

## HYDROGEN PEROXIDE DIRECT SYNTHESIS: FROM CATALYST PREPARATION TO CONTINUOUS REACTORS

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Monometallic Pd and bimetallic Pd-Au catalysts supported on zirconia, sulphated zirconia, silica and sulphated ceria were prepared by different methods and tested for hydrogen peroxide direct. The effect of the addition of gold to Pd enhance the selectivity and the yield of H<sub>2</sub>O<sub>2</sub>. The best results were obtained with bimetallic Pd-Au catalyst on sulphated zirconia (PdAu-ZS). Activity was tested at both atmospheric and high pressure, batch and semi-batch wise. Decomposition, hydrogenation and direct synthesis of H<sub>2</sub>O<sub>2</sub> were assessed on the PdAu-ZS catalyst. Catalysts have been tested also in a trickle bed reactor for the continuous direct synthesis. The H<sub>2</sub>/Pd mol ratio was investigated to enhance both H<sub>2</sub>O<sub>2</sub> concentration and selectivity in batch and TBR. H<sub>2</sub>O<sub>2</sub> concentration was successfully compared between batch and TBR. The TBR shows an enhancement in selectivity towards H<sub>2</sub>O<sub>2</sub> compared to the batch synthesis. Three different liquid flow rates and seven different gas flow rates were used. The combined effect of liquid and gas flow rates, with two different H<sub>2</sub>/O<sub>2</sub> ratio (2/18 and 4/16) in the gas feed, has been studied, by independent variations. The highest H<sub>2</sub>/O<sub>2</sub> ratio always increases production rate and selectivity. PdAu-ZS catalyst shows a remarkable gain in both selectivity and production rate when the 4/16 gas feeding is used. A selectivity up to 90% has been measured on PdAu-ZS with the higher H<sub>2</sub>/O<sub>2</sub> ratio and larger liquid flow rates. The maximum production rate measured is 0.47 mg H<sub>2</sub>O<sub>2</sub>/g CH<sub>3</sub>OH/min with 1 ml/min liquid flow rate and 2.7 ml/min gas flow rate again on PdAu-ZS.

### 1. INTRODUCTION

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a green oxidizer, used as a disinfectant, antiseptic, oxidizer, bleaching agent and as a propellant. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species. The direct synthesis of hydrogen peroxide by heterogeneous catalysis is emerging as a relevant alternative to the anthraquinone autoxidation (AO) process, in view of an integration with other industrial applications, such as the paper bleaching, the water waste treatment, in textile industries and in the synthesis of caprolactam and propylene oxide. The in situ production of H<sub>2</sub>O<sub>2</sub> would reduce or eliminate the costs and hazards of transport and handling of concentrated solutions; moreover, the capital investment and operating costs are expected to be lower than those for the well-known H<sub>2</sub>O<sub>2</sub> manufacturing process (e.g. AO process). Now an increasing number of processes (from chemical to environmental applications) would benefit from a small on site H<sub>2</sub>O<sub>2</sub> production, eliminating transport costs and avoiding the hazards connected to the transport of

concentrated  $\text{H}_2\text{O}_2$  solutions. A further advantage is that a highly pure  $\text{H}_2\text{O}_2$  can be used, since the presence of stabilizers necessary for the transport is not needed.

The AO process is currently being used for large scale production, but for on site smaller productions alternative ways are being explored.

One possible route to  $\text{H}_2\text{O}_2$  synthesis that avoids the use of AQ is the direct synthesis from hydrogen and oxygen in the presence of a catalyst. A real improvement in  $\text{H}_2\text{O}_2$  chemistry would be a one-pot process involving the atom efficient direct synthesis of  $\text{H}_2\text{O}_2$  from its elements, and its immediate application in a subsequent reaction. Few attempts in the reactor design and in finding the suitable operation conditions have been made (Biasi et al. 2010, Pashkova et al. 2010 and Piccinini et al. 2010), but the breakthrough in the hydrogen peroxide direct synthesis is still in the future. The two major drawbacks in the direct synthesis of hydrogen peroxide are related to safety and selectivity. Hydrogen/oxygen mixtures are explosive for a wide range of concentrations (Piqueras et al. 2011), therefore the ratio of hydrogen to oxygen needs to be kept outside the explosive region, or an inert gas such as nitrogen or carbon dioxide must be added. This obviously reduces productivity. A way to avoid direct contact between  $\text{O}_2$  and  $\text{H}_2$  lies in the use of a membrane, circumventing the need of diluting with an inert gas. The other major problem resides in obtaining good selectivity for hydrogen peroxide, limiting side reactions, since normally the same catalyst that promotes  $\text{H}_2\text{O}_2$  synthesis also induces decomposition to yield water Fig. 1. An appropriate solvent is also required to carry out the reaction, leading to a three-phase system (solid-catalyst, liquid-solvent, gas-  $\text{H}_2$  and  $\text{O}_2$ ) which is difficult to control and optimize.

These drawbacks, however, appear to be controllable, and a lot of attention from industry has been directed to research dealing with hydrogen peroxide direct synthesis.

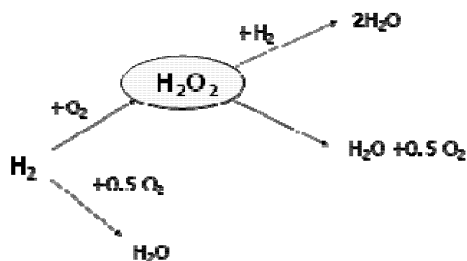


Figure 1: Reactions involved in the direct synthesis of  $\text{H}_2\text{O}_2$ .

We investigated the opportunities of engineering the reaction by moving from batch to continuous operation, with a trickle bed reactor (TBR). A common industrial reactor is easily scalable for the purposes (i.e.  $\text{H}_2\text{O}_2$  synthesis) and can be integrated to already existent processes.

This work is based on the early studies conducted by Menegazzo and coworkers, who synthesized a number of promising catalysts, based on Pd (Melada et al. 2006), Pd-Au (Menegazzo et al. 2008, 2009) and Pd-Pt (Bernardotto et al. 2009) and by Biasi and coworkers (Biasi et al. 2010), who described a method to enhance selectivity in hydrogen peroxide direct synthesis. One of the promising catalyst based on Palladium and Gold, supported on sulphated zirconia (ZS) is compared with a deep analysis of operation conditions in different reactors. In addition, gas and liquid residence time are independently manipulated to affect the extent of reaction and the gas-liquid mass transfer effectiveness (a compensation for small reagents solubility, even lower if operating in the non-explosive region). Two gas  $\text{H}_2/\text{O}_2/\text{CO}_2$  mixtures are used, namely 2/18/80% and 4/16/80% mol and the advantages of using the richest  $\text{H}_2$  mixture are explained. Further, a significant improvement in hydrogen peroxide direct synthesis, compared to semi-batch reactor, is reported.

## 2. EXPERIMENTAL

### 2.1 Catalyst preparation and testing

The catalysts were prepared with different methods as reported elsewhere (Bernardotto et al. 2009, Melada et al. 2006 and Menegazzo et al. 2008). The best catalytic results were obtained with bimetallic Pd-Au catalyst on sulphated zirconia prepared by incipient wetness coimpregnation of  $\text{H}_2\text{PdCl}_4$  and  $\text{HAuCl}_4$  aqueous solutions, followed by calcination at  $500^\circ\text{C}$  in flowing air (30 ml/min) for 3 hours (Menegazzo et al. 2008).

Slurry reactors used the catalyst powder as prepared. For TBR, the powder was compressed to obtain pellets, which were crushed and sieved to obtain particles with a diameter between 0.5-1 mm; subsequently, 0.16 grams of catalyst particles were mixed with 0.2 grams of  $\text{SiO}_2$  and used as catalytic bed (Biasi et al. 2010).

Catalytic tests were carried out both at atmospheric pressure and under pressure. Atmospheric tests were carried out in a constant temperature (293 K) glass reactor according to a previously described procedure (Menegazzo et al. 2008). Mixing was obtained with a Teflon-made rotor operating at 1000 rpm.  $\text{O}_2$  and  $\text{H}_2$  were bubbled directly into the liquid phase by a gas diffuser, with a total flow of 50 ml/min and a mixture composition of  $\text{H}_2/\text{O}_2 = 4/96$  (lower limit for nonflammable mixture). The reaction medium was 100 ml of a 0.03 M  $\text{H}_2\text{SO}_4$  methanolic solution and was presaturated with the gas mixture before introduction of the catalyst (135 mg).

Activity tests at high pressure were carried out in two different reactors.

