors the reduction of hydrogen peroxide and decreases its concentration. The results of Ng et al. [5] showed that an excess of oxygen (O_2:H_2 2:1) gave the highest concentration of hydrogen peroxide (0.25 M). High selectivity (85%) and yield (77%) were also achieved at the O_2:H_2 ratio of 3:1 [19]. On the other hand, Wang et al. [10] reported that the best results were obtained with a stoichiometric feed of hydrogen and oxygen.

CONCLUSIONS

The microreactor technology can offer advantages when producing hydrogen peroxide directly from oxygen and hydrogen gases. Hydrogen gas forms easily explosive mixture with oxygen and air, and therefore the synthesis requires safe production technology. Microreactors with small channels and low internal volumes enable safe operation in challenging conditions. They represent an inherently safe production technology. Direct synthesis in a microreactor is very suitable for on-site production of hydrogen peroxide. There might be no need to concentrate the hydrogen peroxide solution, because dilute hydrogen peroxide can be used directly in various applications.

Literature study reveals that microreactors have been applied successfully in the direct synthesis in laboratory conditions. Research groups reported high conversions, yields, selectivities, and mass fractions of hydrogen peroxide up to 90, 77, 100% and 5 wt %, respectively. So far, only Pd and Pt catalysts have been used in microreactors. The use of Au catalysts can improve productivity. The development work both in the field of catalysis and in the field of reactor technology continues actively, since direct synthesis in microreactors seems a very promising technology to produce hydrogen peroxide in future.

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