Continuous H_2O_2 direct synthesis over PdAu catalysts

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ABSTRACT

H_2O_2 direct synthesis over two bimetallic, palladium-gold catalysts based on sulfated ceria (PdAu-CeS) and on sulfated zirconia (PdAu-ZS) has been studied in a continuous, trickle-bed reactor, at $-10\,°C$ and 10 bar. 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_2/O_2 ratio (2/18 and 4/16) in the gas feed, has been studied, by independent variations. The highest H_2/O_2 ratio always increases production rate and selectivity. In the case of 4/16 ratio, PdAu-CeS catalyst shows an enhancement in selectivity only, while the increase in H_2O_2 production rate is not significant compared to the 2/18 ratio case. PdAu-ZS catalyst shows a remarkable gain in both selectivity and production rate when the 4/16 ratio in gas feeding is used, outperforming the PdAu-CeS catalyst. The enhancement of the catalytic activity is more pronounced in the case of PdAu-ZS, compared to PdAu-CeS, when the highest H_2/O_2 ratio is used. A selectivity up to 90% has been measured on PdAu-ZS with the higher H_2/O_2 ratio and larger liquid flow rates. The maximum production rate measured is 6 $\mu mol/min$ (i.e. a productivity 0.18 mol $H_2O_2\,g_{Pd}^{-1}\,h^{-1}$) with 1 ml/min liquid flow rate and 2.7 ml/min gas flow rate again on PdAu-ZS.

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1. Introduction

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 paper bleaching, waste water treatment, textile manufacturing, and caprolactam and propylene oxide synthesis. The in situ production of H_2O_2 would reduce or eliminate the costs and hazards of transport and handling related to concentrated solutions, moreover the capital investment and operating costs are expected to be lower than those for the well known H_2O_2 manufacturing process (autoxidation of anthraquinone). The numerous steps included in the AO process as extraction, concentration and purification of the working solution, that embody the hydrogen peroxide, can be avoided. Direct synthesis will therefore result in a simpler process and plants. The direct reaction of hydrogen and oxygen to form hydrogen peroxide is in principle the best atom-efficient method for producing H_2O_2, but still insufficiently developed. The reaction is thermodynamically favored, but as shown in Fig. 1, the reaction of H_2O_2 hydrogenation and water formation can affect selectivity and production rate of hydrogen peroxide formation. One of the main problems concerning direct

synthesis lies in the fact that the catalyst promotes both hydrogen peroxide formation and the unwanted reactions (Fig. 1).

Both academia and industry have been extensively investigating direct synthesis, with a large number of studies being continuosly published [1–8]. However, the main effort in the direct synthesis is still focused on the synthesis of new catalysts [2,9–13] that can reduce or avoid the parallel and consecutives reaction involved in the reaction to form H_2O_2 (Fig. 1). Investigations on reactor design and operation conditions are increasing in recent years [1,4,14–18], but the industrial breakthrough is still far away. The most important issue in hydrogen peroxide direct synthesis concerns the safety this is one of the reasons why microreactors and membranes reactors are emerging as important alternatives [15,18].

Microreactors are expected to improve safety at high concentration of hydrogen and different H_2/O_2 ratios, even inside the presumed flammability limit [18] measured in standard, low surface-to-volume vessels. Channel width in microreactors can be made smaller than the quenching distance of hydrogen/oxygen flames, which are thus expected to self extinguish. The same issue can be easily solved with a packed bed [18]. In addition, the bed can be formed by inert particles (e.g. SiO_2) or catalyst powder. The possibility of using microreactors is further limited by the low conversion of the reagents inside the reactor (e.g. when H_2 conversion is around 35% selectivity is around 30% and when H_2 conversion is around 2% selectivity is 100%) [19,20] and their cost, still high to be scaled up for industrial purpose [17–21]. The use of Membrane

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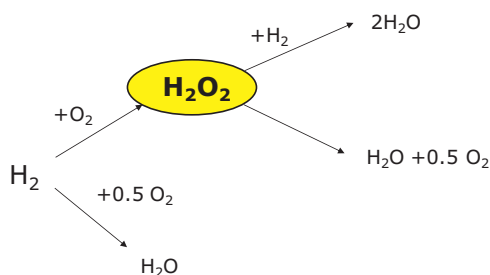 E-mail address: bpierdom@abo.fi (P. Biasi).