The scheme of the batch reactor is reported in the Figure 1. This reactor (12) is an autoclave with an internal volume of 100 ml (Autoclave Engineers), made of Hastelloy C steel. Stirring is realized with a magnetically coupled electric engine (MagneDrive, Autoclave Engineers) and a radial turbine. The reactor is fitted with a thermocouple connected to a computer that allows to register temperature values for the duration of experiments. Gases are loaded in the reactor directly from the gas cylinders:  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2$  (1, 2, 3 and 15 in the scheme, respectively). Three on/off valves are located between the gas cylinders and the batch reactor to allow for separation and control (4). Regulation valves are used to carefully dose gas amount from the cylinders (5), and also for liquid (7) and gas sampling (6). Two one-way valves (10 and 11) are used to ensure no backmixing from the reactor environment to the pipelines. A safety valve is added to guarantee safe operation in case of uncontrolled pressure increase (23). Pressure is constantly monitored through a pressure transducer (9), the values are then registered by the computer. A mechanical pressure gauge is used to control pressure conditions (8). A three way valve is located close to the back pressure controller (14), with one end connected to the nitrogen cylinder (15), one to the reactor and the last one to the back pressure controller (18). A high pressure pump was employed to feed the liquid inside the reactor at the beginning and during the experiments. The standard operating procedure loaded the gases first ( $\text{CO}_2$  and  $\text{O}_2$ ), and then the given amount of liquid solvent (39.5 gr of  $\text{CH}_3\text{OH}$ ) with an HPLC pump,  $\text{H}_2$  (the limiting reactant) was fed by a MFC (mass flow controller) after the vapor liquid equilibrium between  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CH}_3\text{OH}$  was reached. The reactor operated at 20 bar and  $-10^\circ\text{C}$ . Recirculation of the liquid phase was also included, through the HP pump (17) coupled with a six-way valve (20). Before the HP pump, a tank with fresh methanol (21) was also added. The reasons behind that were: i) precise liquid sampling in terms of quantity and time; ii) GC analysis of the liquid phase thanks to the six-way valve connected to the GC. However, GC analysis of the liquid phase were not performed, because some difficulties still existed: the liquid phase could contain some by-products from the direct synthesis reaction (e.g.  $\text{O}_2$ ), and the heater before the GC, used to gasify the liquid, could decompose  $\text{H}_2\text{O}_2$ . Thus quantifying  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$  and water with a GC analysis on the liquid phase is not straightforward.

Another significant improvement from the initial set-up was the addition of three mass flow controllers (MFC) (24) after the gas cylinders, which allow for precise gas loading. All the species could then be exactly measured before the reaction started. The MFC were also equipped with a by-pass valve (22) to allow for direct gas loading from the cylinders, if required.

Finally, with thermodynamic predictions, quantification of the amount of reactants in the liquid phase can be obtained.

The implemented modifications lead to a more versatile and precise set-up for batch operations.

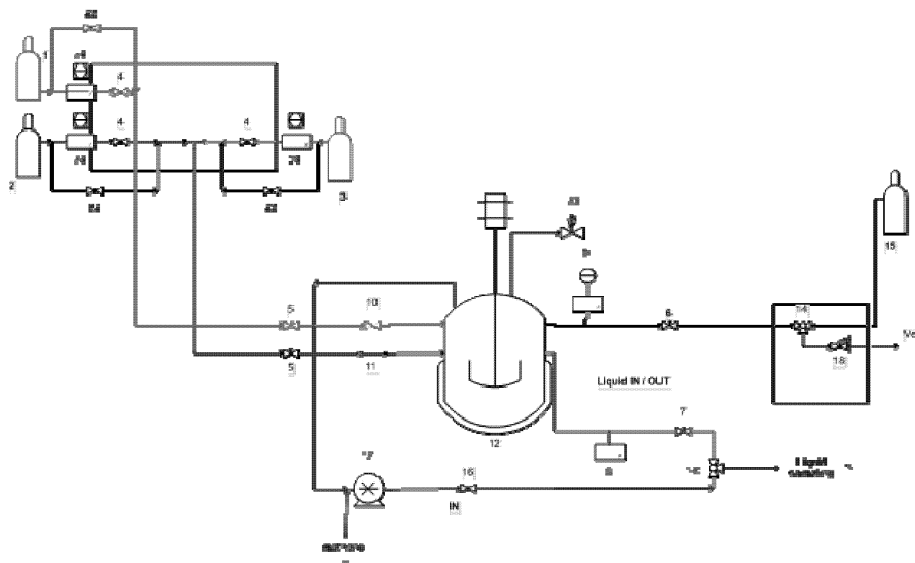


Figure 2: Schematic of the experimental Batch apparatus.. (1, 2, 3) Gas bottles: H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, respectively. (12) Batch Reactor. (17) High Pressure pump. (19) Liquid sampling. (23) Rupture disk. (24) Mass flow controller (MFC).

