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Hydrogen Peroxide Direct Synthesis: Enhancement of Selectivity and Production with non-Conventional Methods

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The present work is part of a comprehensive study on the direct synthesis of hydrogen peroxide in different fields, from chemistry to chemical engineering. Working on the different fields of the direct synthesis gave the possibility to look at the results and the challenges from different viewpoints. Here was investigated one parameter that enhances the direct synthesis. The H_2/Pd ratio is the key parameter that has to be investigated and optimize to enhance the hydrogen peroxide direct synthesis. Two reactors were built to study deeply the H_2/Pd ratio and to demonstrate how this parameter can affect the direct synthesis both in batch and continuous reactor with non-conventional experiments/methods. 1) A batch reactor was utilized as a "starving reactor" to enhance the productivity of hydrogen peroxide and to try to keep constant the selectivity. The starving method consists in refilling the hydrogen when it is consumed in the reactor. 2) A trickle bed reactor was utilized with a gradient of catalyst along the reactor to maximize both production and selectivity of hydrogen peroxide. The distribution of the catalyst along the bed gave the possibility to significantly improve the selectivity and the production of hydrogen peroxide (up to 0.5% in selected conditions). Higher production rate and selectivity were found when the catalyst concentration decreases along the bed from the top to the bottom compared to the uniformly dispersed catalyst. Selectivity in the batch reactor was enhanced by 5% and in the continuous reactor of 10%. The non-conventional experimental methods have been found to be novelty concepts to enhance the hydrogen peroxide direct synthesis.

1. Introduction

Hydrogen peroxide is considered an inherently green oxidant, one of the cleanest, most versatile chemical oxidants available, since it decomposes to yield only water and oxygen as the reaction products. H_2O_2 is also one of the most efficient oxidizing agents by virtue of its high active oxygen content (about 47%), only next to molecular oxygen.

Hydrogen peroxide was discovered by the world-famous French chemist Louis-Jacques Thénard in 1818. Since then to the beginning of the 20th century, 3% H_2O_2 solutions were obtained from the hydrolysis of barium peroxide with sulphuric acid. Several alternative processes, such as electrochemical and chemical (oxidation of isopropanol or methylbenzyl alcohol, or antraquinone oxidation) processes have been developed and are available for the production of H_2O_2.

Today, hydrogen peroxide is manufactured almost exclusively by the Riedl-Pfleiderer process and the Hydrogen peroxide annual production is nowadays around three million tons and the growth of its market is estimated around 4%/year (Arkema Website).

The main uses of hydrogen peroxide in europe are summarized below in the Figure 1 below. As revealed by the Figure 1, the major part of the hydrogen peroxide, more than 80% is used for paper bleaching and chemical synthesis.

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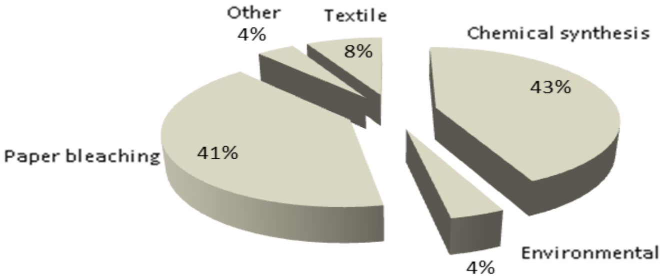

Figure 1: Uses of hydrogen peroxide in Europe.

1.1 Why direct synthesis?

The "Strategic Research Agenda" (SRA) of the European Technology Platform for Sustainable Chemistry reports that the direct synthesis of the H_2O_2 from H_2/O_2 and its integrated use in chemical processes is one of the priorities for a sustainable chemistry (Centi, 2009). H_2O_2 is an ideal clean reagent, but its industrial use is inhibited from the high cost of the H_2O_2. This is reflected by the complains of the H_2O_2 users, which suffer rising in prices due to a market strictly constrained by few large producers (Centi, 2009).

The direct synthesis from H_2/O_2 with catalysts based on Pd allows to decrease more than half the cost of commercial H_2O_2, making economically feasible the following processes: direct synthesis of phenol, propene oxide, caprolactam. Moreover, the following industries will also benefit from the direct synthesis: paper industry (as a bleaching, chlorine-free chemical), textile industry (as a bleaching agent replacing sodium chlorite and hypochlorite or a component in many detergents), chemical industry itself (in oxidations, epoxydations, hydroxylation, as an initiator in polymerisations) and in the electronic industry (to clean semiconductors). Other potential applications of the direct synthesis are primary and waste water treatment (as a disinfectant or sulphite odour control), several inorganic syntheses (manufacture of sodium percarbonate and sodium perborate, used as mild bleaches in laundry detergents) and several domestic use (disinfectant, bleaching of hairs and tooth whitener, detergents).

Most of the applications mentioned call for a capillary network of distribution, in relatively limited individual quantities. This fragmentation of usage, together with the hazard of transportation, suggests another breaking observation: developing small-scale production units would be a much required, a further goal for a new process. Again, this is in conflict with the actual situation where almost universally H_2O_2 is produced through a complex process, with a critical environmental impact, which is economically feasible only at large scale. Consequently, the H_2O_2 production is presently concentrated in a few large plants and little space for competition is left to small and medium producers (Campos-Martin et al., 2006), unless a new, economically viable technology emerges (Centi et al., 2009).

The H_2O_2 effectiveness as an oxidant is also due to the large abundance of oxygen in its molecule (47%), where only pure O_2 has a higher value. In addition, use of H_2O_2 produces harmless water and oxygen, as required by a green chemical.

The arguments above lead to the choice of investigating the process of direct synthesis of H_2O_2 from H_2 and O_2. The reaction is apparently extremely simple, but unfortunately side reactions are likely to occur, partly connected with the reactivity of H_2O_2, that causes hazard in manipulation and transportation, but it is also the reason for its countless applications, partly because they involve water, an extremely stable molecule, as product.

The technology related to the direct synthesis will benefit the industries lowering the price of hydrogen peroxide and reducing the wastes related to the auto-oxidation process. The direct synthesis of hydrogen peroxide is the most promising alternative to the auto-oxidation process. Table 1 compares the benefits and drawbacks of the auto-oxidation process and the direct synthesis. The direct synthesis is still not well enough developed to be considered as an alternative to the auto-oxidation process, but research efforts will be helpful to solve all the issues related to the selectivity and safety issues of the direct synthesis process.

Table 1: Comparison between auto-oxidation process and direct synthesis of hydrogen peroxide.

PROCESS	Indirect synthesis auto-oxidation process	Direct synthesis
PRINCIPLE	Sequential hydrogenation and oxidation of organic molecules, release of H_2O_2 and recycle of the organic molecules	$H_2+O_2=H_2O_2$
GENERAL FEATURE	A very famous, well-known and complex process developed during a very long time	A very simple process but still lack of maturity
CATALYST	Pd in the hydrogenation step	Pd- and Au-based catalysts
REACTION ENVIRONMENT	Working solution of a mixture of organic molecules	H_2O, MeOH or EtOH, CO_2 used as a co-solvent
REACTOR SYSTEM	A complex system that counts of numerous and sequential big reactors	Synthesis done in one reactor
SELECTIVITY	High	It is an issue
SAFETY	Safe	Can be made safe
ON SITE PRODUCTION	Impossible	Possible

1.2 Scope of the research on the H_2O_2 direct synthesis

The present research is part of the research strategy on the hydrogen peroxide direct synthesis. The combination of catalysis and chemical engineering applied to the hydrogen peroxide direct synthesis is fundamental to understand this complicate reaction. The general aim of the work is to demonstrate that is necessary to understand both the catalytic and reactor effects on the direct synthesis (Biasi et al., 2012a, Gemo et al., 2012; Kilpio et al., 2012). The development of new catalysts has to be investigated coupled to reactor development in order to find the most suitable conditions for high production rate and selectivity towards hydrogen peroxide (Biasi et al., 2010; Biasi et al., 2011a; Biasi et al., 2011b; Biasi et al., 2012b). The all work was structured as reported in the research diagram flow-sheet in Figure 2.