Fig. 1. Reactions involved in the direct synthesis of H_2O_2.

reactors is an alternative for direct synthesis [15,16,22]. The catalyst is deposited into the pores of a fine-porous surface layer, while O_2 and H_2 are kept separated by a membrane [15]. It is reported that the best configuration is dissolving H_2 in the liquid phase while O_2 is supplied in the coarse–porous side [16]. Tubular membranes can be used in continuous reactors [15,16]. To avoid explosions membrane reactors are perhaps the best configuration, but the drawback of mass transfer limitation of the gaseous reagents in the catalytic layer is still an issue (e.g. in the continuous H_2O_2 direct synthesis performed with catalytic membranes, the laminar flow conditions in the empty membrane tube allows H_2 mass transfer from the centre to the walls, where the catalytic material is deposited, only by molecular diffusion) [16].

The effects of the reaction conditions were recently investigated by Piccinini et al. [14] and by Moreno et al. [4]. These contributions provide a new interpretation of the results obtained in the direct synthesis. Moreover, our previous work [1] demonstrates how studying the operation conditions allows to find the suitable combination between catalyst and reaction conditions to increase H_2O_2 selectivity and production rate.

Selectivity in most of the cases is enhanced by adding some stabilizers, like alogens (NaBr, HBr) or acids (H_2SO_4) [9,10,12,20,23], to the reaction medium (e.g. methanol, water, ethanol), to support H_2O_2 production by suppressing water formation and H_2O_2 decomposition. We aim at finding suitable operation conditions in a TBR allowing to produce H_2O_2 in situ for other processes (e.g. peroxycarboxylic acid) without using any stabilizer or additive. At these conditions, the highest productivity achieved is 0.18 mol H_2O_2 g_{Pd}^{-1} h^{-1}, comparable to catalytic membrane results (continuous operations, TiO_2 membrane, active phase Palladium, at 30–50 bar, water as a solvent, 0.03 mol/l H_2SO_4, 15 mg/l NaBr) [16].

Two drawbacks of the TBR are that (i) the reaction mixture must fall outside the flammability limits and (ii) the low contact time between the small catalytic bed and the liquid phase leads to low conversion of the reagents. The production rate in the TBR is still low for industrial applications: and the increase of it is an open issue to be addressed with different catalysts and different feeding policies in the reactor.

Here we investigate the opportunities of engineering the reaction by implementing continuous operation with a trickle bed reactor (TBR). A common industrial reactor permits to be easily scalable for the purposes (i.e. H_2O_2 synthesis) and integrated to already existing processes.

This work is based on previous studies conducted by Menegazzo et al., who synthesized a number of promising catalysts, based on Pd [12], Pd-Au [24] and Pd-Pt [9] and by Biasi et al. [1], who described a method to enhance selectivity in hydrogen peroxide direct synthesis. Two promising catalyst based on palladium and gold, one supported on sulfated zirconia (ZS) and the other one on sulfated ceria (CeS) are compared with an in depth analysis of operation conditions. In addition, gas and liquid residence times are independently manipulated to affect the extent of the reaction and gas–liquid mass trans-

fer effectiveness (a compensation for small reagents solubility, even lower if operating in the non-explosive region). Two $H_2/O_2/CO_2$ gas mixtures are used, namely 2/18/80% and 4/16/80% mol and the advantages of using the richest H_2 mixture are explained. Furthermore, a significant improvement in hydrogen peroxide direct synthesis, compared to semi-batch reactor, is reported.

2. Experimental

2.1. Materials

$ZrOCl_2$ (Sigma–Aldrich), $(NH_4)_2Ce(NO_3)_6$ (Sigma–Aldrich), $(NH_4)_2SO_4$ (Merck), were used for catalyst synthesis as received. Methanol for HPLC was used as reaction medium (J.T. BAKER 99.99%), H_2O_2 30% w/w (Merck) for decomposition tests, while potassium iodide (Sigma–Aldrich), Hydranal-Composite 2 (Fluka), dry methanol for KFT (Fluka), Acetic Acid (Sigma–Aldrich), Sodium Thiosulfate penta-hydrate 99.5% (Sigma–Aldrich), Starch (Sigma–Aldrich), Potassium dichromate (Riedel de Haën) were used for analysis. The catalysts were prepared as already reported [12], and pre-reduced in situ before using. The catalyst powder was compressed to obtain pellets, which were then crushed and sieved to get particles with a diameter ranging between 0.5 and 1 mm; subsequently, 0.16 g of the catalyst particles were mixed with 0.2 g of SiO_2 and used as catalytic bed.

2.2. Reactor set-up for the experiments

A cocurrent, downflow TBR, previously developed and tested [1], was used. Besides the advantages already mentioned, the TBR allows short liquid residence time, if required for improving selectivity. It is a steady-state reactor, so that chemical analysis has no limitation on the sampled quantity and does not affect reactor operation.

The experimental reactor set-up is described in details elsewhere [1]. Briefly, 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_2O_2 decomposition due to accessible Fe^{3+} 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_2, CO_2/H_2 97.5/2.5%, CO_2/H_2 95/5%, and O_2) were fed independently by mass flow controllers (MFC), that were calibrated on actual mass flow; volumetric flow rates reported in the figures were 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 was controlled and regulated with a back pressure controller. A rupture disc was installed for safety reasons. A bypass was used to achieve the desired pressure inside the reactor more rapidly. The liquid phase was fed in through a syringe pump with temperature control, connected to a pressure transducer and computer controlled. Gas and liquids mixed before the reactor. A regulation valve was used to sample the instantaneous liquid phase. The catalyst bed (0.6 cm long) was placed between two quartz wool plugs. Temperature inside the reactor was measured with a K thermocouple before the catalyst bed.

2.3. H_2O_2 experiments and analyses

The experiments of direct synthesis were carried out at 10 bar and $-10\,°C$, in methanol, the liquid flow rates tested were 0.5, 1 and 2 ml/min. Two gas $H_2/O_2/CO_2$ mixtures were used, namely 2/18/80% (denoted 2/18) and 4/16/80% mol (denoted 4/16). The total gas flow rates tested were 1, 2, 2.7, 4, 6, 9 and 12 ml/min. The volumetric total flow rates correspond to specific mass flow

rates ranging between 0.063 and 0.254 kg/m²s for the liquid and between 0.0021 and 0.0433 kg/m²s for the gas. All the experiments were carried out well in the trickling regime, according to typical flow maps [25,26].

We chose to operate the reactor at −10 °C because (1) the decomposition and hydrogenation of H_2O_2 are slower, while synthesis is less affected by temperature (2) solubility of CO_2 in methanol rises, thus increasing hydrogen solubility in the mixture [27] (3) it is a low temperature condition industrially feasible without a significant increase of costs.

Fresh catalyst was introduced in the reactor without pretreatment. In situ reduction with H_2 (20 ml/min) at room T and P for 1 h followed. The reduction state (Pd^0) is expected to remain after the liquid feed is started and pressurization with a mixture CO_2/H_2 (97.5/2.5% mol) achieved. Eventually, O_2 is also fed and the oxidation state becomes less obvious. Although water formation (experimentally measured) is considered an indication of Pd^{2+} oxidation state, in the absence of promoters (e.g., halide ions and acids) [10,13,28–31], their addition causes Pd^{2+} to be active for H_2O_2 production as well [9,10,12,24,32]. The actual oxidation state may vary due to the presence of both O_2 and H_2, whose concentration varies along the bed, because of the reaction and different solubility. The O_2/H_2 ratio increases along the bed, possibly changing the local Pd oxidation state.

During each single test, the liquid phase was sampled at the reactor exit, and water (volumetric Karl Fischer) and H_2O_2 (iodometric titration) concentrations measured. Errors in H_2O_2 measurements were in the interval of ±3% and for the measurements of water content in the range of ±4%. Water content was also measured prior to each experiment, before feeding O_2. Production rate is defined as moles of H_2O_2 produced/min, which is given by the H_2O_2 concentration measured in the liquid sampled (almost pure methanol, after flashing) times the methanol flow rate set on the syringe pump, as representative of the liquid flow rate. Given that all experiments used the same amount of catalyst (0.16 g, with a nominal metal loading of 2.5% and a real Pd loading of 1.22% in the PdAu-ZS catalyst and 1.01% in the PdAu-CeS catalyst), specific production rate in units of mol H_2O_2 g_{Pd}^{-1} h^{-1} can be obtained by multiplying the reported data in µmol H_2O_2/min by 0.0307 for the PdAu-ZS catalyst and 0.037 for the PdAu-CeS catalyst. These values were obtained with the following equation:

$[10^{-6} \times 60/1 \, (min/h)]/[0.16 \, (g) \times Pd \, (\%)]$; where 10^{-6} is the conversion factor from µmole to mole, 60/1 to convert the result in hours, 0.16 are the grams of catalyst used during the experiments and Pd is the percentage of palladium loaded in the catalyst (note that our results are in µmol/min). However, it should be pointed out that catalyst particles prepared from impregnated powders do not take advantage of all the metal, mostly inaccessible in the particle interior, so that the conversion factor overestimates the real palladium availability. Selectivity is defined as $100 \times [H_2O_2]/([H_2O_2] + [H_2O]_{prod})$; it is equal to the moles of H_2O_2 produced, divided by the moles of H_2 consumed.

Hydrogen peroxide at 30% w/w was diluted in methanol to a concentration of 1% w/w of H_2O_2. The stability of the solution at ambient pressure and temperature was tested for 12 h. The concentration remained constant. The solution was than used to test the decomposition of H_2O_2 on the catalyst support and in the reactor. H_2O_2 decomposition tests were carried out on pure and sulfated ceria and zirconia at 20 °C and 1 bar for 5 h. Decomposition in the reactor was tested by filling the TBR with inert silica and the solution of H_2O_2 was then fed into the reactor. The temperature values used for the tests were −10 °C and 20 °C at 10 bar. At the lowest gas and liquid flow rate (largest contact time) the concentration of the solution did not vary by passing through the reactor. The tests were also performed at the end of the experiments of direct synthesis in order to check the stability of the reactor system.
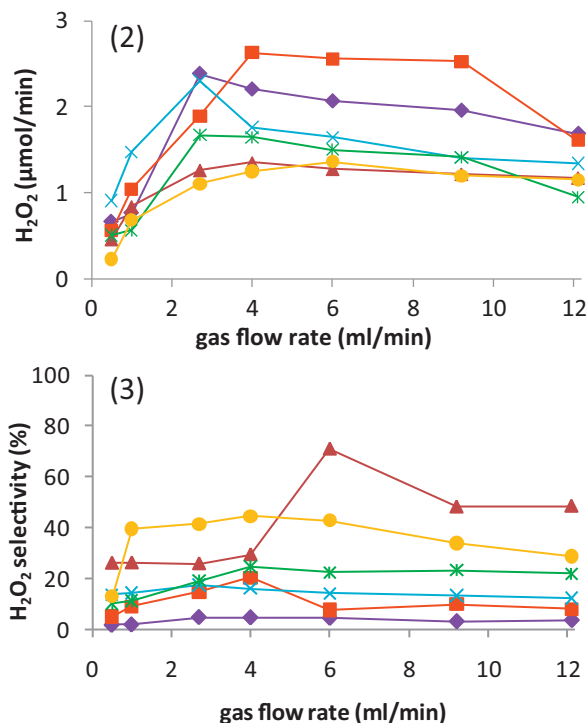

Fig. 2 (above) and Fig. 3 (below). Production rate and selectivity of H_2O_2 over PdAu-CeS catalyst. Combined effect of gas and liquid flow rates at 10 bar and −10 °C. Methanol flow rate: 0.5 ml/min 2/18 (light blue, exes), 1 ml/min, 2/18 (green, stars), 2 ml/min 2/18 (yellow, circles). Methanol flow rate: 0.5 ml/min, 4/16 (purple, diamonds), 1 ml/min 4/16 (red, squares), 2 ml/min, 4/16 (brown, triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.4. Catalyst preparation and properties

The Zirconia (Z) and Ceria (Ce) supports were sulfated by incipient wetness method with $(NH_4)_2SO_4$ to yield an 8 wt% of anion loading. The amount of sulfate was determined by ion chromatography after dissolution of materials and showed a loading of 4.2 wt% in Z and 6.9 wt% in Ce. The metals were then deposited again by incipient wetness with H_2PdCl_4 and $HAuCl_4$ aqueous solutions to give a nominal 2.5 wt% metal loaded catalyst. BET characterization showed a specific surface area (SSA) for the ZS support of 129 m²/g and a SSA for the CeS support of 29 m²/g. The pore diameter and volume for the ZS sample were respectively 11.1 nm and 0.332 cm³/g and for the CeS were 19.5 nm and 0.099 cm³/g. The nominal value of Pd and Au loaded on the ZS and CeS supports were 1.25 wt% for each metal, but atomic absorption spectroscopy (AAS) reported an actual loading of 1.22 wt% for Pd and 0.92 wt% for Au on ZS, and 1.01 wt% of both Pd and Au on CeS. The particle size distribution measured by HRTEM indicated that the average size of the particles observed in the PdAu-ZS catalyst was 4.5 nm and for the PdAu-CeS catalyst was 1.5 nm. A more detailed characterization is reported elsewhere [12].

3. Results and discussion

The results of the experiments to produce H_2O_2 from its elements in a TBR are shown in Figs. 2–5, with both PdAu-CeS (sulfated ceria) and PdAu-ZS (sulfated zirconia) catalysts, reporting either H_2O_2 production rate or selectivity, as previously defined. Different gas and liquid flow rates as well as different H_2/O_2 ratio in the gas phase were investigated.

The two catalysts were already developed and tested in a semi-batch reactor [12], showing a promising activity for H_2O_2 direct
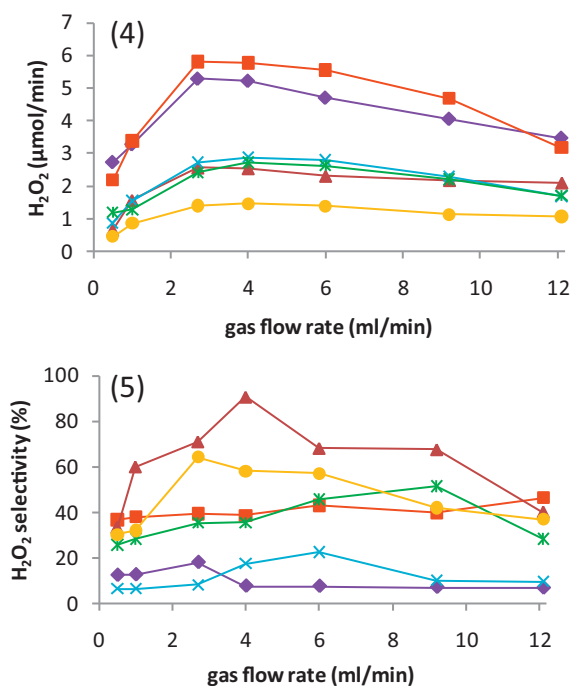
Fig. 4 (above) and Fig. 5 (below). Production rate and selectivity of H_2O_2 over PdAu-ZS catalyst. Same conditions of Figs. 2 and 3.

synthesis. The PdAu-ZS catalyst showed a 60% selectivity and the PdAu-CeS catalyst presented a maximum in selectivity approaching 50%, at ambient temperature and pressure with H_2SO_4 as stabilizer [12]. In this work, the same catalysts were tested in a continuous reactor that allows to manipulate the local reaction environment, possibly leading to a gain in selectivity, as previously shown for a Pd-based catalyst [1]. Here a maximum productivity of 0.18 mol H_2O_2 g_{Pd}^{-1} h^{-1} was measured. The optimum in selectivity and production rate is also heavily affected by the type of catalyst used. Both aspects of catalyst activity and reactor type and operation play an important role to direct the synthesis across the reaction path of Fig. 1 [1,11].

Preliminary tests with a catalyst bed of 10 cm were performed. Mostly water was produced, indicating that stabilizers are required to preserve all the H_2O_2 formed, before hydrogenation and decomposition in a longer catalyst bed take place. For the above reason a much shorter (0.6 cm) catalyst bed was chosen, aiming at capturing the maximum of H_2O_2 production before side reactions consume it, without adding any stabilizer.

3.1. PdAu-CeS catalyst

H_2O_2 production rate and selectivity for the PdAu-CeS catalyst are reported in Figs. 2 and 3 for different gas and liquid flow rates, with two different H_2 and O_2 concentration in the gas feed. Gas composition was 2% (or 4%) of H_2, 18% (or 16%) of O_2 and always 80% of CO_2.

Production rate (Fig. 2) always showed a maximum varying the gas flow rate, more pronounced at the lowest liquid flow rate. Accordingly, an optimum gas flow rate could be identified for every liquid flow rate examined. The maximum value achieved depended both on the liquid flow rate and H_2/O_2 ratio. The Best results were obtained with the smaller liquid flow rate when the H_2/O_2 ratio is lower, and with the intermediate liquid flow rate with higher H_2/O_2 ratio. However, differences were small as well as absolute values. Interestingly, non-linear effect of the liquid flow rate implies that the kinetics grows more than linearly with residence time, recall-

ing that production rate is defined as the product of liquid flow rate times the outlet H_2O_2 concentration and increases with smaller liquid flow rate.

H_2O_2 selectivity was heavily affected by the gas and liquid flow rates, as shown in Fig. 3. While at the lower H_2/O_2 ratio a maximum selectivity of 40% was achieved, comparable with the one measured in the semi-batch reactor [12], increasing the H_2/O_2 ratio allowed a sharp gain, up to 70% selectivity. Interestingly, we achieved a comparable selectivity (approx 70%) with a catalyst based on Pd alone, again on sulfated ceria, with the same operative conditions [1]. Note that Pd-Au catalysts yielded better productivity and selectivity in a semibatch reactor than a Pd based catalyst using the same support [12]. Again, these are evidences of the extreme influence of the operating conditions (i.e. reactor type and operating mode) in addition to the catalyst nature, as already discussed in a previous work [1].

3.2. Effect of H_2 concentration

In Fig. 2 no relevant differences can be noted when H_2 concentration is either 2% or 4% in the total gas flow fed into the reactor, with a liquid flow rate of 0.5 ml/min. We speculate that at longer contact time between liquid and solid phase, hydrogen concentration does not significantly impact on the production rate. However, in relation to selectivity, as shown in Fig. 3, a significant difference between the higher and lower H_2/O_2 ratio exists when operating with the maximum liquid flow rate.

The production rate with PdAu-CeS catalyst was constant, although we expected the reaction rates to be different. When the concentration of H_2 is higher, H_2O_2 direct synthesis reaction rate was expected to be larger. At the same time H_2 concentration also affected the hydrogenation reaction, increasing its rate (thus reducing selectivity) with larger H_2 concentration. As displayed in Fig. 2, H_2O_2 production rate was higher when 4% of hydrogen was used, with a liquid flow rate of 1 ml/min. Thus PdAu-CeS catalyst produced more H_2O_2 when more H_2 was available (with excess O_2); however selectivity is not enhanced by a larger amount of H_2 in the liquid phase, as shown in Fig. 3.

When liquid contact time was too short (i.e. the maximum liquid flow rate used, 2 ml/min) and with low gas flow rates (i.e. gas flow rates lower than 4 ml/min), production rate was approximately halved in comparison to the lower liquid flow rates, as shown in Fig. 2. On the other hand, there was a remarkable increase in selectivity (Fig. 3), which reached 70%, with 4% H_2 in the gas feed.

3.3. PdAu-ZS catalyst

Results for the PdAu-ZS catalyst are presented in Figs. 3 and 4. As previously seen with the PdAu-CeS catalyst, the PdAu-ZS catalyst always showed a maximum in production rate and selectivity with varying gas flow rate. At 0.5 and 1 ml/min liquid flow rates, the highest H_2/O_2 in the gas phase significantly increased the production rate. While keeping the same dependency on the gas flow rate, the production rate of H_2O_2 almost doubled with double H_2 concentration. As expected were the kinetics first order in H_2 and the solubility linear in the gas phase composition. In addition, PdAu-ZS also showed a higher H_2O_2 production rate, approximately doubled, compared to the former PdAu-CeS catalyst. In both these bimetallic catalysts the nominal amount of metal loaded on the support was the same, only the support was different. Results confirmed the crucial role of the support used, as previously investigated [9,12] and of the operative conditions [1].

Larger liquid flow rates (2 ml/min) were not equally productive, and a significant drop in production rate could be observed at any H_2/O_2 ratio, although the beneficial, linear increase with H_2 was still observed.

Selectivity was be quite limited if the contact time between liquid and solid phase was large (0.5 ml/min); again, it increased by lowering the contact time (larger liquid flow rates). The largest liquid flow rate, together with a higher H_2/O_2 ratio yielded an outstanding result for selectivity, close to 90%, approaching the values of commercial anthraquinone process (about 98%).

3.4. Production rate and selectivity optimization

We saw that H_2/O_2 ratio together with flow rates can dramatically affect the catalyst activity and selectivity in a continuous flow reactor. At 1 ml/min and 4% H_2 PdAu-ZS catalyst showed the highest production rate, while at small gas flow rate and with 2% of H_2 in the gas feeding there was no significant variation between the two catalysts in terms of H_2O_2 production rates. Catalysts behavior with different operative conditions did not yield comparable selectivities. We conclude that different operative conditions affect catalyst behavior in 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 H_2O_2 presented in Figs. 2 and 4 show that an optimum between gas and liquid flow rates exsists, to maximize H_2O_2 production [1,14]. When the H_2 concentration in the feed is 2% mol, an optimum in H_2O_2 production rate was achieved with a gas flow rate between 2 and 6 ml/min, at any liquid flow rate. When H_2 was 4% in the feed the optimum was always found between 2.7 and 4 ml/min gas flow rate. Selectivity is defined as H_2O_2 produced with respect to water and H_2O_2 formed and reflects the relevance of unwanted side reactions. To increase selectivity, H_2O_2 production needs to increase, or the rate of water formation to decrease, or both of them together. It is reported [19,20] that stabilizers and small H_2 conversion can increase selectivity up to 100%. In our case reagents conversion was rather low due to the short contact time between the liquid phase and the catalytic bed. Furthermore, without using stabilizers the consecutive reactions reported in Fig. 1 cannot be neglected. Selectivity dropped down when the contact time between liquid and solid phase was larger. Moreover the water production by direct formation was likely due to surface changes in the active metal, as already reported [1]. The selectivity behavior is also to be ascribed to the reactor used. We assume that direct synthesis is active throughout the whole reactor but when the concentration of H_2O_2 increases the reactions of decomposition and hydrogenation become important. Various aspects are emerging as relevant for discussing selectivity results, such as 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 liquid and catalyst is the highest. The H_2O_2 produced has enough time to be hydrogenated or decomposed by the catalyst reducing the selectivity, as reported in Figs. 3–5, below 30% for the PdAu-CeS catalyst and 40% for the PdAu-ZS catalyst. If the gas flow rate is increased, the contact time between liquid and solid decreases. When the gas flow rate is increased up to the maximum value (i.e. 12 ml/min), channeling is likely to occur so that a higher liquid velocity than the nominal one can be reached. In this case the mass transfer rate from the gas to the liquid phase is enhanced and modifications on the catalyst surface happen. Most probably, due to the higher concentration of H_2 in the liquid phase, the reaction of water formation is increased by catalyst surface reduction. In principle, in the case of hydrogen at 2% or 4%, with the lowest and the intermediate liquid flow rates, selectivity does not change sharply with the gas flow rate due to the complex phenomena mentioned above (e.g. change of the catalyst oxidation state, H_2 mass transfer in the liquid phase). With these reaction conditions there is an increase/decrease of water formation during the reaction (hydrogenation, decomposition and direct water formation) that results in a change of H_2O_2 production rate but not in selectivity. When H_2 is 2% or 4% molar in the feed, with the highest liquid flow rate (2 ml/min), selectivity behavior changes compared to the previous conditions. At the lowest gas flow rate, hydrogen has enough time to reduce the Pd oxidation state thanks to the high contact time. The same phenomenon occurs when the gas flow rate is the highest, but this time because hydrogen mass transfer from the gas to the liquid phase is enhanced. The results in selectivity are obviously comparable. On the other hand, selectivity changes sharply with the intermediate gas flow rates and the highest liquid flow rate. The reason of this situation can be ascribed to the mass transfer between gas and liquid: the different velocities of gas and liquid flow rates probably result in different concentrations of H_2 in the liquid phase (the differences in H_2 and O_2 concentrations probably are wider compared to the previous conditions analyzed, due to the highest liquid flow rate used). The amount of H_2 and O_2 dissolved in the liquid phase is higher and all the reactions in Fig. 1, except for decomposition, are expected to accelerate. The modification of the catalyst oxidation state plus to the low contact time between liquid and solid, with the highest gas flow rate used, have a greater impact on selectivity in the reaction of hydrogen peroxide direct synthesis, compared to the other liquid flow rates used. The peak observed in both cases (70% for PdAu-CeS and 90% PdAu-ZS, Figs. 3 and 5) 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 water formation. 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 et al. [12]. When the surface of the catalyst is reduced, unwanted reactions are enhanced [9,12,24,33].

We underline that we did not use any additive or stabilizer in the reaction medium, in order to elucidate how the operative conditions impact on the reaction pathway evolution. Stabilizers are used to suppress series reactions [9,10,12,24,34], but here we aimed first at optimizing the conditions by engineering the reaction, trying to understand how the reaction conditions influence the catalyst performance, in order to enhance H_2O_2 direct synthesis, before further improvements that can be achieved by chemically altering the reaction conditions, i.e. adding stabilizers or other additives.

It is well known that H_2 promotes direct H_2O_2 synthesis but also its hydrogenation when no promoters are added to the reaction medium. In earlier studies [11,35] it was suggested that H_2O_2 production and selectivity are positively improved by H_2 refilling during batch experiments. The mechanism appears to be a refreshing of the catalyst surface by H_2, preventing parallel reactions to grow faster than direct synthesis, when H_2 is lacking. The concept of maintaining a stable quantity of hydrogen in the liquid phase during the reaction can be applied in a continuous reactor by 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 [11,35]. Taking this idea into account, the experiments where 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 (Figs. 4 and 5) show the remarkable gain in both production rate and selectivity.

3.5. Catalyst stability

The catalyst stability was assessed by carrying out daily cycles of 16 h of activity (gas and liquid flow rates of 2.7 ml/min and 1 ml/min, respectively), and 8 h (overnight) decompression and

conditioning with N_2. During operation, liquid samples at time 4, 10, 16 h were collected and production rate and selectivity quantified. As already observed [1] with Pd-CeS, the production of H_2O_2 remained constant within the same day and for several days until a sudden drop after the fifth cycle (day). Afterwards, the catalyst was still active, as indicated by the amount of water formed. Pellets disaggregated, thoroughly broken into a powder, providing a dramatic increase in specific surface that determined a much larger contact time with the same flow rates. Disaggregation was likely caused by the repeated compression–decompression cycles, which stressed the catalyst particle structure leading to collapse. Also liquid expansion by CO_2 might have played a role.

4. Conclusions

A continuous reactor for hydrogen peroxide synthesis is successfully used to enhance catalyst activity. Bimetallic catalysts confirm to be promising for H_2O_2 direct synthesis, best results being obtained with a PdAu-ZS catalyst. The H_2/O_2 ratio in the gas phase has different effects on different catalysts: the catalyst based on PdAu-ZS shows better activity with a 4% H_2 compared to the same experiments carried out with 2% H_2. PdAu-CeS catalyst provides better selectivity with 2% H_2 with a liquid flow rate of 0.5 ml/min than with a liquid flow rate of 1 ml/min, when the selectivity is almost not affected by H_2 concentration, and finally with a liquid flow rate of 2 ml/min, the selectivity is better with 4% H_2. This means that H_2 concentration plays an important role on production rate and selectivity, but in combination with other operative conditions, such as 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 are 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 particles stability under pressure swings, while the original catalyst powder preserves its activity. Pressure cycles however are unlikely to happen in a continuous industrial reactor, making this process and catalysts attractive from an industrial perspective.

Acknowledgments

References

[1] P. Biasi, F. Menegazzo, F. Pinna, K. Eränen, P. Canu, T.O. Salmi, Ind. Eng. Chem. Res. 49 (2010) 10627–10632.
[2] E. Ghedini, F. Menegazzo, M. Signoretto, M. Manzoli, F. Pinna, G. Strukul, J. Catal. 273 (2010) 266–273.
[3] P. Li, C. He, S. Campestrini, B. Corain, W. Yuan, Y.-F. Han, Phys. Chem. Chem. Phys. 12 (2010) 2170–2176.
[4] T. Moreno, J. Garcia-Serna, M.J. Cocero, Green Chem. 12 (2010) 282–289.
[5] J.-L. Dubois. (Arkema France), EP2276695, 2009.
[6] T. Hass, G. Stochniol, J. Rollmann. (Degussa AG), US Patent 6,764,671, 2004.
[7] R. Miglio, G. Paparatto, G. De Alberti. (Polimeri Europa S.p.A.), WO 2005/063620 A3, 2005.
[8] B.E. Solsona Espriu, J.K. Edwards, G.J. Hutchings, A.F. Carley. (University College Cardiff Consultants Limited), WO/2007/007075, 2007.
[9] G. Bernardotto, F. Menegazzo, F. Pinna, M. Signoretto, G. Cruciani, G. Strukul, Appl. Catal., A 358 (2009) 129–135.
[10] R. Burch, P.R. Ellis, Appl. Catal., B 42 (2003) 203–211.
[11] J.K. Edwards, B. Solsona, N.E. Ntainjua, A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Science 323 (2009) 1037– 1041.
[12] F. Menegazzo, P. Burti, M. Signoretto, M. Manzoli, S. Vankova, F. Boccuzzi, F. Pinna, G. Strukul, J. Catal. 257 (2008) 369–381.
[13] C. Samanta, V.R. Choudhary, