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## Engineering in direct synthesis of hydrogen peroxide: targets, reactors and guidelines for operational conditions

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The demand for hydrogen peroxide is booming since it is considered as one of the most environmentally friendly and versatile chemical oxidants available and has a wide range of applications. The annual market, close to 3000 kt per year being produced via the auto-oxidation process (with 2-ethyl anthraquinone (traditional) or amyl anthraquinone for mega-plants), is mostly supplied by the company Solvay (30%), followed by Evonik (20%) and Arkema (13%). Nevertheless, the dream of a direct synthesis process is close to a century old and it has gained momentum in research efforts during the last decade with more than 15 groups active in the world. In this review, we focus the discussion on the targets, e.g. plant tonnage, the reactors and the most feasible industrial operational conditions, based on our experience and point of view using the chemical engineering tools available. Thus, direct synthesis can be competitive when on-site production is required and capacities less than 10 kt per year are demanded. The total investment cost should be approximately  $40.3 \pm 12.1$  MM\$ (in 2012) for a 10 kt per year size process to be comparable to the traditional process in terms of costs. Moreover, all kinds of reactors used are hereby discussed emphasizing the pros and cons; the most common ones are batch

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and semi-continuous modes of operation. However, at the moment, demonstrations of continuous operations as well as carefully determined kinetics are needed in order to scale up the process. Finally, operational conditions, including the catalyst composition (active metal, oxidation state and support), promoters (halides and acids—pH—isolectric point), solvents, pressure and temperature need to be carefully analysed. In our opinion, as we try to show here,  $\text{H}_2\text{O}_2$  direct synthesis is a competitive process and is ready for larger scale demonstration. Also, more than a hundred patents within the area support this claim, although the barriers of technology demonstration and further licensing are still pending.

## 1. Introduction

Known since the onset of the 20<sup>th</sup> century when Hugo Henkel and Walter Weber patented the first method for the production of  $\text{H}_2\text{O}_2$  *via* direct synthesis in the presence of water and a suitable catalytic agent in 1914,<sup>1</sup> the direct synthesis of hydrogen peroxide has only become a truly promising alternative to the auto-oxidation route over the last few decades.<sup>2,3</sup>

Only during the last decade (from 2004 to 2013 included) *ca.* 70 patents have been granted (more than 30 between 2004 and 2006). In light of this, it appears that the technology is well protected but, apparently, there is still scope for development. Therefore, the process could be developed if companies found the niche or the eco-efficiency opportunity over the traditional auto-oxidation process (AOP). Moreover, the safety issues should always be considered in detail.

An apparently simple reaction, such as the direct reaction between hydrogen and oxygen to produce  $\text{H}_2\text{O}_2$ , is, in fact, much more complex than it seems at first glance. Issues such as the requirement of a selective catalyst and three-phase reaction conditions, together with the existence of side reactions that seriously affect the selectivity of the process, *i.e.* the formation of water, the decomposition of hydrogen peroxide, and the reduction of hydrogen peroxide, are the most important chemical and technical challenges for this process.

Benchmarking against the current amyl anthraquinone high-productivity technology, the last improvement over the traditional ethyl anthraquinone process (both Solvay's proprietary)<sup>4</sup> is not trivial.

Campos-Martin, Blanco-Brieva and Fierro reviewed the hydrogen peroxide synthesis process analysing the market, applications and the large-scale conventional auto-oxidation synthesis process.<sup>2</sup> They also reviewed the different emerging alternatives, such as direct synthesis, photocatalysis, fuel cells, plasma reactors (from carbon monoxide, oxygen and water), direct reduction of oxygen among others. This work represents an excellent basis to overview the past, present and future hydrogen peroxide technologies. A couple of years later, Samanta reviewed the direct synthesis process thoroughly. He focused on the operational aspects of the direct synthesis by analyzing the factors that affect the secondary reactions, *i.e.* decomposition and hydrogenation.<sup>3</sup> He also analyzed the parameters that influence the selectivity towards  $\text{H}_2\text{O}_2$ , such as solvent, concentration of  $\text{H}^+$  ions, palladium oxidation state, support, metal additives,  $\text{H}_2/\text{O}_2$  ratio and reaction time. An inspiring book chapter was more recently written by Centi, Perathoner and Abate affording a longitudinal industrial perspective in order to better understand the reactor conditions and fundamental aspects. The authors also reviewed the most recent patents and open literature on the direct synthesis reaction.<sup>5</sup>



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The three approaches are necessary to understand the hydrogen peroxide synthesis, from the current industrial process to the most promising alternatives. Nevertheless, there has been little discussion on the targets, the reactors and the most feasible industrial conditions to be used. There are still several issues that must be addressed: first, the best techniques to cost-effectively study the process from both industrial and basic research points of view; second, the recent advancements and protection of the technology *via* patents; and third, the design criteria for process development, including a review of the reaction kinetics and mass transfer phenomena.

In particular, when discussing the kinetics, we profoundly believe that kinetic studies are the key issue to understand the fundamentals, to determine trends with a physico-chemical basis and to develop not only industrial processes but also relevant apparatus to be used in laboratory and pilot scales. In this sense, we encourage the researchers in the topic to analyze the effects and behavior of the reaction system from the view of kinetic mechanisms and transport phenomena.

In this review, we focus the discussion on the targets (*e.g.* plant tonnage), the reactors (including pros and cons) and the most feasible industrial operational conditions to use, from our experience and point of view using the chemical engineering tools available.

## 2. What are the targets to be achieved for hydrogen peroxide direct synthesis?

Currently, the biggest share of the world production capacity for  $\text{H}_2\text{O}_2$  is provided by Solvay, accounting for approximately 906 kt per year (30.3%), followed by Evonik with 587 kt per year (19.6%) and Arkema with 401 kt per year (13.4%) (according to

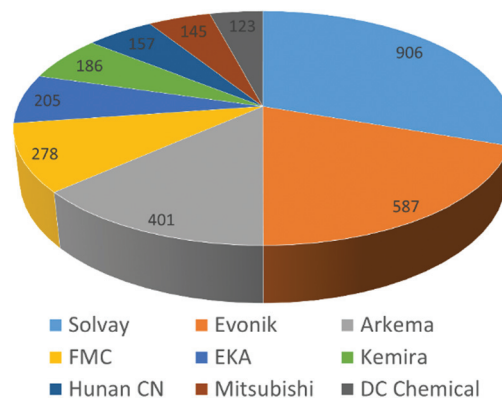


Fig. 1 Leadership positions in the hydrogen peroxide world market (values in kt per year).<sup>4</sup>

data from 2010, see Fig. 1). Solvay predicted that, in 2015, the market will be based on two strong pillars, *i.e.* pulp & paper and propylene oxide processes.<sup>4</sup> According to some reports, China is the world's largest hydrogen peroxide producing and consuming country. China has increased its hydrogen peroxide production rapidly reaching approx. 910 kt per year in 2008.<sup>6</sup>

There have been several attempts to bring the  $\text{H}_2\text{O}_2$  direct synthesis into reality. Thus, in 1988, DuPont patented a method to manufacture hydrogen peroxide solution directly from hydrogen and oxygen by a palladium-catalyzed reaction in an aqueous medium using acid and bromide as promoters.<sup>7</sup> According to SRI Consulting, the company had planned to commercialize the direct technology in Western Canada before 1990. Their idea was that the direct synthesis would be facilitated either as on-site units of 1.8 to 6.0 kt per year or as small plants of up to 10.0 kt per year in close proximity to the clients.<sup>8</sup>

SRI reviewed the technology patented by DuPont, concluding that the direct synthesis technology for on-site use could not compete in terms of economics with the conventional



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*working parties. He has published 300+ research papers, 3 patents and 2 books.*



AOP, arguing that the CAPEX (capital expenditure) costs were too high due to the high pressures required. They also advised that any reduction in the reaction pressure (that, consequently, would decrease the investment costs in reactors, pumps and compressors) will aid considerably, as long as the selectivity and conversion were not significantly dwindled.

The most recent trial was done by DegussaHeadwaters, a joint venture between Degussa AG (Düsseldorf, Germany) and Headwaters Incorporated (South Jordan, Utah, USA). They claimed to have successfully integrated a pilot plant for direct synthesis of hydrogen peroxide in the vicinity of the pilot plant for manufacturing propylene oxide using Degussa-Uhde technology in 2005.<sup>9</sup> In this case, they expected a cost-reduction by one-third to one-half in the total investment cost for integrated H<sub>2</sub>O<sub>2</sub> plants with propylene oxide technology. However, no news from that and no more plants using this technology have been reported ever since.

In a patent by Vandenbussche *et al.* granted to Solvay SA, it is indicated that the current production capacities vary from about 40 to 330 kt per year (the largest being 230 kt per year in Antwerp and 330 kt per year in Thailand). In order to facilitate this capacity, fixed bed reactors operating at up to 50 kt per year and fluidized bed reactors operating at over 50 kt per year were utilized.<sup>10</sup>

Considering this, research efforts have to be clearly targeted at either reducing the CAPEX by smoothing the pressure requirements or decreasing the OPEX (operational expenditure) by increasing the selectivity and efficiency.

What is then the target? Analyzing the H<sub>2</sub>O<sub>2</sub> research literature over the past 20 years, one is easily confused: conversions from 0.1% to 100% and selectivity values varying from non-reported to 90–95% (maximum at low H<sub>2</sub> conversions <10%) and 50–60% (at higher H<sub>2</sub> conversions >10%) are reported.

From the point of view of project and cost engineering, the total investment cost of a chemical plant can be grossly estimated using a potential law. In 2003, Degussa commissioned a new H<sub>2</sub>O<sub>2</sub> plant in Québec for a capacity of 65 000 t per year with a reported cost of \$100 M at that time.<sup>11</sup> Consequently, the current investment cost can be estimated using the Chemical Engineering Plant Cost Index, in this case CEPCI<sub>2003</sub> = 402.0, while CEPCI<sub>2012</sub> = 584.6. Therefore, the estimated cost of a H<sub>2</sub>O<sub>2</sub> plant like the one in Québec in 2012 would be roughly 145.4 MM\$ (*e.g.* 100 × 584.6/402.0). For a chemical plant like this a coefficient of 0.5 can be assumed, using eqn (1) to estimate the cost in 2012:<sup>12</sup>

$$(TCI_1)_{2012} = (TCI_0)_{2003} \left( \frac{Q_1}{Q_0} \right)^{0.5} \left( \frac{CEPCI_{2012}}{CEPCI_{2003}} \right) \quad (1)$$

where  $Q_0 = 65\,000$  kt per year and  $(TCI_0)_{2003} = 100$  MM\$.

Admittedly, the nature of this kind of evaluation has a large estimated error in the range of ±30% (Fig. 2).<sup>13,14</sup>

Therefore, considering that direct synthesis can be competitive when on-site production is required, capacities lower than 10 kt per year are demanded. Thus, the CAPEX of a direct synthesis plant should be approximately between  $40.3 \pm 12.1$  MM\$

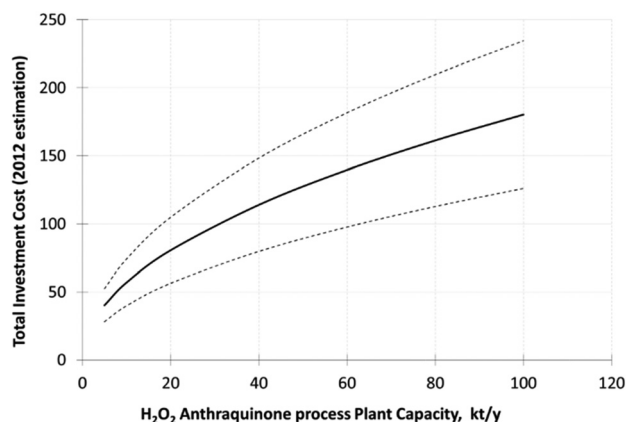


Fig. 2 Price estimation of a H<sub>2</sub>O<sub>2</sub> plant via traditional auto-oxidation process (2012 price basis).

(in 2012) for a 10.0 kt per year basis to be comparable with the traditional process.

The estimation of the total production cost (TPC = MC + GC) is the sum of the manufacturing costs (MC) plus the general costs (GC). When considering the manufacturing costs (MC = DC + FC + PO), one must estimate the direct costs (DC), the fixed charges (FC) and the plant overheads (PO). The direct costs primarily comprise raw materials, utilities, man labor and maintenance. The fixed charges comprise the depreciation, taxes, insurance, *etc.* Finally, the plant overheads take into account all the external facilities, medical costs, *etc.* In the case of the general costs (GC), one must sum the administrative, marketing, research & development and financing costs. In order to compare the traditional AOP with that of direct synthesis, a careful estimation of all these is needed. However, it is not easy for the researchers to have access to such information.

Simplifying the problem, we can consider that the general costs will be similar in both cases. So we focus our analysis on the manufacturing costs that are in the scientific part of the equation.

Similarly, the plant overheads will be comparable, maybe the direct synthesis process (DSP) slightly lower as it requires less space due to the lower amount of equipment needed. The fixed charges are also expected to be comparable in both cases.

This simplification brings us to the comparison of the direct costs only. For that, we should compare the raw materials, utilities, man labor and the maintenance costs. Chemical plants follow similar protocols in maintenance; therefore similar values can be expected in these terms as well. For the comparison of the man labor, we should estimate the number of operators per shift in both plants. The AOP comprises at least four to five subunits; hydrogenation, catalyst recovery, oxidation, extraction and product concentration. Because of this, it will be normally a shift of 4 to 6 employees. The direct synthesis process only consists of the reaction step and, depending on the requirements, a further concentration

step. For that reason, a shift of 2 to 3 employees is expected. In the case of the utilities, both plants will need cooling water, instrument and process air, inert gas and electricity; we can assume that for a similar tonnage, these values will be similar, as the reaction takes place at comparable temperatures. The AOP requires a steam utility for the distillation columns. On the other hand, the consumption of electricity in the DSP will be much higher due to the compression of the gases. If the steam consumption is comparable to the electricity use then the utility costs will be in the same magnitude of order.

So far, only total investment costs and labor costs have really made a difference. Finally, the big difference is unearthed from the raw material consumption. Hydrogen is expensive and is one of the major products needed. In the AOP, the hydrogen may represent between 50 and 60% of the total raw material costs. In the case of DSP, both hydrogen and oxygen must be considered, and both are expensive. This makes a difference. The prices for hydrogen by steam reforming (80% of the production) vary from 1200 \$ per t (large scale) to 8000 \$ per t (small scale), and by electrolysis from 2400 (large scale) to 6400 \$ per t (small scale).<sup>15</sup> Similar prices have been reported for educational use by IChemE, with hydrogen (3.19 \$ per kg or 6.38 \$ per kmol) and oxygen (0.10 \$ per kg or 3.19 \$ per kmol) in 2002 (based on the rate £/\$ = 1.4227).<sup>16</sup> As the direct synthesis requires a large excess of oxygen-to-hydrogen (5 : 1 to 10 : 1) and the price of oxygen is really high, it is the key economic parameter when estimating the competitiveness of the direct synthesis process. For both processes, several stabilizers (AOP) and promoters (DSP) are needed and the cost of those should normally reside between 5 and 10% of the raw material costs. In addition, the catalyst deactivation (*e.g.* active metal leaching, *etc.*) is reported to be higher in the DS process.<sup>17</sup> This point can be improved substantially in the near future, since new catalysts are under development for this process.

In summary, the direct synthesis process can compete only if it avoids CAPEX in further concentration steps, *i.e.* if it can produce H<sub>2</sub>O<sub>2</sub> solutions equivalent to the current technology after dilution. Recent economic analysis carried out by Chem-Systems considered the following concentration levels: (1) Ethyl Anthraquinone (EAQ) Standard Productivity Technology at concentrations of 43 and 70 wt%, (2) Amyl Anthraquinone High Productivity Technology at 40 and 70 wt%, (3) a direct synthesis process in aqueous reaction medium at 15 wt% from the reaction (similar to indicated by Vandenbusshe, of 1 to 15 wt% at the customer site for its specific local application<sup>10</sup>) and also 70 wt% concentrated and (4) direct synthesis in methanol reaction medium at 9 wt%.<sup>18</sup> Ideally, the direct synthesis will be produced on-site and on demand so the transportation costs are avoided. The man labor costs are 30–60% lower than in the AOP. Avoiding the use of pure oxygen is a target, either by using air (using N<sub>2</sub> as the inert for safety reasons), by using a lower O<sub>2</sub>/H<sub>2</sub> ratio, or most importantly by recycling the off-gas. The use of hydrogen relies on the selectivity levels achieved.

### 3. Which are the experimental devices to study direct synthesis of H<sub>2</sub>O<sub>2</sub>?

The direct synthesis reaction (DSR) is a heterogeneous reaction where three phases are involved, the reagents (H<sub>2</sub> and O<sub>2</sub>) and the diluents (He, Ar, O<sub>2</sub>, N<sub>2</sub> or CO<sub>2</sub>) are gases, the reaction medium (H<sub>2</sub>O or alcohols) are liquids and the catalyst is a solid. Analyzing the transport phenomena of the process one can find these steps in series:

- (1) Convection in the gas phase.
- (2) Gas-liquid equilibrium at the interphase.
- (3) Convection in the bulk liquid phase.
- (4) Adsorption of H<sub>2</sub> and O<sub>2</sub> to the catalyst sites.
- (5) Surface reaction between adsorbed H<sub>2</sub> and O<sub>2</sub>.
- (6) Desorption of H<sub>2</sub>O<sub>2</sub> to the bulk liquid phase.
- (7) Convection in the bulk liquid phase.

The limiting steps will limit the global rate of the process. Therefore, in order to increase the overall conversion level, it is crucial to identify which of the steps are the limiting ones.

The selection of the appropriate experimental device to carry out direct synthesis influences the results that can be obtained. In most cases, the reaction has been studied in batch-mode, in agitated vessels. Several researchers have used semi-continuous agitated vessels as an advancement over the batch mode, in many occasions upgrading the earlier applied batch apparatus. From the viewpoint of industrial application, the most common reactors for three-phase reactions are continuous slurry bubble columns, trickle bed reactors and structured reactors.

Furthermore, alternative reaction systems such as micro-reactors<sup>19–23</sup> and catalytic membranes<sup>24–26</sup> have been successfully employed in direct synthesis of hydrogen peroxide during the last few years. There are also other systems, such as fuel cells for electrochemical synthesis,<sup>27–34</sup> which strictly speaking can be considered as “direct synthesis” because they only use hydrogen and oxygen, but they are beyond the scope of this review.

The main experimental set-ups are analyzed next, indicating the strengths and weaknesses of those.

#### *Safety notice emphasis*

Before getting into the core of the topic, we would like to stress once more that manipulating hydrogen and its mixtures with oxygen is a major issue to be carefully considered. Hydrogen and oxygen can create explosive mixtures. Among the different factors which define flammability, the flammability limit is the most relevant one. It indicates the range of fuel concentrations needed for flame propagation to occur. Most of the experimental data and estimation methods available have been collected for pure substances in air (and other diluents in combination), under atmospheric conditions. Furthermore, in many cases, significant differences can be found in the tabulated values. In the case of H<sub>2</sub>, the lower flammability limit (LFL) is between 4.0 and 4.5 mol%, depending on the

source. The operation at high pressures is likely to change these safety limits, and it is necessary to know the actual, true values for safe operations. Luckily, an increase in pressure has, as a general rule in this case, a positive effect reducing the flammability interval.<sup>35</sup>

Operations inside the flammability limits have been an option for decades, although the risk is high. As Centi *et al.* emphasized, nowadays in reality, almost all the research groups have abandoned this idea and operate in the inherently safer gas concentration interval.<sup>5</sup> Process industries have learned their lesson during the last century with a number of incidents and accidents and make the effort to always reside on the safe side of the equation, as the visionary of process safety Trevor Kletz proclaimed years ago.<sup>36,37</sup>

### 3.1. Batch reactor

Batch reactors have been used and are used extensively to produce very precise kinetic data. Most of the experiments in DSP have been carried out in stirred batch reactors made of glass for reactions under mild conditions<sup>25,38–44</sup> or autoclaves generally made of stainless steel or Hastelloy when working at higher pressures or temperatures.<sup>45–54</sup> Generally, the reactor volumes used have been varied from 50 to 600 mL. As a common safety measure in all the systems where the catalyst is a powder, a slurry with a solvent or deionised water has been prepared before feeding the gaseous reactants since upon contact a H<sub>2</sub>–O<sub>2</sub> mixture and a dry Pd-catalyst may result in an explosion.<sup>5,35</sup>

When stainless steel is used, it is recommended to initially passivate the system with 35% HNO<sub>3</sub> for 4 h and 30% H<sub>2</sub>O<sub>2</sub> for 10 h to minimize H<sub>2</sub>O<sub>2</sub> decomposition under reaction conditions. Although in our experience decomposition is not always observed, even in a raw stainless steel system the passivation is recommended. As a troubleshooting rule of thumb, one could say that if no H<sub>2</sub>O<sub>2</sub> is detected in the reaction mixture when it should be there, it is highly probable that it is

because some iron ions are present (*e.g.* due to rust) in the solution. In this sense, special care has to be taken if highly corrosive solutions are used in the reaction system, such as HCl or similar solutions.

An example flow diagram of the system is shown in Fig. 3. H<sub>2</sub> and O<sub>2</sub> were stored in high pressure cylinders; the outlet pressure was set by using self-regulated valves (V1 and V4, respectively). An inert gas is used to flush out the system, either N<sub>2</sub>, H<sub>2</sub>, Ar or CO<sub>2</sub> before each experiment.

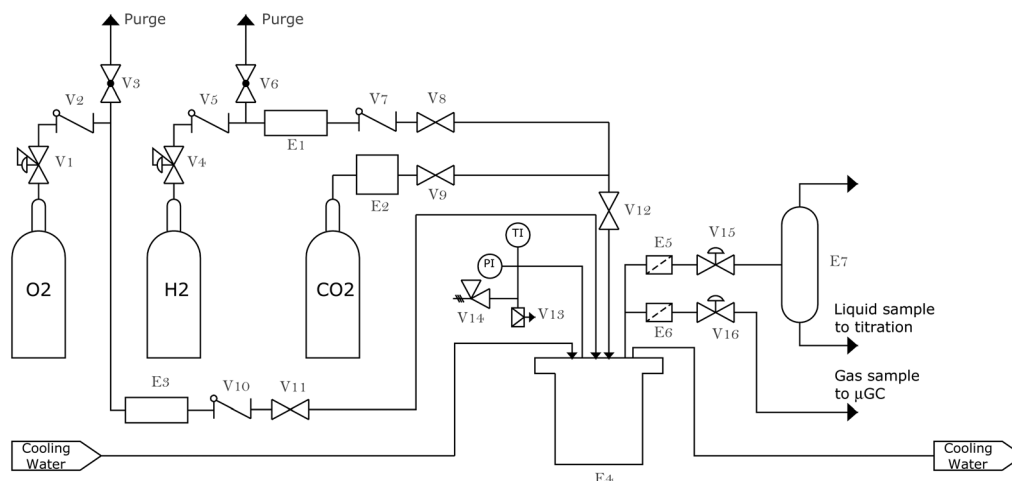
The mixture of gases inside the reactor was calculated in most cases by controlling the pressure and estimating the composition using the equation of state (EoS), such as Peng-Robinson or Soave-Redlich-Kwong.<sup>55,56</sup> The total volume of the reactor is known and, consequently, the initial liquid volume is known too. Nevertheless, estimating the real pressure of the gases injected using water is not trivial. When using alcohols and CO<sub>2</sub>, CO<sub>2</sub> expands the liquid phase<sup>57,58</sup> dissolving quickly, and controlling the exact amount of solutes is difficult. The use of the semi-continuous mode mitigates somehow this inconvenience, but the difficulty remains unless the liquid phase is continuous.

Thus, hydrogen and oxygen have been usually introduced at the beginning of the experiment in order to pressurize the reactor, although in some cases they were bubbled by a gas diffuser directly into the liquid phase throughout the experiment.<sup>25,38,41,42,44,59</sup>

The catalyst can be charged in several ways:

- directly in the liquid phase before closing the reactor; this implies that the reaction starts from the very moment that H<sub>2</sub> and O<sub>2</sub> are entering the system, but during the first minutes the gas phase is not stable and analyzing the gas phase is highly recommended.

- the catalyst is added when all liquids and gases have been charged and the system is at the desired initial pressure. For this, a flushing device is needed in order to control the catalyst insertion.



**Fig. 3** Experimental set-up for direct synthesis of H<sub>2</sub>O<sub>2</sub>. Equipment, E1: mass flow controller, E2: HPLC pump, E3: mass flow controller, E4: Reactor, E5: 1 μm online filter, E6: 5 μm online filter, E7: flash separator, V1, V4: pressure regulators, V2, V5, V7, V10: check valves, V3, V6: globe valves, V8, V9, V11, V12: ball valves, V13: rupture disc, V14: pressure safety valve, V15 and V16: back pressure regulators.

The flow of  $H_2$  and  $O_2$  can be controlled by means of mass flow controllers or on-off valves. Since the maximum pressure considered in open literature to perform tests in a batch reactor/a semi-batch reactor is around 10.0 MPa, gas compressors (gas boosters) to compress the gases were not required as hydrogen and oxygen cylinders operate well beyond such pressure. On the other hand,  $CO_2$  is pumped as a liquid by a refrigerated pump (E2) from a cylinder (max. 5.5 MPa). This is convenient since it can be controlled by means of a volumetric pump (e.g. a HPLC pump).

Different reactors can be found, starting from an autoclave, e.g. Parr reactor, to "home-made designs" normally in AISI 316 SS. Often these types of reactors are agitated by means of magnetic stirring. The reactor has frequently an internal coil in order to remove the reaction heat, but an external heating jacket can be used as well.

Sampling of the liquid and gas phases is usually facilitated by means of on-off valves or six-way valves. Normally the gas phase must pass a knock-out drum to remove all the liquid droplets. For depressurization, backpressure valves coupled with automation are used.

The advantages and disadvantages of batch operation are summarized below:

*Advantages:*

- Controllable mixing with the stirring speed, reducing mass transfer limitations.
- Good heat release due to agitation.
- Low amount of chemicals consumed.
- High production of experimental data.
- High precision of the data, provided that the chemical analysis of both liquid and gas phase is at a high level.

*Disadvantages:*

- Concentration of the gas and liquid phases change over time, which makes the kinetic analysis more difficult (but possible).
- Difficult control of the initial composition; in many cases this is performed by controlling the pressure of each gas.
- Catalyst attrition due to the stirrer.
- Low  $H_2O_2$  percentages achieved unless high gas volumes and pressures or small liquid volumes are used.

### 3.2. Semi-continuous reactor

The semi-continuous reactor is commonly conceived in the  $H_2O_2$  direct synthesis as a batch in terms of the liquid phase and as continuous in terms of the gas phase. Thus, the  $H_2O_2$  and  $H_2O$  formed accumulate in the liquid phase. At low percentages of  $H_2O_2$ , the decomposition and hydrogenation can be rendered negligible and thus the concentration increases almost linearly with time (at a constant  $H_2$  feed and conversion).

Most of the batch systems used for  $H_2O_2$  direct synthesis have been or can be adapted for the semi-continuous mode. The only difference is that the gas phase must be continuously evacuated from the reactor and a backpressure valve or a pressure controller is needed.

The gas phase can be analyzed by means of a GC or, often more conveniently, micro-GC. The analysis using a normal GC requires the use of two columns; one of them should be a molecular sieve to trap the light gases and a valve-split flow is required. The analysis time varies from 10 to 20 min. Using a micro-GC a back-flush is used and times reduce up to 2–4 min.

Blanco-Brieva presented important advancements using a semi-continuous system in her doctoral thesis. The authors obtained concentrations up to 10 wt% of  $H_2O_2$  in a linear trend which indicates that decomposition and hydrogenation were still at a low level. In their studies, nitrogen was used as the inert gas, with conversions ranging from 76 to 83% and selectivities up to 82%.<sup>60</sup> The best value was obtained at  $P = 9.5$  MPa,  $T = 40$  °C, total gas flow of 2500 N mL min<sup>-1</sup> and gas inlet of  $N_2/O_2/H_2 = 50.0/46.4/3.6$ , liquid volume of 190 mL, catalyst 1.6 g of 0.26–1.92 wt% Pd (4.2 to 30.7 mg Pd) supported on a sulphonated resin. The group has published many papers and patents.<sup>61–63</sup>

Menegazzo *et al.* operated a glass reactor at atmospheric pressure and at 20 °C. Nitrogen was applied as the inert dilutant and a total gas flow of 50 mL min<sup>-1</sup> was used. In this work up to 0.43 wt% of  $H_2O_2$  in methanol with a 61% selectivity was reported and the system was stable even after 5 h of operation. The endeavor was to test the beneficial effects of Au addition in a bimetallic catalyst containing also Pd.<sup>44</sup> High pressure tests were conducted in an autoclave of 250 mL of total volume, with 100 mL of liquid volume. The conclusions were that the best catalyst was 1.5% of Pd/SiO<sub>2</sub> with a maximum selectivity of 60% resulting in *ca.* 0.3 wt% of  $H_2O_2$ .<sup>64</sup>

Moreno *et al.* studied the reaction in water using  $CO_2$  as the inert gas, at pressures of 6.0–8.0 MPa and at temperatures between 25 and 60 °C. A maximum concentration of 4.3 wt% of  $H_2O_2$  after 8 h of operation was obtained with a turnover frequency (TOF) of 158 mol <sub>$H_2O_2$</sub>  kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> using a commercial 5% Pd/C. A high amount of catalyst was charged into the reactor in order to demonstrate that under such conditions the productivity only depends on the mass transfer (more than 5 mg of Pd in such a system), and is also under a kinetic regime (at low catalyst amounts lower than 1.5 mg Pd in that system).<sup>65</sup> In an earlier paper, the authors studied the reaction under semi-continuous operation mode using methanol at low pressures and thus established the limits of operation upon using promoters.<sup>56</sup>

*Advantages:*

- Controllable mixing through stirring speed, reducing mass transfer limitations in a lab scale reactor, while in industrial reactors special design is needed to achieve good mass transfer (*i.e.* stirrer and baffles).
- Good heat release due to agitation in a small scale reactor while in an industrial reactor a better design is needed.
- Constant gas phase after stabilization of the gas phase.
- Constant pressure controlled by the gas phase.
- Higher concentrations of  $H_2O_2$  can be achieved as  $H_2$  is added continuously.



*Disadvantages:*

- Requires mass flow controllers and a continuous back-pressure regulator in the gas phase.
- Catalyst attrition due to the stirrer.
- High consumption of gases, due to continuous flow.

**3.3. Slurry bubble column reactor**

A slurry bubble column reactor (SBCR) is a bubble column reactor that operates with a solid phase dispersed in the liquid. The solid phase is or contains the active catalyst. A bubble column is a tubular reactor operating with the liquid phase flowing downwards or upwards whereas the gas flows upwards with a gas sparger in the bottom to improve bubble generation.

The importance of this kind of reactor is clearly demonstrated by their extended use in chemical, petrochemical, biochemical and metallurgical industries. In the case of chemical industries, the most typical reactions to take advantage of this apparatus are oxidations, hydrogenations (such as hydrotreating or hydrocracking), chlorination, alkylation and polymerization. Biological processes, such as fermentations and wastewater treatment using loop reactors, also use SBCR technology.

The main difference between the continuous stirred tank reactor equipment (with continuous liquid and gas phase) and the slurry bubble columns (with a low length, *i.e.* shallow) could be considered the better mixing in the CSTR compared

with the SBCR. Normally, the residence time of the gas is one or two orders of magnitude lower than the residence time of the liquid.<sup>66</sup>

The gas can be considered operating in plug flow mode with minor back mixing effects.<sup>67</sup> The liquid, in contrast, due to the hydrodynamic restrictions at the outlet and due to the turbulence caused by the intense bubbling, behaves more like a perfectly mixed bulk phase (Fig. 4).<sup>68,69</sup>

So far, no papers published using SBCR in the direct synthesis of hydrogen peroxide can be found in the open literature. However, there are several on-going studies conducted at the University of Valladolid presented at a conference,<sup>70</sup> but the results have not yet been released.

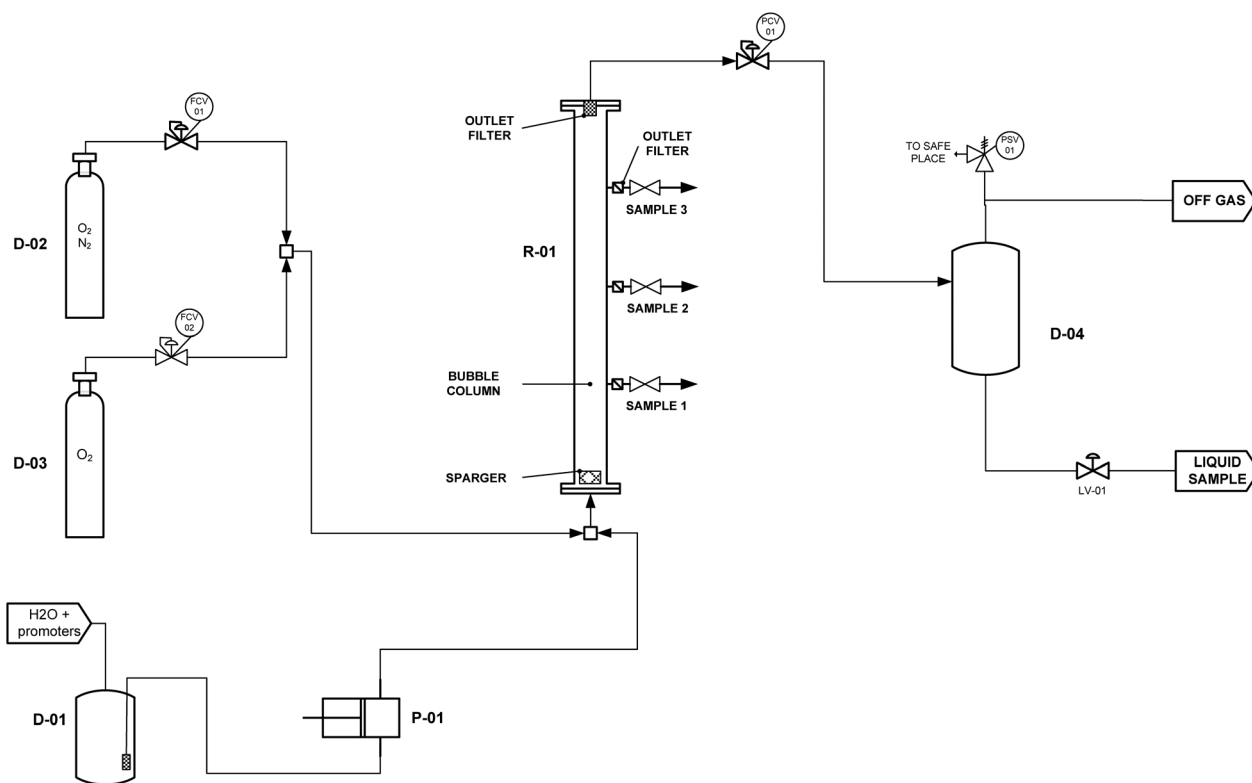
In the patents by Degussa AG considering the direct synthesis route, they conducted experiments in a SBCR with a 80 mL bed volume (I.D. 1.6 cm, length 40 cm) at 25 °C and 5.0 MPa and applying nitrogen as the inert gas.<sup>71</sup>

*Advantages:*

- Good heat release due to intense bubbling agitation, which also minimizes problems with runaway reactions as the catalyst cannot easily develop hotspots.
- Constant gas phase and constant liquid phase operation.
- Constant pressure controlled by the gas/liquid phase.

*Disadvantages:*

- Requires mass flow controllers and a continuous back-pressure regulator in the gas/liquid phase.
- Needs catalyst recovery at the liquid outlet.



**Fig. 4** Schematics of a slurry bubble column reaction system. Equipment, D1-0 liquid feed vessel, D-02 air cylinder, D-03 hydrogen cylinder, P-01 HPLC pump, R-01 slurry bubble column reactor, D-04 product vessel, PCV-1 backpressure valve.



• The concentration of  $\text{H}_2\text{O}_2$  is difficult to maintain at high levels unless long liquid residence times or high  $\text{H}_2$  quantities are used. This limits the experimental system.

### 3.4. Fixed bed reactor

Fixed bed reactors are widespread in the petrochemical industry and for the production of bulk chemicals. They consist of a family of reactors, where gas and liquid flow in a downward direction (gravity) or upflow direction over a bed of solid catalyst particles. Trickle bed reactors operate with downflow, in terms of both liquid and gas, whereas counter-current reactors operate with liquid flowing downwards and gas upwards. Upflow reactors operate with both liquid and gas stream flowing upwards. The name 'trickle bed' comes from the special liquid operation mode, in which the liquid flows down intermittently wetting the solid particles in the form of droplets, films or rivulets.<sup>66</sup>

The gas flow may be conducted either in an upward or downward manner, depending on the application. The co-current downflow is the best option for the hydrogen peroxide direct synthesis, since we should avoid contact between  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  to avoid hydrogenation of  $\text{H}_2\text{O}_2$ . An upflow gas configuration would allow the gas inlet with the maximum concentration of hydrogen to encounter the liquid outlet with the maximum concentration of  $\text{H}_2\text{O}_2$  and the undesired side-reactions like hydrogenation would thus be favored.

The catalyst may be packed in a structured, semi-structured or random manner.

When designing the experimental system, it is crucial to consider the design parameters affecting the hydrodynamics in order to assure a proper flow in the TBR, as illustrated in Fig. 5. Upon trickle flow, the reactor basically operates under restricted liquid or gas availability characterized by Reynolds numbers in the order of  $\text{Re}_\text{G} < 10^3$  and  $\text{Re}_\text{L} < 10^3$ . Nevertheless, most of the experimental trickle bed reactors operate under conditions characterized by  $\text{Re}_\text{G} < 10^1$  and  $\text{Re}_\text{L} < 10^2$ .<sup>66</sup>

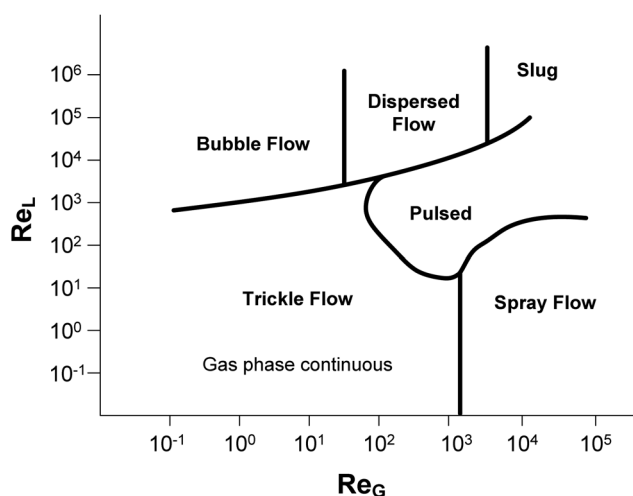


Fig. 5 Flow regimes in downflow packed beds (adapted from ref. 66).

An example of the fixed bed reactor (trickle bed)<sup>72</sup> is reported in Fig. 6. The system consists of four sections, liquid inlet, gas inlet, three-phase reaction, and biphasic separation, respectively. Liquid is pumped at room temperature with an HPLC pump (P-01) and is then heated in a preheater or in the first part of the reactor. The gases are introduced continuously from the bottles by means of mass flow controllers. The reactor is filled with the support and the catalyst, and the bed is immobilized by using either metal filters or glass wool at the entrance and outlet.

The pressure inside the reactor can be controlled using a backpressure automatic controller installed at the off-gas outlet (PCV-01) or a backpressure valve directly at the outlet of the reactor. A rupture disc and/or a pressure safety valve is strongly recommended in the off-gas line. The liquid entrance is commonly inserted inside the bed, so that the quartz acts as a liquid distributor. It is extremely important to start-up the reactor at medium liquid flow rates assuring proper wetting of the bed. At the entrance of the reactor, a small void chamber (*ca.* 3 mL) acts as a pressure compensator and a gas distributor. A manual globe valve can be used to sample the liquid phase instantaneously.

The use of TBRs for direct synthesis has been extensively studied by the group at Åbo Akademi University. In one of the first studies, the effects of various gas and liquid flow rates and different palladium catalysts were studied in terms of the  $\text{H}_2\text{O}_2$  selectivity, at concentrations up to 0.012 wt%  $\text{H}_2\text{O}_2$ .<sup>73,74</sup> The activity of several catalysts, *i.e.* Pd-SiO<sub>2</sub>, Pd-Z, Pd-CeS, Pd-ZS being Z = zirconia and ZS = sulphated zirconia, were compared in light of the previous results obtained in semi-batch reactors, and it was revealed that a considerable increase in the selectivity can be achieved when operating under continuous flow. Most recently Biasi *et al.* have reported values of  $\text{H}_2\text{O}_2$  up to 1.2 wt%.<sup>72</sup>

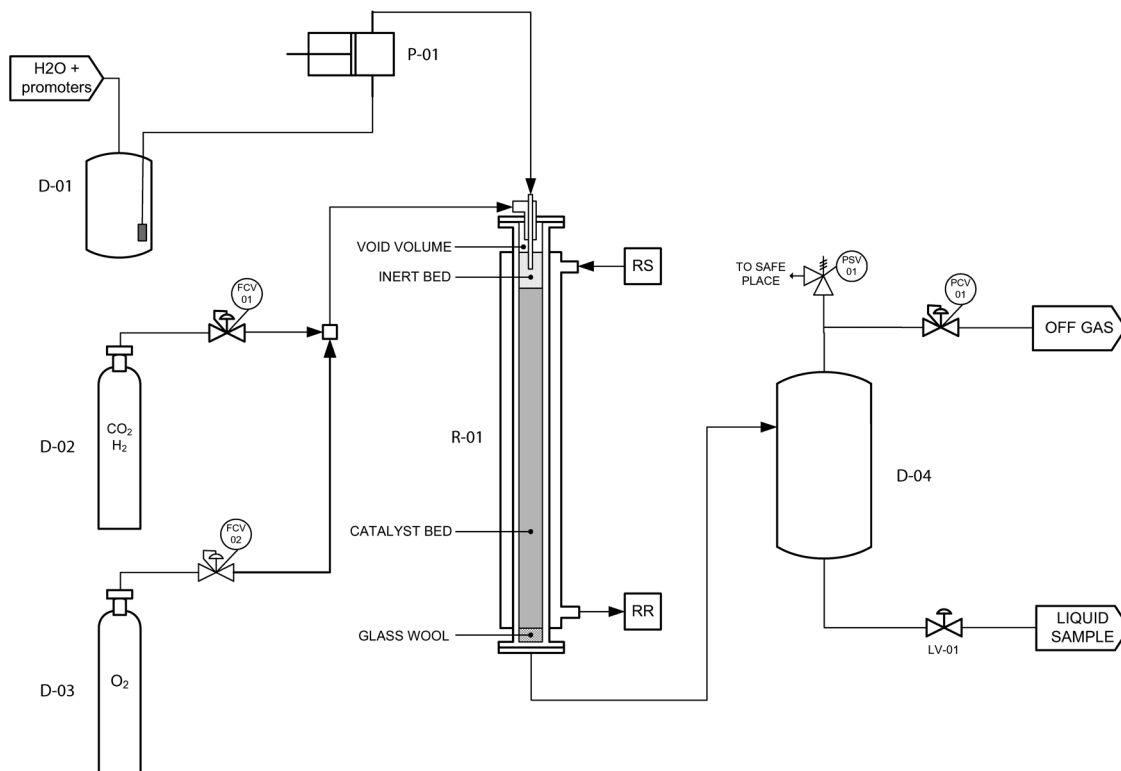
The use of TBRs has been also mentioned in several of the early patents concerning  $\text{H}_2\text{O}_2$  direct synthesis.<sup>7,75,76</sup> TBRs together with the slurry bubble column are the two most evident options for the industrial operations at large scale.

#### Advantages:

- Enormous mass transfer area in the solid and catalyst particles.
- Easy operation of the liquid and gas phase and pressure control.
- Low catalyst attrition.
- No back-mixing, so the concentration of the reagents is maximized and so is the reaction rate.
- Easy and low cost closures, compared to the stirred reactor.

#### Disadvantages:

- Requires mass flow controllers and a continuous back-pressure regulator.
- Liquid maldistribution.
- Easy to form hotspot which can lead to temperature runaway.



**Fig. 6** Schematic flow diagram of a trickled bed reactor (TBR) system. Equipment, D-01 = Water and promoters inlet vessel, P-01 = HPLC pump, D-02 = H<sub>2</sub> + CO<sub>2</sub> cylinder, D-03 = O<sub>2</sub> cylinder, D-04 = liquid product collecting vessel, FCV-01 = gas flow controller, FCV-02 = gas flow controller, LV = liquid sampling valve, R-01 = TBR (RS = refrigerant supply, RR = refrigerant return).<sup>72</sup>

- Heat release for high reactor diameters might be a problem. For experimental devices, in practice, there are no heat release problems.

- Adding more catalyst implies changing the catalytic bed.

### 3.5. Microreactors

The use of microreactors is an innovative and recent approach to the direct synthesis of hydrogen peroxide. The most important feature of these microstructured reactors is safety, which derives from increased heat dissipation owing to higher surface-to-volume ratios<sup>77</sup> and also thanks to the small volumes used. This also provides a significant enhancement in the mass transfer. Moreover, the dimensions of the microchannels are smaller than the quenching distance for hydrogen, the critical distance below which no flame can propagate. All these features make microreactors very well suited for reactions that are highly exothermic or involve explosive mixtures, such as the direct synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>78</sup>

As an example, in the system described by Voloshin *et al.*,<sup>22</sup> the configuration is similar to the one used for other microreactors found in the literature (see Fig. 7).

Inoue *et al.*<sup>20</sup> designed a multichannel microreactor with packed-bed Pd/C, Pd/alumina and Pd/silica catalysts. In order to load the microchannels, the catalyst was suspended in de-ionized water and introduced by means of a micro-syringe, subsequently loading inert silica particles to minimize the void space. Deuterium was used as a reactant to distinguish the

water produced during the reaction from that in the reaction solution. The feed solution also contained diluted sulphuric acid, phosphoric acid and sodium bromide. They obtained higher yields with the Pd/C catalyst after an oxidative pre-treatment, rather than after a reducing pre-treatment (0.15–0.24 wt% vs. 0.02–0.07 wt%). Somehow, this contradicts the results obtained in conventional reactors.<sup>45,46</sup> On the other hand, they confirmed the positive effect of Br<sup>−</sup> as an inhibitor for the decomposition of H<sub>2</sub>O<sub>2</sub>, and reported that, at high Br<sup>−</sup> concentrations, the selectivity to H<sub>2</sub>O<sub>2</sub> was *ca.* 100% and no measurable H<sub>2</sub>O<sub>2</sub> decomposition was observed. Interestingly, they observed a significant increase in the peroxide yield when placing two microreactors in series, attributed to an improved gas–liquid distribution in the second reactor.<sup>20</sup> They probably found this improvement because the H<sub>2</sub> (or D<sub>2</sub>) conversion was very low, the H<sub>2</sub>/Pd ratio was kept high and the promoters used and detailed in the Degussa AG patent series were applied.<sup>71,79</sup> In their most recent work Inoue *et al.* have demonstrated that H<sub>2</sub>O<sub>2</sub> solutions from 1 wt% to 11.3 wt% can be produced with a selectivity ranging from 78% to 53%.<sup>19</sup> It is a clear breakthrough in the technology, demonstrating that it is feasible to achieve high concentrations in a glass microreactor. Ideas on how to upscale this process into a reasonable tonnage for on-site consumers will be of use.

Wang *et al.*<sup>80</sup> studied the results obtained in single and multichannel microreactors over Pd catalysts. They reported higher productivities (6.53 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> mol<sub>Pd</sub><sup>−1</sup> h<sup>−1</sup>) with the

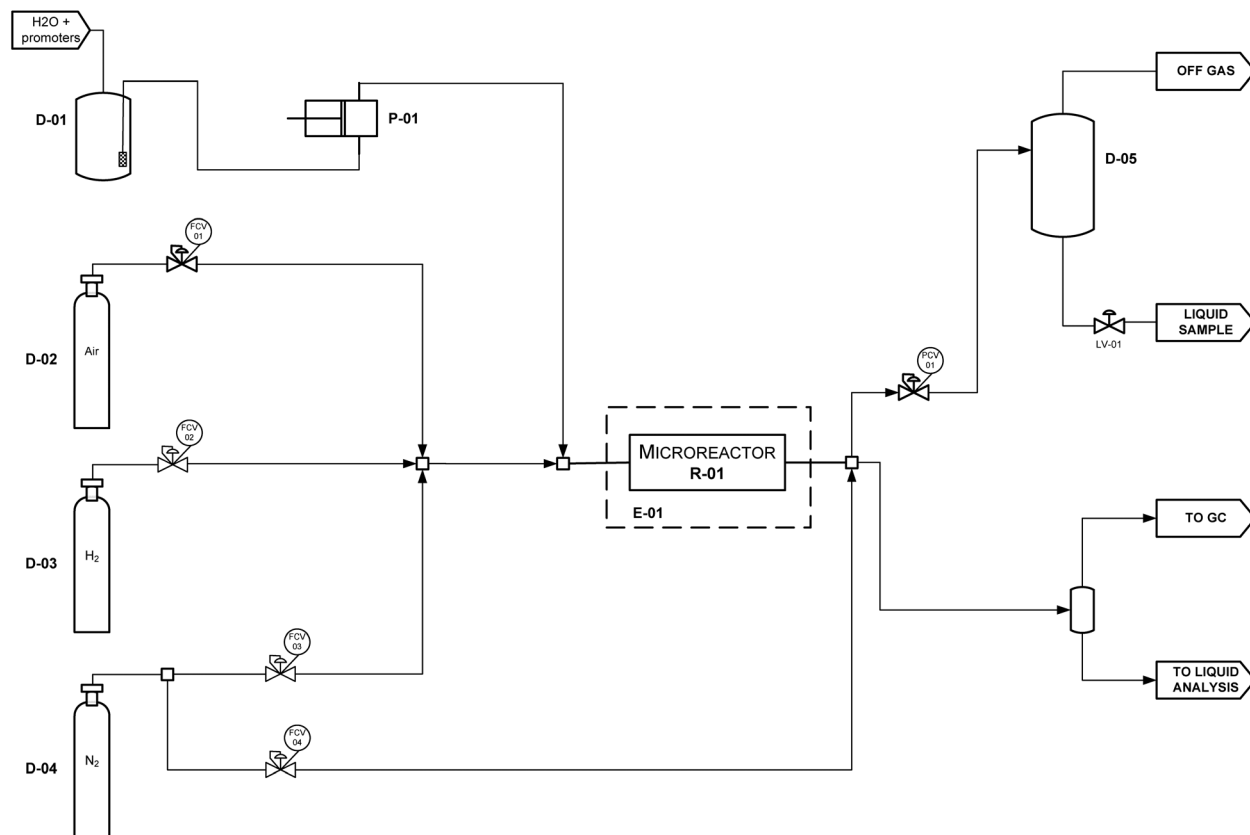


Fig. 7 Schematic flow diagram of a microreactor system (similar to Voloshin *et al.*<sup>22</sup>). D-01 = solvent and promoters inlet vessel, P-01 = high pressure liquid pump, D-02 = air cylinder, D-03 = H<sub>2</sub> cylinder, D-04 = N<sub>2</sub> cylinder, D-05 = liquid product collecting vessel, FCV-01/04 = gas flow controllers, PCV-01 = backpressure controller, LV-01 = liquid sampling valve, R-01 = microreactor, E-01 = water temperature controlled bath.

highest solvent flow rates (2 mL h<sup>-1</sup>). The best solvents turned out to be acidified alcohols, with a much improved solubility of the reaction gases, in agreement with earlier results.<sup>81</sup> Siliceous zeolites gave the best results, with a selectivity up to 43%. Multichannel reactors gave worse results than single channel reactors due to a lower linear velocity, which led to a reduced gas-liquid-solid mass transfer rate. It can be also due to hydrogenation and decomposition reactions playing an important role when the H<sub>2</sub>/Pd ratio is not high enough.<sup>55</sup> Maehara *et al.*<sup>82</sup> designed a compact system for direct synthesis of H<sub>2</sub>O<sub>2</sub> in which reacting gases (H<sub>2</sub> and O<sub>2</sub>) were produced in a flow-through electrolysis cell rather than supplying them from gas cylinders. Pd/C catalysts were applied in capillary and packed microreactors for the synthesis of H<sub>2</sub>O<sub>2</sub>. It was observed that a small quantity of peroxide was electrochemically formed in the electrolyzer before entering the reactors and, in the capillary microreactor, the rates of peroxide formation and decomposition were fully balanced, therefore stabilizing the H<sub>2</sub>O<sub>2</sub> concentration. In the stack microreactor, higher H<sub>2</sub>O<sub>2</sub> concentrations were observed, at lower oxygen flow rates, due to the enhanced mass transfer properties of the microchannels, achieving a peroxide concentration of  $8.3 \times 10^{-3}$  M (at 10 °C in an aqueous HCl solution). Lower concentrations were obtained when using pure water as a solvent. Voloshin *et al.*<sup>21</sup>

studied the kinetics of hydrogen peroxide synthesis in a microreactor under a Pd/silica catalyst with very low conversions (1–2%). The production of 1 wt% of peroxide was obtained at approximately 2.0 MPa and 35–50 °C. Working under these conditions, the reaction was kinetically controlled, and internal mass transfer and heat transfer limitations were found to be negligible. Langmuir–Hinshelwood rate equations for different mechanisms proposed were obtained. Later, they studied the decomposition and hydrogenation reactions<sup>22,83</sup> and were finally able to propose and verify an overall rate expression for H<sub>2</sub>O<sub>2</sub> production in a microreactor.<sup>23</sup>

#### Advantages:

- Low reagent consumption.
- Easy operation of the liquid and gas phase and pressure control.
- Low catalyst attrition.
- No back-mixing, so the concentration of the reagents is maximum and so is the reaction rate.

#### Disadvantages:

- Safety measures.
- Requires miniature catalyst particles to avoid clogging, and this may cause problems upon catalyst separation.
- Low capacity so far.
- Expensive to construct.

### 3.6. Membrane reactors

In recent years, the use of catalytic membranes for the direct synthesis of hydrogen peroxide has developed. The main feature of membranes is safety, owing to the fact that they allow keeping hydrogen and oxygen gases separate. Safety is also indirectly improved by avoiding the formation of fine catalyst particles in the reactor, which usually remain in the peroxide solution and can catalyze decomposition and explosions.

Choudhary *et al.*<sup>84</sup> developed a novel Pd-membrane catalyst which gave rise to high conversions (up to 100%) and selectivity (over 60%). The membrane separates hydrogen gas from the aqueous liquid medium, through which oxygen is bubbled. Only hydrogen atoms penetrate through the membrane, and react with oxygen over the surface of the Pd film, forming  $\text{H}_2\text{O}_2$  which is absorbed by the aqueous medium. They observed a large increase in the  $\text{H}_2\text{O}_2$  selectivity when depositing a thin film of pure Pd on a stable Pd–Ag alloy on  $\alpha$  and  $\gamma$  alumina. Such an increase was likely due to the bulk oxidation of the Pd film. The deposition of a thin film of a hydrophobic polymer membrane that prevents further contact of the produced  $\text{H}_2\text{O}_2$  with the catalyst surface slightly enhanced the selectivity. Nevertheless, slow diffusion of hydrogen through the membrane limited the overall rate of the process and led to low productivities ( $1.5 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{Pd}}^{-1} \text{ h}^{-1}$ ).

Melada and his co-workers successfully produced hydrogen peroxide on a carbon-coated ceramic Pd–Pt membrane using an aqueous solvent,<sup>85</sup> and later reported the use of these catalytic membranes in methanol solutions,<sup>24</sup> obtaining higher productivities than in water although the selectivities were still far below those of industrial interest. This could be remedied by working at higher pressures, which favors the  $\text{H}_2\text{O}_2$  synthesis over  $\text{H}_2\text{O}$  formation. The use of promoters, such as  $\text{Br}^-$ , was necessary to prevent the peroxide decomposition. Moreover, they found that the rate of  $\text{H}_2\text{O}_2$  reduction or hydrogenation is about one order of magnitude higher than that of  $\text{H}_2\text{O}_2$  dismutation, suggesting that the first is the most likely decomposition mechanism of the peroxide. Wang *et al.*<sup>86</sup> successfully produced  $\text{H}_2\text{O}_2$  using Pd–Ag ceramic composite membranes. When a second layer of Pd was deposited on the Pd–Ag/alumina membrane, the concentration of peroxide increased, although it was still too low for industrial interest (up to  $0.95 \text{ g l}^{-1}$  after 4 hours at  $20^\circ\text{C}$  and with a transmembrane pressure difference of 0.25 bar).

All the experiments mentioned above were carried out under atmospheric pressure or at slightly increased liquid pressure. Pashkova *et al.*<sup>26</sup> investigated the effect of higher pressure on the  $\text{H}_2\text{O}_2$  productivity. For a constant differential pressure of 5 bar, the increase of the liquid pressure led to a distinct increase of the  $\text{H}_2\text{O}_2$  formation rate as a consequence of the increased concentration of the dissolved gaseous reactants in the liquid phase. Additionally, the concentration profiles tended to become linear at higher pressures, suggesting a decrease of the decomposition rate compared to the formation rate. The effect of the solvent was studied too, and pure

methanol yielded the best results ( $1.65 \text{ mol}_{\text{H}_2\text{O}_2} \text{ g}_{\text{Pd}}^{-1} \text{ h}^{-1}$  after 1000 minutes working at  $20^\circ\text{C}$  and 6.9 MPa in the gas phase, 6.4–6.7 MPa in the liquid phase), compared to water. Methanol productivity was 7-fold higher than water as a solvent. Finally, a different approach for reactants supply was tested:  $\text{O}_2$  was supplied from the dry part of the membrane, while  $\text{H}_2$  was bubbled in the liquid phase. Higher productivities were obtained ( $1.96 \text{ mol}_{\text{H}_2\text{O}_2} \text{ g}_{\text{Pd}}^{-1} \text{ h}^{-1}$  after 20 hours working at  $20^\circ\text{C}$  and 6.7 MPa in the gas phase, 6.4 MPa in the liquid phase), but still much lower than those obtained with a commercial powder Pd catalyst (5 wt% Pd/alumina) tested under similar conditions ( $6.5 \text{ mol}_{\text{H}_2\text{O}_2} \text{ g}_{\text{Pd}}^{-1} \text{ h}^{-1}$ ).

#### Advantages:

- Oxygen and hydrogen are not in direct contact in the gas phase, so pure  $\text{H}_2$  and  $\text{O}_2$  can be used without safety problems.

- Catalyst separation from the working solution

#### Disadvantages:

- Specialised membranes are expensive.

- Mass transfer limitations due to the Taylor flow.

## 4. What are the best operational conditions to increase conversion and selectivity towards $\text{H}_2\text{O}_2$ ?

### 4.1. Catalyst

**4.1.1. Active metal.** All catalysts described in the literature reviewed were based on noble metals supported on different substrate materials. Palladium, gold, silver and platinum are the most commonly employed metals. Of these, Pd and Au are generally the catalysts of choice, usually in a supported form although Dissanayake *et al.*<sup>39,40</sup> showed that colloidal Pd is also very active for  $\text{H}_2\text{O}_2$  synthesis under ambient conditions. Landon *et al.*<sup>47</sup> obtained selectivities up to 90% using a 0.6 wt% Pd/sulfonated carbon catalyst at a low reaction temperature ( $1\text{--}2^\circ\text{C}$ ). At higher temperatures, the selectivity towards  $\text{H}_2\text{O}_2$  decreased dramatically, which was attributed to its decomposition or hydrogenation. Li *et al.*<sup>87</sup> also compared the performance of various metals on a zeolite-Y support, at a low temperature, and found Pd to have the best productivity ( $8 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ), followed by Pt ( $4 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) and Au ( $3 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ). Other metals such as Ag, Cu, Rh and Ru demonstrated very low productivities.

Olivera *et al.*<sup>88</sup> predicted that Au could be more active than Pd or Pt for  $\text{H}_2\text{O}_2$  synthesis, based on a theoretical study of the energetics of the reactions involved. Li *et al.*<sup>52</sup> tested different zeolite-supported Au catalysts ( $20^\circ\text{C}$  and 3.7 MPa) and achieved  $3.61 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  with a non-calcined catalyst and  $2.99 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  with a calcined catalyst (both 4.3% Au/Y zeolite). However, non-calcined catalysts were proven unstable and lost Au upon operations so they could not be successfully recycled. Hutchings and co-workers<sup>47,89,90</sup> focused on investigating the combination of Au and Pd to improve the production rate and selectivity to hydrogen peroxide in reactions, at low temperatures ( $2^\circ\text{C}$ ) and short



residence times (30 minutes). Landon *et al.*<sup>47</sup> reported significantly higher production rates of  $\text{H}_2\text{O}_2$  using a 5 wt% Pd–Au/alumina catalyst ( $4.46 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) than either the Au-only ( $1.53 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) or the Pd-only ( $0.37 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) catalysts. They found that Pd acts as a promoter for the Au catalyst, and that the catalyst was comprised of Pd–Au alloys rather than the two metals separately. Edwards *et al.*<sup>89</sup> extended this study and screened a range of Pd, Au and Pd–Au catalysts supported on different materials. The highest yields were observed for Pd–Au catalysts supported on carbon and silica: 110 and  $108 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , respectively. Li *et al.*<sup>90</sup> showed that an enhancement effect of replacing some of the Au with Pd in a zeolite supported catalyst is much more pronounced for zeolites than that observed with  $\text{TiO}_2$ , silica or iron oxide as supports. They suggested that the best catalyst composition is 2.5 wt% Au/1.8 wt% Pd ( $101.6\text{--}138.3 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).

Ishihara *et al.*<sup>91</sup> studied the effect of different metal additives on a silica supported Au catalyst. They observed that  $\text{H}_2\text{O}_2$  formation is much improved by addition of Pd, but impaired by addition of other metals, such as Re or Co, probably due to an increased activity for  $\text{H}_2\text{O}_2$  decomposition and/or hydrogenation. In turn, Li *et al.*<sup>90</sup> studied the addition of different metals on a zeolite supported Au catalyst, and also obtained the best results with the Au–Pd catalyst. The addition of Ru or Rh had no notable effect, but the addition of Pt resulted in a clear enhancement in the yield of hydrogen peroxide, which is consistent with the suitability of Pt for  $\text{H}_2\text{O}_2$  production as reported elsewhere.<sup>42,85</sup>

Other bimetallic catalysts, such as Pd–Ag or Pd–Pt, have been studied too. Abate *et al.*<sup>85</sup> investigated the performance of alumina supported Pd–Ag and Pd–Pt catalysts on membranes through which hydrogen was introduced into the reacting system. On alumina ceramic membranes, Pd–Ag showed better results (12% selectivity), whereas for the same ceramic membrane covered with a surface of thin carbon layer prior to the addition of the metal, Pd–Pt bimetallic catalysts were superior ( $0.5 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  and 29% selectivity after 1 hour at room temperature and atmospheric pressure). Liu *et al.*<sup>42</sup> analyzed the effect of adding Pt onto a Pd/silica catalyst and found that the addition of only 5 atom% Pt to a catalyst that contained 0.5 wt% Pd resulted in a 2.5-fold increase in the rate of peroxide formation with only a small decrease in selectivity, whilst the addition of more Pt did cause a decrease in the selectivity. This fact was also confirmed by Bernardotto *et al.*,<sup>92</sup> who showed that the addition of 0.1 wt% Pt to a zirconia supported Pd catalyst enhanced the yield of  $\text{H}_2\text{O}_2$  with respect to the monometallic catalyst under ambient conditions, whilst the same results for a combination of Pd and Au were obtained with much higher amounts of Au (1.2 wt%).

The quantity of precious metal used in the catalyst is important at the industrial scale. The price of palladium per kilo in 1990 was close to 2100 \$ per kg. One decade later, in 2000, it was close to 26 000 \$ per kg; the prices have risen since to near 52 000 \$ per kg (a factor of 25 in two decades). This becomes clear when one examines the quasi-constant prices of

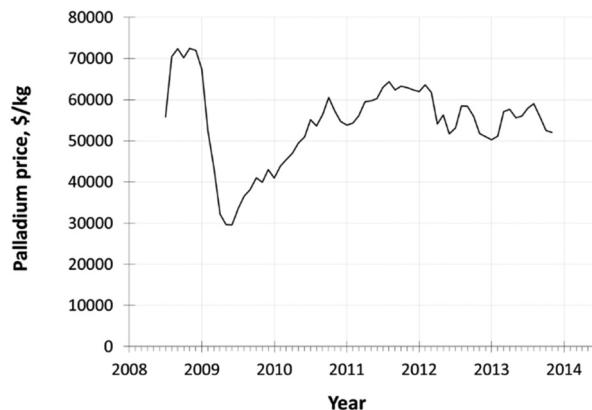


Fig. 8 Palladium average market prices by month according to the London Palladium & Platinum market.<sup>97</sup>

palladium in the market in the last lustrum (Fig. 8). The precious metal market is complex and clearly complicated. Most companies do not own the metals that they use; it is a symbiotic leasing where the company pays a fee for using/storing the metal in their reactors, knowing that the leached or deactivated metal must be recovered, as it must be available if the lease ends. The petrochemical and refining companies do not buy the metal itself to avoid excessive cash consumption. Most of the precious metals are owned by financial, trading and metal refining companies. If they keep them just stored they lose money, if they lease the metals, then they produce money and reduce the liability. As an example, in order to produce 10 kt per year of  $\text{H}_2\text{O}_2$  of 17 wt% *via* direct synthesis (as explained before in section 2), and estimating a conservative value of productivity of  $30 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  (5% Pd/C according to Edwards<sup>93</sup> with a 20% selectivity), the reactor will need at least 61 kg of catalyst, which implies at least 10.5 kg of pure palladium. Consequently, the circulating capital of this precious metal stock will be approximately 0.54 MMS\$. On the other hand, the leasing habitually charges between 3 and 5% of the base cost per annum. This quick number confirms why, for most industrial processes, the percentage of active metal is below 3 wt%. There will be a compromise between having the required active metal loading, the needed surface area for mass transfer in the support and the smallest reactor volume possible. In summary, a realistic value used in the industry is between 2.5 and 3 wt%, although values from 0.5 to 10 wt% are used in the bulk and fine chemical industry.<sup>94</sup> In the case of  $\text{H}_2\text{O}_2$  even pure  $\text{Pd}^0$  black can be used. The catalyst life is usually lower than 2 years on average, after which it needs to be recovered and reactivated.<sup>95,96</sup> Nevertheless, the catalyst lifetime depends strongly on the operational conditions, such as temperature, pH (that may cause leaching of the active metal *via* dissolution), promoters (that may cause leaching of the active metal due to complex formation), flow rate, *etc.* It is common in industrial practice to control the catalyst activity by changing the operational parameters linearly with time (*e.g.*  $\pm 0.03$  to  $0.2^\circ\text{C}$  per day), creating mass balances at start of run (S.O.R) and end of run (E.O.R).

**4.1.2. Oxidation state.** The effect of the palladium oxidation state on the catalytic activity has also been widely discussed in the literature, although the results are somewhat contradictory. Hăncu *et al.*<sup>45</sup> explored the use of both Pd<sup>0</sup> and Pd<sup>2+</sup> catalysts in the direct synthesis of hydrogen peroxide using liquid CO<sub>2</sub> as the solvent. They took advantage of the rapid reaction between cyclohexene and hydrogen peroxide to minimize H<sub>2</sub>O<sub>2</sub> decomposition, and used cyclohexene oxide formation to indirectly measure H<sub>2</sub>O<sub>2</sub>. Indeed, it was confirmed that Pd<sup>0</sup> catalysts have significantly superior activity in the generation of H<sub>2</sub>O<sub>2</sub> after three hours of reaction, at room temperature, and high pressure (17.0 MPa). This was later confirmed by Burch *et al.*,<sup>46</sup> who reported that the reduced catalysts demonstrated improved hydrogen conversion and hydrogen peroxide selectivity when compared to their unreduced counterparts. Liu *et al.*<sup>98</sup> also concluded that Pd<sup>0</sup> is the active phase in the direct formation of H<sub>2</sub>O<sub>2</sub> when they observed that the PdO/SiO<sub>2</sub> catalyst only showed some activity after a short period under a N<sub>2</sub>/H<sub>2</sub> flow, which presumably was enough to reduce a part of the PdO since they also observed a change in the color of the slurry from brown to grey. The rate of H<sub>2</sub>O<sub>2</sub> formation observed then was about 1/3 of that observed for the fully reduced catalyst (4.1 vs. 10.9 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>-1</sup> min<sup>-1</sup>).

A contradictory conclusion was reached by Melada *et al.*,<sup>25</sup> who took a different approach and tried a pre-activation process consisting of particle surface oxidation: the zirconia supported Pd catalyst was reduced *in situ* by passing a pure hydrogen flow into the reaction medium, and then pure oxygen was fed. After removing excess oxygen, the H<sub>2</sub>/air/N<sub>2</sub> mixture was fed and H<sub>2</sub>O<sub>2</sub> synthesis started. They observed that surface oxidation induced very high catalytic activity, the maximum productivity being over 800 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup> working at 20 °C and atmospheric pressure. Furthermore, they changed the H<sub>2</sub>/air/N<sub>2</sub> mixture for an undiluted H<sub>2</sub>/O<sub>2</sub> mixture with oxygen in large excess (H<sub>2</sub>:O<sub>2</sub> = 4:96) and noted that the productivity was lower at the beginning of the reaction, but increased notably after long reaction times (up to 550 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup> after 5 h). Besides, the water production rate was 50 times lower than in air, which corresponds to a significantly higher selectivity towards H<sub>2</sub>O<sub>2</sub> (around 40%) that remained extremely stable for several hours.

The work on monometallic palladium by Rossi *et al.* from University of Padova is particularly interesting. Their claim is that model catalysts in the form of ideal Pd surfaces, either single (100) or poly crystalline can have even higher catalytic activity than the supported catalysts. They also indicate that it is important to define the productivity of the catalyst not only as per gram of catalyst or metal, but per mol of real-active metal. They tested bulk metal and a structured non-porous disk, where the number of available active sites on a Pd disk is expected to be so small that any activity could be measured, and they found an unexpected high activity.<sup>99</sup>

**4.1.3. Catalyst support.** Acidic supports such as carbon, silica, zirconia and zeolite generally give better results due to the higher stability of hydrogen peroxide on an acidic

environment.<sup>91</sup> Another acidic support, titania, has also been proved suitable for H<sub>2</sub>O<sub>2</sub> synthesis, with formation rates usually higher than the corresponding alumina supported catalysts.<sup>50</sup> Other supports such as alumina<sup>46,47,100</sup> and iron oxide<sup>49</sup> have also been successfully employed in hydrogen peroxide synthesis, although productivities are lower than those obtained with the acidic supports. This was confirmed by Edwards *et al.*,<sup>51</sup> who showed that the support has a great influence on the productivity. A range of Pd–Au supporting materials prepared by impregnation are compared and the order of reactivity found was C > TiO<sub>2</sub> > SiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > Fe<sub>2</sub>O<sub>3</sub>. A common factor in all these studies is the fact that calcined catalysts are more stable, and, therefore, can be reused several times without metal losses. Ntainjua *et al.*<sup>101</sup> identified the isoelectric point of the support as the major parameter affecting the selectivity towards H<sub>2</sub>O<sub>2</sub>. In their experiments, supports with low isoelectric points such as carbon and silica gave the highest synthesis rates. This observation is intimately related to the acidic promoters in the system, as will be discussed later.

In one of the latest patents from Degussa-Huls AG, oxidic and silicate supports, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, SiO<sub>2</sub>, Ce<sub>2</sub>O<sub>3</sub> and zeolites were regarded as the most desirable support materials.<sup>102</sup> Curiously, carbon was not considered, maybe because its use at the industrial scale can be compromised due to the options of it being burnt under an oxidising atmosphere. A recent patent filed can be found in 2012 under the name of Solvay SA, and it claims the use of catalysts with total active metals *ca.* 5% with mixtures of Pd and Au,<sup>103</sup> and considers a number of supports from activated carbon, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, iron oxides, SiO<sub>2</sub>, silica-alumina and zeolites or any mixture thereof.

Functional resins have also been reported as suitable supports for H<sub>2</sub>O<sub>2</sub> synthesis.<sup>104</sup> Blanco-Brieva *et al.*<sup>48</sup> reported that the anchorage of Pd<sup>II</sup> ions into mesoporous ion-exchange resins functionalized with sulfonic groups produced highly efficient catalysts, resulting in hydrogen peroxide production rates close to 1100 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup> when using methanol as a solvent at 40 °C and 10.0 MPa. This high performance was attributed to the ability of the sulfonic acid groups of the resin to interact with and stabilize the Pd<sup>II</sup> ions without further reduction to Pd<sup>0</sup>. However, they did not study in-depth the state of Pd<sup>II</sup> at the end or during the catalytic reaction. Neither was the catalyst reusability studied, as pointed out by Burato *et al.*,<sup>105</sup> who confirmed the catalytic potential of the previously described catalyst. This is true even under conditions somewhat different (2.0 MPa and –10 °C), although it was found that the catalyst colour turned gray after the first run, which suggested at least a partial reduction of Pd<sup>II</sup> to Pd<sup>0</sup> as later confirmed by TEM analysis. Furthermore, they tested the catalyst after pre-reduction of Pd<sup>II</sup> to Pd<sup>0</sup>, and found it to be remarkably more active and stable, increasing the molar yield from 35 to 46%.

The addition of different dopants to the supporting material has also been investigated. Melada *et al.*<sup>25</sup> successfully tested different Pd catalysts supported on SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>,

F<sup>−</sup> and Br<sup>−</sup> doped zirconia for hydrogen peroxide synthesis under mild conditions (20 °C, 1 bar). Using a doped support generally improved the production rate and selectivity towards H<sub>2</sub>O<sub>2</sub>, although it also depended on the solvent of choice. Recently this group<sup>44</sup> has also reported the benefits of support sulfonation for ceria and zirconia supported Au–Pd catalysts. They also compared the performance of Pd and Pd–Au supported on sulfonated zirconia after a redox pre-treatment and reported that H<sub>2</sub>O<sub>2</sub> productivity increases from 670 for the monometallic catalyst to 1270 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>−1</sup> h<sup>−1</sup> for the bi-metallic catalyst after 3 hours of reaction at 20 °C and 1 bar, while the selectivity increased from 50 to 61%. It is noteworthy that the rate H<sub>2</sub>O<sub>2</sub> formation increased whereas that of direct water formation decreased, a fact that explains the increase in selectivity with respect to the monometallic catalysts. Sulfonic acid functionalized silica has also been successfully used upon H<sub>2</sub>O<sub>2</sub> synthesis,<sup>106</sup> showing significantly higher selectivity, yield and final concentration of peroxide than the non-functionalized silica-supported catalysts. The authors also found that the functionalization did not affect the hydrogenation reaction of H<sub>2</sub>O<sub>2</sub>, but it did greatly inhibit the decomposition reaction, therefore increasing the selectivity. Blanco-Brieva *et al.*<sup>107</sup> recently reported remarkable results when carrying out the synthesis reaction at high pressure (9.5 MPa) in a methanolic medium using a palladium catalyst supported on sulfonic acid-functionalized silica, achieving a productivity of 335 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> and H<sub>2</sub>O<sub>2</sub> concentrations up to 8 wt%.

## 4.2. Promoters

As explained above, supported noble metals such as Pd and Au are the most typically employed catalysts for direct synthesis of hydrogen peroxide. However, their major drawback is the fact that they are also active for the combustion of hydrogen to water and the decomposition of hydrogen peroxide. This can be controlled to some extent with the addition of promoters, which fall into two categories: halides that act as catalysts poisons retarding water production and increasing hydrogen peroxide selectivity; and acids that retard base-catalyzed decomposition and hydrogenation of H<sub>2</sub>O<sub>2</sub>. It is worth noting that for some particular Au–Pd catalysts the use of these promoters has been reported to result in a loss of catalytic activity;<sup>89</sup> however, the use of promoters is generally considered crucial, especially for monometallic Pd catalysts.

**4.2.1. Halides.** Pospelova *et al.*<sup>108</sup> reported early on the beneficial effect of adding a mineral acid such as HCl to the solution to inhibit the decomposition of the peroxide. Nowadays, chlorides and bromides are the most commonly employed halides. They have been found to cause a drastic decrease in the activity of Pd catalysts related to the side reactions responsible for H<sub>2</sub>O<sub>2</sub> destruction, increasing the selectivity toward hydrogen peroxide.<sup>109</sup> This is believed to be caused by the blockage of high energy sites of the catalyst responsible for the dissociative chemisorption of O<sub>2</sub> and re-adsorption of H<sub>2</sub>O<sub>2</sub>.<sup>44</sup> This is consistent with previous results by Dissanayake and Lunsford,<sup>40</sup> who used Raman spectroscopy to determine that only diatomic oxygen is responsible for the formation of

H<sub>2</sub>O<sub>2</sub> on palladium. The optimization of the amount of halide is usually referred to its concentration, although some authors have suggested that it should be more related to the ratio between halide and Pd in the catalyst.<sup>107</sup>

Landon *et al.*<sup>47</sup> studied the effect of the addition of HBr (1.8 × 10<sup>−5</sup> M) and found that hydrogen conversion, at a given temperature, decreased compared to a similar reaction without Br<sup>−</sup> present whereas the selectivity towards H<sub>2</sub>O<sub>2</sub> remained high at temperatures up to 20 °C. This is consistent with a poisoning of the active sites responsible for hydrogen combustion. Liu *et al.*<sup>43</sup> thoroughly studied the role of Cl<sup>−</sup> anions in the direct formation of H<sub>2</sub>O<sub>2</sub> over a silica supported Pd catalyst in a H<sub>2</sub>SO<sub>4</sub>–ethanol system and the kinetic data obtained suggested that Cl<sup>−</sup> had a positive effect on the net formation of peroxide. The plausible mechanism involves combustion of firstly inhibiting hydrogen and, secondly, limiting the reduction and decomposition of H<sub>2</sub>O<sub>2</sub>. Choudhary *et al.*<sup>110</sup> employed a Pd/C catalyst in aqueous acidic medium containing different halide anions to study the hydrogenation of H<sub>2</sub>O<sub>2</sub>, and showed that the electronegativity of the anion directly influenced the inhibiting action, I<sup>−</sup> being the most inhibiting and F<sup>−</sup> the least. However, I<sup>−</sup> caused complete catalyst deactivation due to poisoning. Therefore, in the presence of Cl<sup>−</sup> and, especially, Br<sup>−</sup>, the hydrogenation or reduction of H<sub>2</sub>O<sub>2</sub> is appreciably inhibited with increasing halide anion concentration. It was also found that this hydrogenation is zero order with respect to the H<sub>2</sub>O<sub>2</sub> concentration, and its activation energy is higher in the presence of Br<sup>−</sup> than Cl<sup>−</sup>.

Ntainjua *et al.*<sup>111</sup> studied the effect of a bromide pretreatment on MgO and C supported Au–Pd catalysts which only provided an enhancement in productivity for the MgO based catalyst but had no significant effect on the carbon catalyst. Even without pretreatment, the catalyst demonstrated a higher productivity than the best result obtained with the pretreated MgO catalyst (96 vs. 73 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>). This was attributed to the nature of the Au–Pd particles present on the catalyst: the carbon based catalyst presents homogeneous Au–Pd alloy nanoparticles (very active in direct synthesis), whereas the MgO supported catalyst has Au–Pd alloys with a Pd-rich surface and an Au-rich core (with much lower activity).

The research group at Yoshizawa investigated theoretically the effect of bromide on the palladium surface, particularly in the face Au–Pd (111). They claimed that pretreated palladium catalysts with strong acids or halide ions to weaken the interaction between the metal surface and the reagents lead to higher selectivity and productivity towards H<sub>2</sub>O<sub>2</sub>.<sup>112</sup>

**4.2.2. Acids, pH and isoelectric point (IEP).**<sup>44,113</sup> Ntainjua *et al.*<sup>101</sup> have established that the role of the acid is intimately related to the catalyst support, particularly to its isoelectric point, which controls the degree of surface charging. They observed that supports with low isoelectric points, such as carbon and silica, provide the highest productivities for Pd-only and Pd–Au supported catalysts. Specifically, for a Pd–Au/C catalyst, they observed a maximum in the activity at pH ≈ 2.<sup>114</sup> Apparently, the crucial parameter is pH rather than acid concentration.

Hydrogen halides are a common choice as promoters, as they combine the function of the acidic proton with the effect of the anion described above, and so HCl and HBr are usually employed.<sup>38–40,47,48</sup> Sulphuric acid is also often used as a promoter.<sup>25,42–45</sup> Han and Lunsford<sup>41</sup> studied the role of HCl and H<sub>2</sub>SO<sub>4</sub> as promoters. The system H<sub>2</sub>SO<sub>4</sub>–ethanol yielded better results than HCl–ethanol, reaching 32 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>Pd</sub><sup>−1</sup> min<sup>−1</sup> after 7 hours at atmospheric pressure and 10 °C over a Pd/silica; instead, they observed no net formation of peroxide in a H<sub>2</sub>SO<sub>4</sub>–water system. They also suggested that one of the roles of protons is to prevent hydrogenation or reduction of H<sub>2</sub>O<sub>2</sub>, rather than the base-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> as stated by other authors.<sup>47</sup> At least under their experimental conditions and using ethanol as a solvent this can be stated. The dependence of the H<sub>2</sub>O<sub>2</sub> formation rate on pH in catalyst suspending solution was studied by Ishihara *et al.*,<sup>91</sup> who used H<sub>2</sub>SO<sub>4</sub> or NaOH to control pH. As expected, no peroxide formation was found under very basic conditions, and the optimum condition for peroxide synthesis over an Au/silica catalyst was found at around pH 7.

Phosphoric acid is also found in the literature to be a suitable acid promoter.<sup>46</sup> Choudhary *et al.*<sup>110</sup> compared the role of phosphoric acid with that of different mineral acids such as sulphuric acid, nitric acid and hydrogen halides in the hydrogenation of H<sub>2</sub>O<sub>2</sub>. They highlight the fact that H<sub>3</sub>PO<sub>4</sub> is less corrosive and the phosphate anions act as a H<sub>2</sub>O<sub>2</sub> stabilizer. Moreover, metal leaching from the catalyst was only observed at the highest concentrations of H<sub>3</sub>PO<sub>4</sub> (>0.3 M), whereas appreciable metal leaching was observed in the presence of HCl, HBr and HNO<sub>3</sub>. Abate *et al.* operating at H<sub>2</sub>SO<sub>4</sub> = 0.019 M (approx. pH = 1.4) measured a leaching lower than 5% of the active metal. Similarly, Moreno *et al.* operating at pH = 2.0 with H<sub>3</sub>PO<sub>4</sub> (approx. 0.03 M) reported leaching ranging between 0.6 and 4.0%, and generally below 2%.<sup>65</sup> Biasi *et al.* observed a leaching rate of 2.5% in 4 h operating a continuous trickle bed reactor at a H<sub>3</sub>PO<sub>4</sub> = 0.003–0.005 M (approx. pH = 2.6–2.3). The rule of thumb is to operate at a pH equal to or lower than the value of the isoelectric point of the support.<sup>115</sup> The isoelectric point is determined preparing a suspension of the support and by acid–base titration measuring the electrokinetic mobility.<sup>116,117</sup> According to Toebe *et al.*, the approximate IEPs for the common Pd supports are (values in parentheses):<sup>118</sup>

SiO<sub>2</sub> (1.0–2.0) < MnO<sub>2</sub> (3.9–4.5) < SnO<sub>2</sub> (5.5) < TiO<sub>2</sub> (6.0) < ZrO<sub>2</sub> (6.7) < CeO<sub>2</sub> (6.8) < α,γ-Al<sub>2</sub>O<sub>3</sub> (7.0–9.0) < ZnO (8.7–9.7) < MgO (12.1–12.7).

For the case of carbon black, the IEP can be substantially modified by acid or base treatment. Thus, the IEP for raw carbon black was reported to be 6.7, this value can vary in the interval from 1.3–3.0 (acid treatment) to 7.5–8.8 (basic treatment).<sup>119</sup>

Acid pretreatment of the support has been reported to have a significant effect on the productivity of H<sub>2</sub>O<sub>2</sub> for Au–Pd catalysts, as reported by Edwards *et al.*<sup>120</sup> They found that the acid pretreatment of a carbon support prior to the addition of the active metals led to an important increase in the selectivity

and the complete suppression of the hydrogenation. The beneficial effect of the acid pretreatment was attributed to an enhancement of the gold dispersion in the bimetallic alloy particles that generates smaller Au–Pd nanoparticles. These nanoparticles have a double effect: they increase the activity for the synthesis and switch off the active sites for H<sub>2</sub>O<sub>2</sub> hydrogenation, therefore increasing the selectivity. However, they did not observe this suppression of the hydrogenation reaction for acid pretreated TiO<sub>2</sub> supports, although the pretreatment still produced a significant enhancement in catalyst performance.<sup>93</sup>

#### 4.3. The synergetic effect of the Pd–Au metals coupled with an acidified support: the key challenge of the future green direct synthesis

The key problem in the direct synthesis is that catalysts based solely on palladium, although active for the synthesis of hydrogen peroxide, are also active in its destruction by O–O scission leading to water formation. This problem is reduced by the addition of acids and halides during the reaction, but these additives have to be subsequently removed or reduced. It was found by different research groups that alloying gold with palladium (or making a core shell structure) has, to some extent, the same effect as halides and acids. Unfortunately it is still unclear how the gold addition to the palladium and the acids/halides added to the reaction mixture really work. Some hypotheses were made but a clear confirmation of that is still under investigation.<sup>120–122</sup> Moreover it was suggested that the catalysts calcination ensures that the palladium is present in the cationic form; this leads to catalysts that can have high selectivity for the direct synthesis. At present, the green chemistry community studying the hydrogen peroxide direct synthesis is working on tailored bimetallic AuPd catalysts supported usually on metal oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and their modification)<sup>44,50,92,93,113,120,123–126</sup> and carbon nanotubes or carbon with different acidic properties or functions that have specific acidic properties.<sup>127–129</sup> The aim is to shape the catalysts design for the hydrogen peroxide direct synthesis. The current remaining problem to be solved for these catalysts is that the maximum amount of hydrogen peroxide produced is typically really low (less than 1 wt%); this value has to be increased to at least 10 wt%. The concentration of 10 wt% of hydrogen peroxide in water is typically required for bleaching, disinfection, electronics and chemical synthesis applications. Understanding how the hydrogen peroxide synthesis and hydrogenation can be kept separate without the use of additives is the key challenge for the green chemistry community.

It was reported by Landon *et al.*<sup>47,130</sup> that the addition of small amounts of Au or Pt to Pd leads to a significant enhancement, especially in terms of selectivity in the hydrogen peroxide direct synthesis; however, sometimes the same trend was also observed for the hydrogenation of the hydrogen peroxide that was formed. This effect has been subsequently confirmed in many studies by Edwards *et al.*<sup>50,93,120,124,126</sup>, Bernardotto *et al.*,<sup>92</sup> Menegazzo *et al.*<sup>44,113</sup> and Hutchings *et al.*<sup>125</sup> Notwithstanding, the combination of bimetallic catalysts with a proper



acidified support leads to a decrease of the hydrogenation reaction. It is interesting to see that the addition of Au or Pt improves the selectivity while at the same time reducing the rate of  $H_2$  conversion.<sup>131</sup> The synergetic behaviour of the two metals is usually considered to originate from an electronic effect rather than from a morphological effect, but the precise origin is yet to be determined.<sup>44,92,113,124</sup> Since there are no significant differences in the particle size distribution and particle morphology for these Au–Pd nanoalloy catalysts prepared using different Pd/Au ratios, it is believed, based on the results published in recent years, that the positive effects observed when alloying Pd and Au are caused by an electronic effect where the addition of a small amount of Au affects the electronic nature of Pd.<sup>125,126</sup> However, other authors found that the effect can be ascribed to both the effects: morphological and electronic.<sup>92</sup>

It seems clear that the different preparation methods studied over the years gave different supported nanostructures with different properties for the direct synthesis reaction.<sup>44,64,120,124–126,131</sup> Core shell or alloys of Pd–Au metals were investigated by many authors. The electronic effect between the two metals and between the metals and the support can enhance the catalytic properties making the catalyst more selective towards  $H_2O_2$ , but the real mechanisms of the modifications and of the direct synthesis reaction are still unclear.<sup>44,50,64,92,93,120,123–126</sup> The addition of halides/acids enhances selectivity but it is not yet clear how, and if, their effects are similar to the addition of Au or Pt.

Hutchings and co-workers have recently shown that during the synthesis of supported AuPd nanoparticles, the addition of an excess of halide in the impregnation methodology coupled with a reduction step leads to alloyed nanoparticles that have uniform compositions. Furthermore, the composition in the AuPd system can be controlled by the amount of the excess halide that is used. These materials, when optimized, are very active and reusable catalysts for  $H_2O_2$  direct synthesis.<sup>132</sup>

Menegazzo *et al.* described the synergetic effect of PdAu materials.<sup>44,113</sup> Core shell PdAu materials enhance the production of  $H_2O_2$  diminishing water formation. Palladium doped with Au blocks the formation of  $\beta$ -hydride, which increases selectivity by maintaining the same  $H_2O_2$  rate of formation while diminishing the production of  $H_2O$ . It is possible that the  $\beta$ -hydride can be blocked also by the use of halides/acids combination, but this is a reversible process as opposed to the permanent effect achieved with the addition of Au.

The synergetic effect of the PdAu materials was found to be important in the direct synthesis of  $H_2O_2$  but not the only one regulating the reaction. It is important to mention that the support plays an important role enhancing or diminishing the properties of the PdAu materials. Coupling the PdAu synthesis with an excellent support can improve the materials used as catalysts for the  $H_2O_2$  DS.

It is well known that the direct synthesis reaction needs an acidic environment to better express all its potential. Many studies were focused on investigating how the acidity of the supports can enhance the DS both with Pd and PdAu catalysts.

Strukul *et al.* investigated different modifications on a Zirconia support. They found that the sulphated zirconia was one of the best supports for  $H_2O_2$  direct synthesis.<sup>25,44,113</sup> Sulphated zirconia showed better results compared to plain zirconia for both Pd and PdAu based catalysts, and catalysts based on PdAu were far superior than the Pd based ones. They found that the sulphated zirconia support enhances the rate of the  $H_2O_2$  formation while diminishing both the  $H_2O_2$  hydrogenolysis and  $H_2O_2$  dismutation.<sup>44,113,133</sup> The role of gold in the catalytic reaction seems to be a really complex one, improving the performance of Pd particles by changing their size, morphology and electron density and making them more suited to the reaction requirements. However the role of the sulphated support is not completely understood yet. Moreover, the results obtained by Strukul *et al.* during recent years seem to suggest that the oxide layer formed over the Pd species acts as the activating phase of oxygen in a molecular form, while hydrogen dissociates on clean  $Pd^0$  couples on edges, thereby explaining the selectivity in hydrogen peroxide formation. Looking at these results it is possible that the sulphated zirconia helps to diminish the formation of  $\beta$ -hydride (responsible for the formation of water) as much as the addition of Au to the Pd catalysts. It is also believed that sulphated zirconia helps the dispersion of the gold on the palladium. Pd–Pt catalysts on sulphated zirconia showed excellent results as well, indicating that a small amount of Pt to the catalysts coupled with the acidification of the support aims at switching off or diminishing the formation of water. Pd–Pt catalysts showed good reusability, as well as Pd–Au catalysts.<sup>44,92,113</sup> Platinum metal in this reaction is known to be active (much less than Pd) but poorly selective towards hydrogen peroxide formation. This implies that the residual reactivity of pure Pt in addition to Pd reactivity is negligible, as the performances of the bi-metallic catalysts are better (and not worse) than the mono-metallic ones. The positive effect of Pt addition on activity has been assigned to a Pd particle morphology change and also to a stabilization of the oxidized Pd surface.<sup>25,44,113</sup> On the other hand, the higher selectivity in  $H_2O_2$  formation requires non-dissociative chemisorption of oxygen on the catalyst surface that is favoured on low energy sites and by an electron rich Pd surface. In this respect, close contact with a more “noble” metal such as Pt (as well as Au) would result in a sort of ligand effect increasing the electronegativity of Pd and justifying the better selectivity.

The results obtained with titania and carbon pretreated with  $HNO_3$  used as supports seem to indicate that the shape and the average dimension of the nanoparticles were not affected by the pretreatment of the materials. Pretreatment at lower temperatures leads to an unstable, but even more active, catalyst.<sup>125,126</sup>

Edwards *et al.* observed in their electron microscopy studies that the Au–Pd/C samples (supported on both non-pretreated and acid-pretreated carbon) calcined at 400 °C contained Au-rich nanoparticles and a highly dispersed coverage of atomic and cluster-like Pd species, intermixed with a small amount of atomically dispersed Au. The calcination treatment appears to

improve the overall metal dispersion, but the acid pre-treatment of the support does not seem to affect the morphology or dispersion of the metallic species in the catalysts.<sup>124</sup> This suggests that the change in oxidation state of the Pd to >90% cationic Pd observed by XPS is the most important distinguishing feature between the acid pre-treated and untreated samples.

Edwards *et al.* reported that the acid pre-treatment had no influence on the optimal calcination temperature, although it seems clear that the acid-pretreated samples are more affected by the calcination process with the dried material displaying a very high, but unstable, activity.<sup>93,120,123–126</sup> Although a calcination treatment at 400 °C is required to achieve stability, it seems clear that the acid pre-treated samples are always more active than their untreated counterparts. The metal dispersion and morphologies are essentially identical and so cannot be responsible for this phenomenon.

So far, it has been impossible to separate the different contributions from the metal, the support and the preparation parameters, but what is really important to understand is that a switching-off of the hydrogenation activity for the acid-pretreated sample can be found in the samples calcined at 400 °C. It was shown that the acid-pretreated carbon clearly showed an enhanced concentration of surface carboxylic acid functional groups.<sup>120,124–126,133</sup> These species may play a key role in the enhanced activity of the observed acid-pretreated catalysts and may aid the dispersion of the metals during preparation, but the real role of the acidic functional groups on the surface may be another one. XPS of the untreated set of samples showed that the surface comprises *ca.* 60–70% Pd<sup>2+</sup> with 30–40% Pd<sup>0</sup>, whereas XPS of the acid-pretreated set of samples showed that they contain almost exclusively Pd<sup>2+</sup> on the surface with no Pd<sup>0</sup> being detectable for all samples.<sup>124</sup> This feature may be the cause of the enhanced activity observed with the acid pretreatment method. The amount of Pd<sup>2+</sup> increased gradually with increasing calcination temperature for the pretreated samples. It is quite clear that the H<sub>2</sub>O<sub>2</sub> hydrogenation activity decreases as the amount of Pd<sup>0</sup> in the catalysts diminishes, although this has to be clarified in the case of the PdAu or PdPt catalysts.<sup>44,92,113,120,125,126</sup> Palladium as the only metal supported can lead to other conclusions.<sup>42,127,128,134,135</sup>

As reported earlier, the research in recent years focused on the oxidation state of Pd, which is a crucial parameter along with the PdAu or Pd–Pt alloying and the support for the metals. The oxidation state of Pd in the bimetallic catalysts (or in the monometallic ones) can be related to the initial formation of H<sub>2</sub>O<sub>2</sub>, but also its sequential hydrogenation. PdAu alloys ore core shell differed from the Pd based catalysts (Edwards 2012). For the PdAu catalysts it is essential that the amount of Pd<sup>0</sup> is minimised and the role of the Au and Pd<sup>2+</sup> is essentially to isolate the residual Pd<sup>0</sup> so that the active sites required for synthesis are preserved, but those responsible for the hydrogenation are minimised. Since the H<sub>2</sub>O<sub>2</sub> hydrogenation/decomposition can be switched-off (or diminished in most of the cases), as demonstrated by an oxidation procedure,

it seems clear that the sites for synthesis and hydrogenation of H<sub>2</sub>O<sub>2</sub> are different.<sup>44,92,113,120,124–126</sup> This is the most logical conclusion reached by different research groups, since the sites for synthesis require, most probably, the associative adsorption of O<sub>2</sub> followed by hydrogenation, while the sites for hydrogenation/decomposition will break the O–O bond. Isolating Pd<sup>0</sup> sites on the surface enables high rates of synthesis. It is important to underline that the achievements in high selectivities towards H<sub>2</sub>O<sub>2</sub> are reached with the combination between bimetallic catalysts, acid pre-treatment of the support, calcination temperature and the oxidative thermal treatment. Only with these three parameters a green industrial direct synthesis can be achieved in the future.<sup>125,126</sup> The same considerations were reported previously by Liu *et al.*,<sup>43</sup> but the main difference is that they claimed the same issues reported above but with the use of halides. It is important to note that the research on the H<sub>2</sub>O<sub>2</sub> direct synthesis that focuses in catalysts design aims to substitute the effect of the halides with the use of Au or Pt to block the O–O bond.

The main issue can be summarized as follows: can the particle size distribution and the nanoparticle composition be effectively controlled and tailored for the H<sub>2</sub>O<sub>2</sub> direct synthesis? The answer is yes. The understanding of this fascinating reaction is progressing year by year. All the issues reported in the present work are challenges for the green chemistry community working on the H<sub>2</sub>O<sub>2</sub> DS. It was shown that an industrial direct synthesis can be achieved through the optimization of different parameters; however, of course, there is still room for much improvement, since all the phenomena that regulate the direct synthesis are still unclear. It is important to underline that the bimetallic nanoparticles alone cannot explain all the behaviours of the catalysts for the H<sub>2</sub>O<sub>2</sub> DS. The interface between the nanoparticles and the support can be very important in defining the catalytic activity, as well as the reactor design, reagents contact time and other engineering parameters. In this sense, the synthesis/shaping of the support is equally important as in many cases it is an integral part of the catalyst and of the reactor design. Hence, designing and fabricating active catalysts require the optimization of many factors.

Recently, Edwards *et al.* reached extremely important results combining a pretreated support (carbon pretreated with HNO<sub>3</sub>) and a bimetallic catalyst (PdAu). A 98% selectivity was achieved, shaping the direction of the investigation of H<sub>2</sub>O<sub>2</sub> DS.<sup>120</sup>

In conclusion, the results provide the basis for the commercial design of a green direct synthesis process that can be performed outside of the explosive region and hence can provide safe, efficient and green synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>44,113,120,125,126</sup>

#### 4.4. Solvent

The most common solvent, and the first option for a liquid reaction medium, is water, since it provides the safest conditions, is non-toxic, non-flammable, and highly miscible with hydrogen peroxide. In fact, aqueous reaction media are frequently reported in the literature.<sup>38–40</sup> However, its main

drawback is the low solubility of the reacting gases (hydrogen and oxygen), which strongly limits the rate of peroxide production. This problem was early reported by Krishnan *et al.*,<sup>81</sup> who compared the performance of different organic media (methanol, ethanol, isopropanol, dioxane and acetone) with Pd supported on phosphate viologen phosphonate catalysts working at room temperature and atmospheric pressure. They observed almost no H<sub>2</sub>O<sub>2</sub> formation after 6 hours in a water-H<sub>2</sub>SO<sub>4</sub> system, whereas the organic solvents (especially methanol and acetone)/H<sub>2</sub>SO<sub>4</sub> systems yielded up to 200 mM H<sub>2</sub>O<sub>2</sub> during other similar experiments. However, when HCl was used as acid promoter instead of H<sub>2</sub>SO<sub>4</sub>, production of hydrogen peroxide was found in the aqueous medium (150 mM after 6 hours), which suggested a strong halide effect. Interestingly, this effect did not appear to affect organic solvents. They attributed the differences between water and organic solvents to the liquid film mass-transfer at the gas-liquid interface being rate determining. Ishihara *et al.*<sup>91</sup> later confirmed that H<sub>2</sub>O<sub>2</sub> formation rate monotonically increased with increasing total pressure of H<sub>2</sub> and O<sub>2</sub> gaseous mixture, suggesting that the formation rate is determined by the dissolution rate of these gases into water.

Burch *et al.*<sup>46</sup> studied the effect of the addition to the reaction mixture of different organic compounds, with different polarities and miscibilities in water. Some compounds, such as toluene and hexane, which are known to increase the solubility of H<sub>2</sub> and O<sub>2</sub> in water, were found to increase the conversion but gave very low selectivities towards H<sub>2</sub>O<sub>2</sub>, probably due to their immiscibility with water and therefore deficient contact with the catalyst. Others, such as triethanolamine, which is a strong binding ligand for transition metals, completely suppressed the reaction. Alcohols in general were found to be the best co-solvents for H<sub>2</sub>O<sub>2</sub> production, since they are miscible with water and able to dissolve the promoters. Particularly, it was found that ethanol was a more powerful additive at higher concentrations, giving 34% selectivity with a 75/25 ethanol-water mixture.

Considering the effectiveness of alcohols as co-solvents, some authors have described successful results in pure ethanol<sup>41–43</sup> and methanol,<sup>44</sup> although water-methanol mixtures are more commonly employed as solvents for direct synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>47–50,52,87</sup> Edwards *et al.*<sup>51</sup> studied the effect of water/methanol ratio using a 2.5 wt% Au/2.5 wt% Pd/TiO<sub>2</sub>, short reaction times (30 minutes) and low temperatures (2 °C) without the addition of halide or acid promoters. They found the optimal water/methanol ratio at 80:20 (reaching 90 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup>), attributed to an enhanced solubility of the reaction gases in the solvent. Interestingly, although the rate of hydrogen peroxide synthesis is enhanced by the addition of methanol to the water, when water is used as a reaction medium higher catalyst amounts can enhance the rate of reaction. Thus, they suggest that Au-Pd catalysts can be used with water as a solvent with no need for promoters. Li *et al.*<sup>90</sup> compared the results obtained in water, water-methanol and water-acetone solvents for both Au and Au-Pd zeolite supported catalysts in short reaction times (30 minutes)

and room temperature. The bimetallic catalyst in water-acetone solvent gave the best productivity rate (50.8 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup>).

In the latest patent by Solvay SA, the use of liquids such as water, organic solvents and their mixtures was claimed. As organic solvents they considered the water miscible solvents such as methanol, ethanol, isopropyl alcohol, acetone and glycols.<sup>103</sup> These claims are not very different from the previous claims made by other companies such as Degussa AG.<sup>71</sup> Degussa pointed out that the alcohols are suitable for the further use of H<sub>2</sub>O<sub>2</sub> as an epoxidation agent.

Carbon dioxide has also been successfully employed as a solvent for the H<sub>2</sub>O<sub>2</sub> direct synthesis. It is considered as a “green solvent”, since it is relatively non-toxic, non-flammable, and inexpensive. A wide range of reactions can be carried out using supercritical CO<sub>2</sub> technology, including hydrogenation, Friedel-Crafts alkylation, hydroformylation, etherification and esterification,<sup>136,137</sup> and in particular, hydrogenations are clean, fast and more selective. Diluting the gas phase (H<sub>2</sub> + O<sub>2</sub>) using CO<sub>2</sub> is an alternative that, according to Pande and Tonheim,<sup>138</sup> increases the lower flammability limit (LFL) of H<sub>2</sub>/air mixtures up to 9.5% for H<sub>2</sub> as CO<sub>2</sub> helps absorb the heat generated from H<sub>2</sub> oxidation reactions, achieving greater H<sub>2</sub> concentrations and a better temperature control.<sup>63,139</sup> Unfortunately, the operation under high pressures dealing with flammable mixtures, *e.g.* for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, requires the knowledge of the flammability limits. So far, these data are scarce, and the only modelling made in the field of H<sub>2</sub>O<sub>2</sub> direct synthesis was by Piqueras *et al.*<sup>140</sup>

It is important to underline that CO<sub>2</sub> is an interesting carrier that (a) in water forms carbonic acid and (b) can expand different solvents. It is well known that acidic solutions are used both to stabilize and to enhance the H<sub>2</sub>O<sub>2</sub> direct synthesis, and CO<sub>2</sub> is so far the ‘greenest’ acid that can be used for this scope. Moreover, a solvent expanded by the carbon dioxide under pressure can increase its volume up to 100%, depending on the conditions used during the reaction.<sup>141</sup> When the reaction vessel is decompressed, carbon dioxide is released from the solvent and the final concentration of the products increase. These properties make CO<sub>2</sub> attractive for the direct synthesis reaction since CO<sub>2</sub> helps in achieving higher concentrations and in stabilizing the H<sub>2</sub>O<sub>2</sub> produced.

The use of CO<sub>2</sub>-expanded solvents can improve the performances in various selective oxidation reactions.<sup>57</sup> During the direct synthesis reaction, H<sub>2</sub> is around 4 wt%, oxygen around 20 wt% and the remaining gas is CO<sub>2</sub> or N<sub>2</sub> (inert gases). It was reported recently that by using CO<sub>2</sub>-expanded methanol it is possible to nearly double the selectivity to H<sub>2</sub>O<sub>2</sub> and increase the productivity under mild pressure (around 10 bar) in comparison with the results of the same experiments made using N<sub>2</sub> instead of CO<sub>2</sub>.<sup>142,143</sup> An issue, however, regards the stability in these conditions, and whether the use of CO<sub>2</sub>-expanded methanol may lead to catalyst deactivation.<sup>144</sup> The catalysts used in the direct synthesis of H<sub>2</sub>O<sub>2</sub> are almost all based on supported Pd, with the eventual presence of a second element (particularly noble metals such as Au or

Pt).<sup>2,3,145</sup> Few studies have analyzed the possibility of Pd leaching, with the general conclusion being that it is not relevant and that the leached Pd is not active in the homogeneous solution, *i.e.* if the solid catalyst is removed.<sup>146,147</sup> However, it is not yet completely clear if CO<sub>2</sub> in methanol can also act as a promoter for Pd catalyst deactivation.<sup>144</sup> On the other hand, bi-metallic catalysts can be reused up to three times when operating with CO<sub>2</sub> and CO<sub>2</sub> expanded solvents.<sup>113</sup>

Of particular relevance to the direct synthesis reaction is the fact that H<sub>2</sub> and O<sub>2</sub> are completely miscible with supercritical CO<sub>2</sub> ( $T_c = 31\text{ °C}$  and  $P_c = 7.4\text{ MPa}$ ), and even under subcritical conditions their solubility is much higher than in organic solvents or water, so the mass transport limitations associated with conventional solvents are avoided or greatly diminished. Moreover, the solubility of H<sub>2</sub>O<sub>2</sub> in CO<sub>2</sub> is low, which facilitates its separation from the solvent and minimizes the chances for product degradation through prolonged contact with the catalyst.

As mentioned above, the acidic character of CO<sub>2</sub> also helps the stabilization of aqueous hydrogen peroxide, diminishing the need for acidic promoters. Beckman and co-workers<sup>53</sup> first achieved the direct synthesis of H<sub>2</sub>O<sub>2</sub> in liquid CO<sub>2</sub> following a Pd-catalysed hydrogenation and a subsequent oxidation process of fluorinated and, therefore, CO<sub>2</sub>-philic anthraquinone. Later, they developed CO<sub>2</sub> soluble Pd catalysts,<sup>45</sup> obtaining 30–40% yields after 3 hours when using a Pd<sup>2+</sup> catalyst (22 °C, 17.0 MPa). They also found the activity of the reduced catalyst to be approximately twice that of the unreduced catalyst. However, the synthesis of the CO<sub>2</sub>-soluble palladium catalyst was tedious and expensive, and they studied the possibility of using a regular Pd supported catalyst and a very small amount of water,<sup>148</sup> but the difficulty of accurately measuring the concentration of H<sub>2</sub>O<sub>2</sub> formed remained. For these reasons, although scCO<sub>2</sub> requires relatively mild conditions for a single fluid phase and offers a number of very attractive properties for the DS reaction, this process presents a number of safety and technical problems during the decompression stage after the reaction, as well as the difficulty in finding a suitable soluble catalyst, that limit its technical industrial feasibility. As a result, the less expensive and smarter solution is to operate below the triple point and in the presence of a solvent, *i.e.* a two fluid phase system, the so-called CO<sub>2</sub>-expanded liquid.

#### 4.5. Pressure

The influence of pressure is directly related to the mass transfer of the reactant gases to the liquid phase. Total pressure of the system increases the solubility and decreases bubble size and so it increases the mass transfer efficiency. The higher the concentration of H<sub>2</sub> and O<sub>2</sub> in the liquid phase the higher their concentration in the catalyst sites and, therefore, the reaction rate is enhanced.

The solubility of the reacting gases in the liquid solvent increases with pressure and, for the case of a three phase slurry process, it increases H<sub>2</sub>O<sub>2</sub> yield.<sup>56</sup> This result has been found also by Freakley *et al.* in a continuous microreactor between 0.5 and 1.3 MPa,<sup>149</sup> though they did not observe a

change in selectivity. Voloshin *et al.*, also using a microreactor, observed an increase in the space time yield (similar to turn over frequency as they defined it). They also observed and increase in the selectivity between 0.35 and 0.7 MPa but they did not observe a significant increase in selectivity between 0.7 and 2.1 MPa.<sup>23</sup>

Most of the patents indicated ranges of pressure up to more than 20.0 MPa. At industrial scale, the pressure will be a compromise between expensive equipment and an intensive low-volumetric process.

#### 4.6. Temperature

Pashkova *et al.* working at low conversion (below 20%) studied the effect of temperature for 5% Pd–TiO<sub>2</sub> together with variation of H<sub>2</sub>/O<sub>2</sub> ratio at 27 °C (subcritical) and 40 °C (supercritical) in CO<sub>2</sub> as inert. They found an increase in productivity and conversion with temperature independently on the H<sub>2</sub>/O<sub>2</sub> ratio. This trend was different from the one they encountered under batch conditions.<sup>150</sup>

Moreno *et al.* studied the kinetic temperature dependence in a semi-continuous reactor at low catalyst amounts (corresponding to a kinetic regime, where mass transfer is not controlling). They found a direct dependence of productivity on temperature under those conditions, estimating the values of the observed activation energy and the pre-exponential factor in 11.8 kJ mol<sup>−1</sup> and 188.2 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> h<sup>−1</sup> kg<sub>cat</sub><sup>−1</sup>, respectively.<sup>65</sup>

In the same way, Blanco-Brieva *et al.* found that operating at 9.5 MPa, with methanol–water (96/4) and gases H<sub>2</sub>:O<sub>2</sub>:N<sub>2</sub> of 2.2%:47.8%:50 mol% with 0.8 g of catalyst EG-1 and 6 ppm of HBr in a stirred semi-continuous reactor operating at a temperature of 40 °C (4.1 wt% H<sub>2</sub>O<sub>2</sub>) produced more than twice the amount of H<sub>2</sub>O<sub>2</sub> than at 20 °C (1.7 wt% H<sub>2</sub>O<sub>2</sub>) after 120 min.<sup>60</sup>

In contrast, in a promoter-less reaction, Biasi *et al.* demonstrated in a batch system using methanol as the liquid phase that although the conversion increases with temperature, the concentration of H<sub>2</sub>O<sub>2</sub> reaches a maximum at −5 °C and a minimum at 40 °C, while the production of H<sub>2</sub>O reaches a maximum at 40 °C and a minimum at −5 °C.<sup>55,59</sup>

In summary, we can conclude that the reaction temperatures for direct synthesis were investigated from −10 °C to 60 °C and patented even in a wider range. Working below 35 °C is not recommended from an industrial point of view as it would be difficult to remove the heat produced in the reaction (*i.e.* a low temperature utility is expensive). Cooling water utilities normally operate between 25–28 °C (supply) and 32–38 °C (return). Therefore, operations in the range between 40 and 60 °C should be affordable.

## 5. Conclusions

Hydrogen peroxide is booming as an environmentally friendly and versatile chemical oxidant available with a wide range of applications. The world production is currently dominated by Solvay operating novel mega-plants of about 330 kt per year



producing  $\text{H}_2\text{O}_2$  via the auto-oxidation process with 2-ethyl anthraquinone (traditional) or amyl anthraquinone (for mega-plants).

In this review we have tried to provide an answer to questions such as: which are the targets to be achieved for hydrogen peroxide direct synthesis; which are the experimental equipment to study direct synthesis of  $\text{H}_2\text{O}_2$ ; and which are the best operational conditions to increase conversion and selectivity towards  $\text{H}_2\text{O}_2$ ?

Direct synthesis seems to be attractive in the small market situated on-site with production capacities below 10 kt per year, where the traditional auto-oxidation process cannot compete due to more equipment complexity.

The maximum investment cost of a plant of 10 kt per year can be estimated as around  $40.3 \pm 12.1$  MMS (in 2012) to be comparable & competitive to the traditional process.

Many groups are active in the  $\text{H}_2\text{O}_2$  direct synthesis. Most of them started using a batch reactor that afterwards was transformed into a semi-continuous reactor. Other groups work on microreactors and membranes. Slurry bubble columns and fixed bed reactors (such as trickle bed reactors) are less common, so far, but a number of on-going studies aim at demonstrating together with other continuous systems that the process can be feasible.

Reactors capable of reaching a  $\text{H}_2\text{O}_2$  concentration of at least 15% (aqueous) or 9% (alcohol) are needed to demonstrate the technology and to give the basement for the forthcoming scale-up. Specially those which can work with a high  $\text{H}_2$  conversion (more than 99%) and selectivity values over 20%. The advantages and disadvantages of the various reactor configurations were tackled. Together with the target and the type of reactor used, the selection of the operational parameters is indispensable to be successful.

Thus, the choice of an active catalyst, an appropriate solvent and the optimum promoters are essential factors in the direct synthesis. Palladium catalysts are the most commonly employed, although gold and, especially, gold-palladium catalysts have been reported to successfully produce hydrogen peroxide. The influence of the oxidation state of Pd is today not clearly understood. Some authors have reported that the reduced form  $\text{Pd}^0$  is more active, whereas other investigators claim that surface oxidation induced a very high catalytic activity. The support material also has a strong influence on the productivity. Generally, acidic supports such as carbon, titania, zeolite, silica and zirconia tend to give better results due to the higher stability of hydrogen peroxide in an acidic environment. However, the suitability of the support is dependent on the metal used.

To avoid  $\text{H}_2\text{O}_2$  decomposition and hydrogenation and to improve productivity, the addition of promoters, namely halides and acids, is common practice. HBr and HCl are usually chosen as promoters, since they combine the halide effect (blockage of high energy sites of the catalyst, responsible for the dissociative chemisorption of  $\text{O}_2$  and readsorption of  $\text{H}_2\text{O}_2$ ) with the acid effect (inhibition of the base-catalysed decomposition of hydrogen peroxide). Other usual

combination is  $\text{Br}^-$  and phosphoric acid, which does not induce leaching of the active metal from the catalyst, as opposed to other stronger acids.

The choice of solvent is a very important aspect in direct synthesis and has been thoroughly discussed. The low solubility of hydrogen and oxygen in water usually encourages the use of an organic co-solvent, such as methanol or ethanol. An interesting alternative to the use of organic solvents is supercritical  $\text{CO}_2$ , which eliminates the need for acid promoters and, more importantly, product purification, owing to the total miscibility of the reactant gases and the low solubility of the product, which facilitates its separation from the solvent and minimizes the chances for product degradation through prolonged contact with the catalyst.

Finally, pressure and temperature are highly linked to gas-liquid mass transfer and reaction kinetics respectively. Although the two parameters influence the two phenomena. The selection of pressure at industrial scale will be a compromise between expensive equipment and an intensive low-volume process. Most of the patents point out that high pressures between 8.0 and 12.0 MPa are the most recommended. Reaction temperatures between 40 and 60 °C would be considered as affordable to refrigerate using cooling water utility (or air cooled heat exchangers even better if the reaction temperature is higher than 60 °C).

As a final comment,  $\text{H}_2\text{O}_2$  direct synthesis is currently under intense investigation, with a number of patents considering both the auto-oxidation process and the alternative processes, such as direct synthesis. In direct synthesis, most of the efforts have been directed towards catalyst development. Nevertheless, the latest results of many groups working under continuous mode demonstrate that conversion and selectivity can be effectively tackled by a good combination between catalyst selection and operational conditions.

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