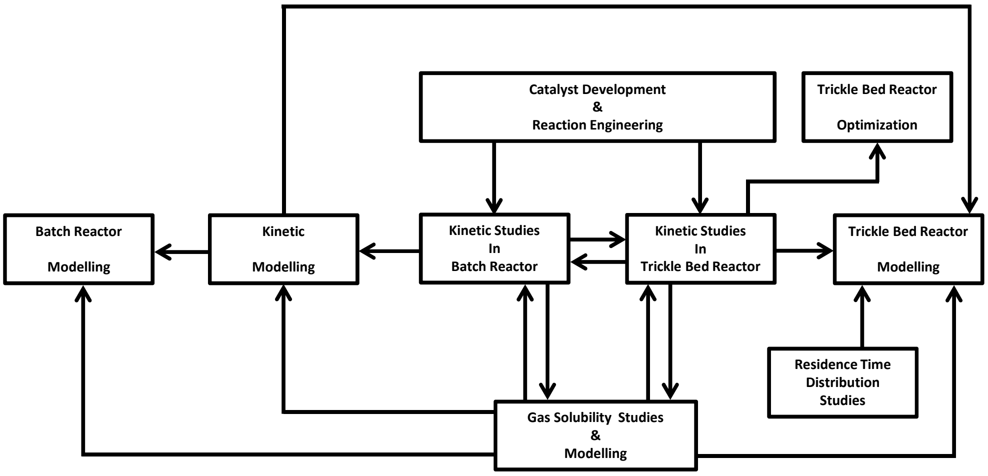

Figure 2: Research diagram flow-sheet for hydrogen peroxide direct synthesis

Here we investigate the H_2/Pd ratio a parameter of particular importance that has been found to be of critical importance in the direct synthesis both in batch and in continuous reactors. H_2/Pd ratio was investigated with new concepts in reactor design like the “starving reactor” and the “catalyst gradient distribution continuous reactor”.

2. Experimental Set-Up

2.1 Batch Reactor

The experiments were performed in a tailored batch reactor, i.e., a stainless steel autoclave reactor (Parr) with a volume of 600 mL and a maximum working pressure of 200 bar. The mixing was performed by a Heidolph RZR 2021 rotor operating at 1000 rpm. The reactor was fitted with a K-type thermocouple connected to a PC that allowed acquisition of temperature data during the experiments. CO_2 and O_2 were loaded into the reactor directly from gas cylinders. Hydrogen was fed by a Brooks mass flow controller to avoid overpressure in the reactor and to ensure a constant and reproducible flow. A 35 mL vessel coupled with a pressure transducer and a heating jacket was placed before the mass flow controller (MFC) for hydrogen feeding. This was used to calculate precisely the amount of hydrogen fed into the reactor.

Before the experimental programme was started, a 4 hour passivation treatment was performed on the reactor, using 30 wt.% nitric acid at 40 °C. Methanol was chosen as reactant medium.

The protocol developed for the experiments was as follows: 0.15 g of a 5% Pd/C (supplied by Degussa) catalyst were loaded in the reactor. Carbon dioxide (18.4 bar) and oxygen (6 bar) were loaded into the reactor directly from the cylinders at 25 °C, followed by the injection of 400 mL of methanol by an HPLC pump. After both pressure and temperature were stable hydrogen was fed from the vessel into the reactor through the mass flow controller. Three different experiments were conducted: 1) synthesis of hydrogen peroxide with one hydrogen filling at the beginning of the reaction (Biasi et al., 2012b); 2) synthesis of hydrogen peroxide with four hydrogen fillings along the reaction, after the totality of the hydrogen dissolved in the liquid phase was completely consumed and 3) synthesis of hydrogen peroxide with four hydrogen fillings, as soon as the hydrogen concentration in the liquid phase started to decrease.

2.2 Trickle Bed Reactor

The system consisted of four sections, liquid inlet, gas inlet, three-phase reaction, and biphasic separation. The liquid was pumped at room temperature using a HPLC pump. The gases were fed independently from gas cylinders (CO_2/H_2 95/5 mol% and with pure O_2) controlled by mass flow controllers (MFC). The TBR was made of AISI 316 stainless steel, 60 cm long and 1.5 cm I.D. (ca. 105 mL) passivated using nitric acid 30 % wt. during 4 h to prevent H_2O_2 decomposition due to iron catalysis. The bed is composed of 2 cm of glass wool at the bottom and up to 110 g of quartz sand mixed with the catalyst (ca. 80-100 mL) reactor can accommodate a catalyst bed up to 50 cm long. The reactor operated in continuous mode, with cocurrent downflow gas and liquid phases. Liquid flow rate: 1 mLmin water (enhancers: 0.0003 M NaBr+ 0.005 M H_3PO_4) and gas flow rate: 4 mL/min.

Water was used instead of methanol in the continuous fixed bed reactor. Water was chosen because the hydrogen solubility is lower than in methanol. If methanol is used as liquid phase there is a risk that the amount of H_2 available for the direct synthesis is too high in the liquid phase, resulting in a fast H_2 consumption. Since the aim of the study was to improve the reaction conditions water was chosen as reactant medium to dose the hydrogen in the liquid phase in all the reactor length.

3. Results and Discussion

3.1 Batch Reactor

The experiments in the batch reactor were performed in order to find a relationship between the selectivity, the production rate and the amount of hydrogen fed into the reactor (Figures 3 and 4). The same amount of hydrogen was fed into the reactor straight after the gas dissolved in the liquid was completely consumed. Both the hydrogen peroxide and water concentrations increased during the reaction. The selectivity had different behaviour though: every time that fresh hydrogen was fed into the reactor, the selectivity towards hydrogen peroxide increased; when hydrogen started to decrease, such selectivity decreased as well. The results prove that the amount of hydrogen plays an important role in the direct synthesis.

Regarding the importance of the H_2/Pd ratio, experiments were conducted avoiding the complete depletion of hydrogen in the liquid phase. In that sense, equal amounts of hydrogen were reloaded into the reactor a certain time after the H_2 peak was recorded with the Fugatron instrument. Such subsequent hydrogen feeding policy demonstrated how a higher selectivity could be achieved compared to the former experiments when the hydrogen was refilled after its complete consumption. The selectivity towards hydrogen peroxide in this case reached a peak around 33 %, compared to only 27 % in the previous case, i.e., when hydrogen was completely consumed (Figure 4). Moreover, the hydrogen peroxide concentration increased constantly until soluble hydrogen was consumed. After this point, the concentration of H_2O_2 remained quite stable. It is interesting to notice that the hydrogen peroxide production was almost equal to the former experiments and moreover, the selectivity reached a higher value (Figures 3 and 4). Hydrogen peroxide formed faster in such experiments due to the amount of hydrogen present in the liquid phase.

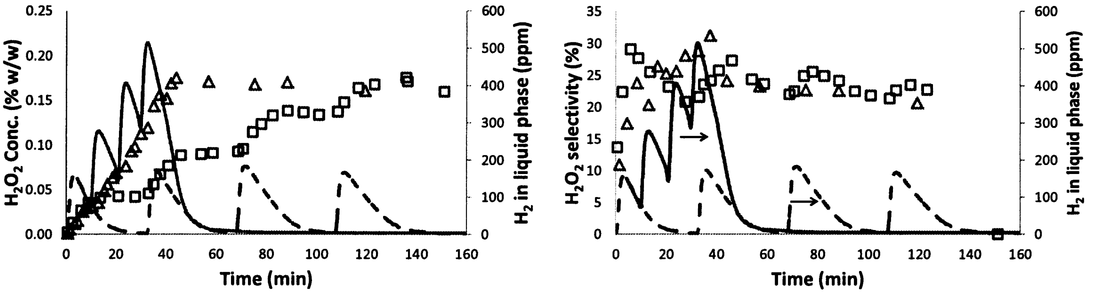

Figure 3 (left) and 4 (right). H_2O_2 concentration (Figure 3) and Selectivity (Figure 4) of H_2O_2 at 10 °C and 18 bar with different hydrogen feeding policies: 1) Hydrogen amount fed after its complete depletion in the liquid phase (solid line) and 2) hydrogen subsequently fed as it decreases in the liquid phase (dashed line). H_2O_2 selectivity under feeding policy 1 (□) and under feeding policy 2 (Δ).star

Comparing the two experiments performed with the hydrogen refilling, an obvious observation concerns the selectivity, which remained stable around a value of 20 % after hydrogen depletion. Moreover, in both cases (Figures 3 and 4), the highest selectivity was reached during the first minutes of the reaction. These results allow the following considerations to be made: 1) hydrogen dissolved in the liquid phase is consumed rapidly (during the first 30 min of reaction time); 2) when hydrogen was not present in the liquid phase, the hydrogen peroxide formed decreased slowly and so did the selectivity; 3) the hydrogen refilled in the reactor enhanced the selectivity; 4) hydrogen refilling before its complete depletion gave better results compared to the case when hydrogen was refilled after its complete consumption and finally 5) hydrogen peroxide production could be increased by regulating the amount of hydrogen dissolved in the reaction medium.

3.2 Trickle Bed Reactor

Following the results in the batch reactor the concept of the "catalyst gradient distribution continuous reactor" was applied. Three different catalyst bed accommodations were designed and fed into the trickle bed reactor to confirm the hypothesis reported above.

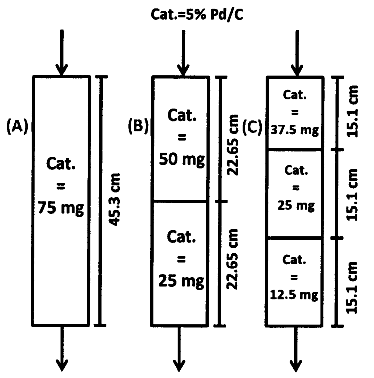

Figure 5: Visual distribution of the catalyst for the configuration A, B and C

Bed A) consisted in 75 mg of catalyst uniformly distributed in 80 mL of quartz sand, while bed B) was composed of 40 mL of quartz on the bottom with 25 mg of catalyst perfectly mixed together and above that 50 mg of catalyst dispersed in 40 mL of quartz sand and, finally, bed C) was divided in three parts of 26.6

mL of quartz sand and from the bottom the quantity of the catalyst was 12.5, 25 and 37.5 mg of catalyst in each part of the quartz sand. The three different bed dispositions are reported in Figure 5.

From those preliminary results from the bed A) to the bed C) (Figure 5) there was an average enhancement of 10 % in the selectivity and a 20 % of the H_2O_2 produced only with a different disposition of the catalyst bed. The best achievement was found at 5 °C where the yield was improved by a value of 11 % from a 50 % with the bed A) to 60 % with the bed C). the production rate was 0.4 wt.% with the bed A) and 0.5 wt.% with the bed C). the amount of the active catalyst was the same and if the hydrogenation (H_2+H_2O_2 over Pd catalyst to give 2 H_2O) was not influenced by the H_2/Pd ratio the results should have been exactly the same. These results showed that the hypothesis made was correct because with this different disposition the hydrogenation is kept lower in the bed C) then in the bed A). All the results made with the bed B) were following the same trend than in the former cases decreasing the production and the yield of H_2O_2 when the temperature is increased from 5 to 35 °C.

4. Conclusions

Different policies of H_2 feeding gave the possibility to enhance the hydrogen peroxide production rate and selectivity in a batch reactor. An improved selectivity was achieved by refilling hydrogen before its complete consumption. These results gave further direction of the investigation on the role of hydrogen dissolved in the direct synthesis. The investigation on the batch reactor was fundamental to program the research activities in a continuous reactor.

A new trickle bed reactor was constructed with the information from the batch experiments. Following the experiments that showed the importance of the H_2/Pd ratio, the concept of “catalyst gradient distribution continuous reactor” was introduced. The bed with a catalyst gradient was found to be very essential to increase selectivity and productivity in a continuous reactor. These results confirmed that if the H_2/Pd ratio goes under some values, hydrogenation takes place as the main reaction.

Finally, the non-conventional methods to operate a reactor as the “starving reactor” and the “catalyst gradient distribution continuous reactor” were a success to enhance the hydrogen peroxide direct synthesis. These new concepts applied to reaction engineering and catalysis engineering will not benefit only the direct synthesis, but also other reactions were selectivity is a really important issue.

References

Arkema Website http://www.arkema.com/sites/group/en/products/spotlight/h2o2.page, 11.01.2013

Biasi P., Menegazzo F., Pinna F., Eranen K., Canu P., Salmi T.O., 2010, Hydrogen Peroxide Direct Synthesis: Selectivity Enhancement in a Trickle Bed Reactor, Industrial & Engineering Chemistry Research, 49, 10627-10632.

Biasi P., Zancanella S., Pinna F., Canu P., Salmi T.O., 2011a, Hydrogen Peroxide Direct Synthesis : from Catalyst preparation to Continuous Reactors, Chemical Engineering Transactions, 24, 49-54 DOI: 10.3303/CET1124009

Biasi P., Menegazzo F., Pinna F., Eranen K., Salmi T.O., Canu P., 2011b, Continuous H2O2 direct synthesis over PdAu catalysts, Chemical Engineering Journal, 176-177, 172-177.

Biasi P., Gemo N., Hernandez Carucci J.R., Eranen K., Canu P., Salmi T.O., 2012a, Kinetics and Mechanism of H_2O_2 Direct Synthesis over a Pd/C Catalyst in a Batch Reactor, Industrial & Engineering Chemistry Research, 51, 8903-8912.

Biasi P., Canu P., Menegazzo F., Pinna F., Salmi T.O., 2012b, Direct Synthesis of Hydrogen Peroxide in a Trickle Bed Reactor: Comparison of Pd-Based Catalysts, Industrial & Engineering Chemistry Research, 51, 8883-8890.

Campos-Martin J.M., Blanco-Brieva G., Fierro J.L.G., 2006, Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process, Angewandte Chemie International Edition, 45, 6962–6984.

Centi G., Perathoner S., Abate S., 2009, Direct synthesis of hydrogen peroxide: recent advances, Modern Heterogeneous Oxidation Catalysis, Wiley-VCH Weinheim, Germany, pp. 253-287.

Gemo N., Biasi P., Salmi T.O., Canu P., 2012, H_2 solubility in methanol in the presence of CO_2 and O_2, The Journal of Chemical Thermodynamics, 54, 1-9.

Kilpio T., Biasi P., Bittante A., Salmi T., Warna J., 2012, Modeling of Direct Synthesis of Hydrogen Peroxide in a Packed-Bed Reactor, Industrial & Engineering Chemistry Research, 51, 13366-13378.