The experimental Trickle Bed Reactor set-up is described in details elsewhere (Biasi et al. 2010). Shortly, the reactor is made of AISI 316 stainless steel, 30 cm long, 1.5 cm I.D., internally lined with Teflon (1.15 cm final I.D.) to prevent H<sub>2</sub>O<sub>2</sub> decomposition due to accessible Fe<sup>3+</sup> ions. The reactor can accommodate a catalyst bed up to 20 cm long. Reactor is temperature controlled through a jacket, allowing temperatures between -20°C and 60°C. Gas (N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> 97.5/2.5%, CO<sub>2</sub>/H<sub>2</sub> 95/5%, and O<sub>2</sub>) are fed independently by mass flow controllers (MFC), that were calibrated on actual mass flow; volumetric flow rates reported in the figures are calculated with mixture densities determined with a Redlich-Kwong-Soave equation of state with Boston-Mathias modification, through the Aspen Properties code. The pressure inside the reactor is controlled and regulated with a back pressure controller. A rupture disc is installed for safety reasons. A bypass is used to achieve the desired pressure inside the reactor more rapidly. The liquid phase is fed in through a syringe pump with temperature control, connected to a pressure transducer and computer controlled. Gas and liquids mix before the reactor. A regulation valve is used to sample the instantaneous liquid phase. The catalyst bed (0.6 cm long) is placed between two quartz wool plugs. Temperature inside the reactor is measured with a K thermocouple before the catalyst bed. The continuous reactor was made of AISI 316 stainless steel, 30 cm in overall length, 1.5 cm I.D., internally lined with Teflon (1.15 cm final I.D.). The reactor can accommodate a catalyst bed up to 20 cm long. An external cooling system uses a chiller. Three mass flow controllers were used to feed the gases into the reactor. Each mass flow controller was connected to a gas cylinder: N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> 97.5/2.5% (or 95/5%), and O<sub>2</sub>. The pressure inside the reactor was controlled and regulated with a back pressure controller. The liquid phase was fed in through a syringe pump. The catalyst bed was normally placed between two quartz wool plugs. Above the upstream quartz wool plug, quartz sand was used to improve gas-liquid mixing. The experiments of direct synthesis were carried out at 10 bars and -10°C, in methanol, the liquid flow rates used were 0.5, 1 and 2 ml/min. Two gas H<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub> mixtures were used, namely 2/18/80% and 4/16/80% mol. The total gas flow rates tested were 1, 2, 2.7, 4, 6, 9 and 12 ml/min.

Reaction progress was always monitored through the liquid phase analysis. Water (volumetric Karl Fischer titrator) and H<sub>2</sub>O<sub>2</sub> (iodometric titration) concentrations were measured. The water content was also measured prior to each experiment, before feeding H<sub>2</sub> (batch reactor) or O<sub>2</sub> (TBR). H<sub>2</sub>O<sub>2</sub> concentration is defined as [(H<sub>2</sub>O<sub>2</sub> mg) / (CH<sub>3</sub>OH g)]. The selectivity is defined as  $100 \times [\text{H}_2\text{O}_2] / ([\text{H}_2\text{O}_2] + [\text{H}_2\text{O}]\text{prod})$ ; it is equal to the moles of H<sub>2</sub>O<sub>2</sub> produced, divided by the moles of H<sub>2</sub> consumed.

### 3. RESULTS AND DISCUSSION

The detailed activity measurements on Pd-Au catalyst on sulphated zirconia (PdAu-ZS) at atmospheric pressure are reported elsewhere (Menegazzo et al. 2008). In the following, high pressure, batch and continuous tests are discussed.

Table 1 summarizes the achievements in a semi-continuous reactor (Menegazzo et al. 2008, Melada et al. 2006, Menegazzo et al. 2009 and Ghedini et al. 2010). The PdAu-ZS catalyst was chosen for its characteristic of activity, selectivity and stability.

Table 1: metal final loading, average of the nanoparticles, activity and selectivity of the catalysts tested in a semibatch reactor (<sup>1</sup>Menegazzo et al. 2008, <sup>2</sup>Melada et al. 2006 <sup>2</sup>Menegazzo et al. 2009 and <sup>3</sup>Ghedini et al. 2010)

catalyst	% Pd (wt %)	% Pd found (wt %)	% Au (wt %)	% Au found (wt %)	particle average diameter (nm)	Productivity (mmol H <sub>2</sub> O <sub>2</sub> /gPd h)	Selectivity (%)
Pd-ZS <sup>1</sup>	2.5	2.44	//	//		6.4	499
PdAu-ZS <sup>1</sup>	1.3	1.21	1.2	0.95	4.5	1027	60
1Pd2Au-ZS <sup>1</sup>	1.3	0.89	1.2	0.74	3	1040	32
1Au2Pd-ZS <sup>1</sup>	1.3	1.17	1.2	0.82	55	1429	54
PdAu-Z <sup>2</sup>	1.25	1.21	1.25	0.95	//	1070	//
Pd-Z <sup>2</sup>	2.5	2.61	//	//	//	100	30
Pd-Ce <sup>2</sup>	2.5	2.68	//	//	//	500	//
Pd-CeS <sup>2</sup>	2.5	2.69	//	//	1.3	245	45
PdAu-Ce <sup>2</sup>	1.25	1.24	1.25	1.10	//	620	//
PdAu-CeS <sup>2</sup>	1.25	1.01	1.25	1.10	1.5	720	50
1.5Pd-SiO <sub>2</sub> <sup>3</sup>	1.5		//	//	2	762	63
1.5Pd-MCM-41 <sup>3</sup>	1.5		//	//	2.9	479	50
1.5Pd-SBA-15 <sup>3</sup>	1.5		//	//	4.5	1134	61
2.5Pd-SiO <sub>2</sub> <sup>3</sup>	2.5		//	//	below 2	443	58
2.5Pd-MCM-41 <sup>3</sup>	2.5		//	//	below 2.9	415	40
2.5Pd-SBA-15 <sup>3</sup>	2.5		//	//	below 4.5	80	52

#### 3.1 Catalyst preparation and properties

The Zirconia (Z) was sulfated by incipient wetness method with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to yield an 8 wt% of anion loading. The amount of sulfate was determined by ion chromatography after dissolution of materials and show a loading of 4.2 wt% in. The metals were then deposited again by incipient wetness with H<sub>2</sub>PdCl<sub>4</sub> and HAuCl<sub>4</sub> aqueous solutions to give a nominal 2.5 wt% metal loaded catalyst. BET characterization shows a specific surface area (SSA) for the ZS support of 129 m<sup>2</sup>/g. The pore diameter and volume for the ZS sample was 11.1 nm and 0.332 cm<sup>3</sup>/g. The nominal value of Pd and Au loaded on the ZS was 1.25 wt% for each metal, but atomic absorption spectroscopy (AAS) reports an actual loading of 1.22 wt% for Pd and 0.92 wt% for Au on ZS. The particle size

distribution measured by HRTEM indicates that the average size of the particles observed in the PdAu-ZS catalyst is 4.5 nm. A more detailed characterization is reported elsewhere (Menegazzo et al. 2008).

### 3.2 Batch runs

Kinetic experiments on hydrogen peroxide direct synthesis, decomposition and hydrogenation were carried out by varying the amount of the PdAu-ZS catalyst. Decomposition of hydrogen peroxide was not observed during the test carried out in the batch reactor in the presence of the catalyst but absence of both  $H_2$  and  $O_2$  (Fig. 1 a). Hydrogenation of  $H_2O_2$  with the catalyst causes a significant loss of  $H_2O_2$  (Fig. 1 b) in a time frame comparable to the synthesis. The amount of catalyst increases the rate of loss.

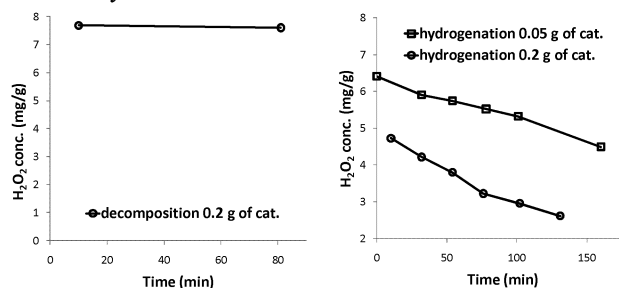


Figure 3 a) decomposition (left) and b) hydrogenation (right) of  $H_2O_2$  on PdAu-ZS catalyst.

In the direct synthesis,  $H_2O_2$  production is dramatically affected by the amount of catalyst. The experiments with 0.05 g of catalyst show a constant increase of the hydrogen peroxide concentration in methanol (Figure 2a). With a larger amount of catalyst (0.2 g)  $H_2O_2$  production increases more rapidly in the first hour passing through a maximum and then its concentration in the products gradually decreases, as shown in Figure 2a.

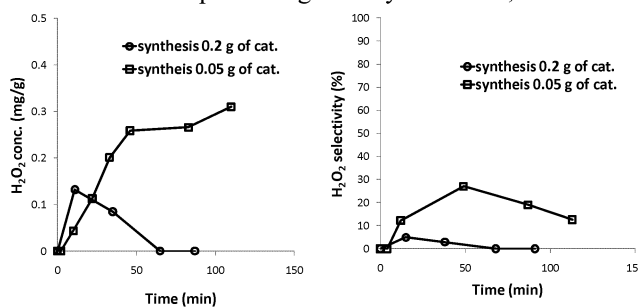


Figure 4 a) concentration (left) and b) selectivity (right) of  $H_2O_2$

At the beginning, the synthesis rate is larger than those of water formation and hydrogenation (0.2 g of catalyst). After ten minutes, the net rate of hydrogen peroxide production begins to decrease while other reactions prevail in the direct synthesis. After one hour,  $H_2O_2$  is not present anymore in the reaction medium. Clearly, hydrogenation and water formation largely prevailed on the  $H_2O_2$  synthesis. Further, all these reactions competes for the same  $H_2$ . Hydrogen peroxide decomposition and hydrogenation further accelerate owing to the increase of the  $H_2O_2$  concentration (Biasi et al. 2010).

The trend is different when the kinetic experiments are carried out with much less catalyst (0.05 g), as evident from Figure 2a: the concentration of  $H_2O_2$  in the solution constantly increases. The reasons of this difference can

be found in the different  $H_2/Pd$  molar ratio on the catalyst surface. When the concentration of  $H_2$  in the liquid phase allows set to a high value of the  $H_2/Pd$  ratio, the direct synthesis is preferred, compared to other reactions (i.e. water formation and hydrogenation).

The selectivity data with the different mass of catalyst are of major importance. The selectivity is also positively affected by the  $H_2/Pd$  ratio as shown in Figure 2 b. The selectivity for the two experiments goes through a maximum, approx. at fifteen minutes when 0.2 g of the catalyst are present and at one hour where the experiments are carried out with 0.05 g of catalyst. Taking into account the results of both  $H_2O_2$  production and selectivity, it is reasonable to state that: 1) the reaction of hydrogen peroxide direct synthesis is very fast at the beginning with a high selectivity; 2) the hydrogenation rate increases as soon as hydrogen peroxide is formed; 3)  $H_2O_2$  production decreases and water formation is favored when hydrogen concentration in the liquid phase lowers.

### 3.3 Trickle bed reactor

A continuous reactor (a trickle bed one) is very attractive and may determine operation conditions to gain in selectivity and productivity.

It was observed that the  $H_2/Pd$  mol ratio together with flow rates can dramatically affect the catalyst activity and selectivity in a continuous reactor, Figures 5 and 6. At 0.5 ml/min liquid flow rate and 4%  $H_2$  in the inlet, the PdAu-ZS catalyst showed the highest production rate, Figures 5a and 6a. Different operation conditions markedly affect the catalyst behavior in a non-obvious way, suggesting that suitable combinations of operating policies might be identified to optimize either the productivity or the selectivity or a function of both.

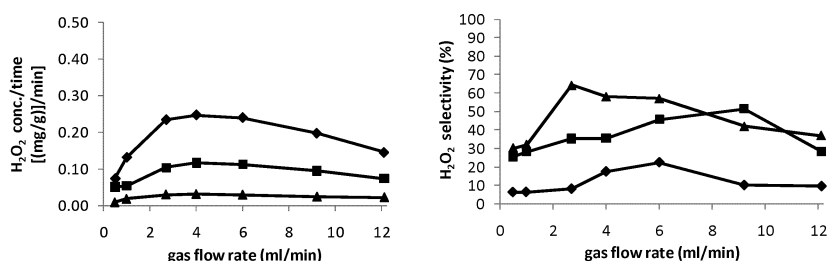


Figure 5a (left) and Figure 5b (right): concentration and selectivity of  $H_2O_2$  over PdAu-ZS catalyst. Combined effect of gas and liquid flow rates at 10 bar and  $-10^\circ C$ . Gas composition  $H_2$  (2%),  $O_2$  (18%) and  $CO_2$  (80%) Methanol flow rate: 0.5 ml/min (diamonds), 1 ml/min (squares), 2 ml/min (triangles).

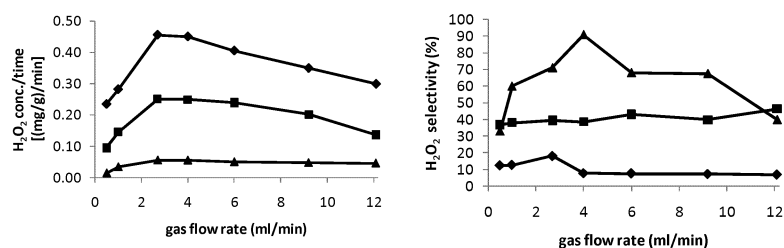


Figure 6a (left) and Figure 6b (right): concentration and selectivity of  $H_2O_2$  over PdAu-ZS catalyst. Same conditions and symbols as in Figure 3, except for gas composition:  $H_2$  (4%),  $O_2$  (16%) and  $CO_2$  (80%).

At 1 ml/min and 4%  $H_2$  PdAu-ZS catalyst shows the highest production rate, while at small gas flow rate and with 2% of  $H_2$  in the gas feeding there is no significant variation between the two catalysts in terms of  $H_2O_2$  production rates. Catalysts behavior with different operative conditions do not yield comparable selectivities. We

conclude that different operative conditions affect catalyst behavior in a non-obvious ways, suggesting that suitable combinations of operating policies might be identified to optimize either production rate or selectivity or a function of both.

The production rates of  $\text{H}_2\text{O}_2$  presented in Figures 5a and 5b show that an optimum between gas and liquid flow rates exist, to maximize the  $\text{H}_2\text{O}_2$  production. When the concentration of  $\text{H}_2$  in the feed is 2% mol, an optimum in  $\text{H}_2\text{O}_2$  production rate is achieved with a gas flow rate between 2 and 6 ml/min, at any liquid flow rate. When the feed is composed by 4% of  $\text{H}_2$  the optimum is always found between 2.7 and 4 ml/min of gas flow rate. Selectivity is defined as  $\text{H}_2\text{O}_2$  produced with respect to water and  $\text{H}_2\text{O}_2$  formed and reflects the relevance of unwanted side reactions. To increase the selectivity, the  $\text{H}_2\text{O}_2$  production has to increase, or the rate of water formation reduced, or both. It is reported (Voloshin et al.) that stabilizers and small conversion of  $\text{H}_2$  can increase the selectivity to 100%. In our case the conversion of the reactants is rather low due to the short contact time between the liquid phase and the catalytic bed; furthermore, without using the stabilizers the consecutive reactions reported in the Fig. 1 can not be neglected. Selectivity falls when the contact time between liquid and solid is larger. Moreover the production of water by direct formation is likely due to surface changes in the active metal; as already reported (Biasi et al. 2010), water formation occurs. The selectivity behavior has to be ascribed to the reactor used, also. We assume that the direct synthesis is active throughout the whole reactor but when the concentration of  $\text{H}_2\text{O}_2$  increases the reactions of decomposition and hydrogenation become important. The main features of selectivity has to be found in the consecutive reactions reported in the Figure 1 and in the contact time between the liquid phase (where the gases are dissolved) and the catalyst. At low gas and liquid flow rates the contact time between the liquid and the catalyst is the highest.

The  $\text{H}_2\text{O}_2$  produced has the time to be hydrogenated or decomposed by the catalyst reducing the selectivity, as reported in figure 5b and 6b, below 40% for the PdAu-ZS catalyst. If the gas flow rate is increased also the contact time between liquid and solid decreases. When the gas flow rate is increased to the maximum value, channeling is likely so that a higher liquid velocity than the nominal liquid velocity can occur. In this case the mass transfer rate from the gas to the liquid phase is enhanced and the modification of the catalyst surface happens. Most probably, due to the higher concentration of  $\text{H}_2$  in the liquid phase, the reaction of formation of water is increased by the reduction of the catalyst surface. In principle, in the case of hydrogen at 2% and 4%, with the lowest and the intermediate liquid flow rates, the selectivity doesn't change sharply with the gas flow rate due to the complex phenomena mentioned above (e.g. change of the catalyst oxidation state,  $\text{H}_2$  mass transfer in the liquid phase). With these reaction conditions there is an increases/decreases of the water formed during the reaction (hydrogenation, decomposition and direct formation of water) that come out in a change of  $\text{H}_2\text{O}_2$  production rate but not in selectivity. When  $\text{H}_2$  is 2% and 4% molar in the feed, with the highest liquid flow rate, the behavior of the selectivity changes compared to the previous conditions. In practice at lowest gas flow rate the hydrogen has the time to reduce the Pd oxidation state due to the high contact time, the same phenomena can be found when the gas flow rate is the highest because the mass transfer of hydrogen from the gas to the liquid phase is enhanced. The results in selectivity are obviously comparable. On the other hand the selectivity changes sharply with the intermediate gas flow rates and the highest liquid flow rate. The reason of this situation is ascribed to the mass transfer between gas and liquid: the different velocities of gas and liquid flow rates probably result in different concentrations of  $\text{H}_2$  in the liquid phase (the differences in  $\text{H}_2$  and  $\text{O}_2$  concentrations probably are wider compared to the previous conditions analyzed, due to the highest liquid flow rate used). The amount of  $\text{H}_2$  and  $\text{O}_2$  dissolved in the liquid phase is higher and all the reactions in the Fig. 1 increases, except decomposition, are expected to accelerate. The modification of the oxidation state of the catalyst added to the low contact time between liquid and solid, with the highest gas flow rate used, have a higher impact on the selectivity in the reaction of hydrogen peroxide direct synthesis, compared with the others liquid flow rates used. The peak observed in both cases (70% for PdAu-ZS with 2% of  $\text{H}_2$  in the feed and 90% PdAu-ZS with 4%  $\text{H}_2$  in the feed, Figures 5b and 6b) at 2 ml/min liquid flow rate can be ascribed to an optimal combination of gas and liquid flow rates, leading to the appropriate contact time which suppresses the reaction of decomposition, hydrogenation and formation of water. Most probably with the correct combination of gas and



liquid flow rate the surface of the catalyst remain oxidized, and the unwanted reactions are suppressed as already reported by Menegazzo and coworkers (Menegazzo et al. 2010). When the surface of the catalyst is reduced, unwanted reactions are enhanced.

It is well known that  $H_2$  promotes direct  $H_2O_2$  synthesis but also its hydrogenation without promoters added to the reaction medium solution. In earlier studies it was suggested that  $H_2O_2$  production and selectivity are positively improved by  $H_2$  refilling during batch experiments (Burato et al. 2009). The mechanism appear to be a refresh of the surface of the catalyst by  $H_2$ , to promote direct synthesis, preventing parallel reactions to grow faster than the direct synthesis, when  $H_2$  is lacking. The concept of maintaining the same quantity of hydrogen in the liquid phase during the reaction can be applied in a continuous reactor increasing the amount of hydrogen in the liquid phase as it is consumed while reducing the contact time between solid (catalyst) and liquid (reaction medium) phase. Taking into account this concept the experiments were performed with a catalyst bed of 0.6 cm and increasing the concentration of  $H_2$  from 2% to 4%. The results in selectivity for a PdAu-ZS catalyst (Figure 6a and 6b) show the remarkable gain in both production rate and selectivity

#### 4. CONCLUSIONS

Bimetallic catalysts confirmed to be promising for the  $H_2O_2$  direct synthesis. Best results being obtained with the PdAu-ZS catalyst. Batch and continuous reactors were successfully used to enhance catalyst activity compared to semibatch reactor (Menegazzo et al. 2008). At higher  $H_2/Pd$  mol ratio there is an enhancement of both  $H_2O_2$  maximum concentration achievable and selectivity in both batch and TBR. The  $H_2O_2$  concentration is comparable between the batch and the trickle bed reactor, while much higher selectivities were measured in the TBR, which is promising to make industrial feasible the hydrogen peroxide direct synthesis. A continuous reactor for hydrogen peroxide synthesis is successfully used to enhance catalyst activity. Bimetallic catalysts confirmed to be promising for  $H_2O_2$  direct synthesis. The  $H_2/O_2$  ratio in the gas phase has a really important effects on the catalyst: the PdAu-ZS catalyst shows better activity with a 4%  $H_2$  compared to the same experiments carried out with 2%  $H_2$ . This means that  $H_2$  concentration plays an important role on production rate and selectivity, but in combination with other operative conditions, as the flow rate. The maximum selectivity achieved is about 90% with the PdAu-ZS catalyst, which is quite high and very promising for industrial application. The experimental conditions in this case were 2 ml/min MeOH as the liquid flow rate, 4% hydrogen in the total gas feed with 4 ml/min gas flow rate, 10 bar and  $-10^\circ C$ . Importantly, under these conditions  $H_2O_2$  production rate is also the highest measured.

Catalyst stability test shows a weakness due to the particles stability under pressure swings, while the original catalyst powder preserves its activity. Pressure cycles however are unlikely in a continuous industrial reactor, making this process and catalysts attractive from an industrial perspective.

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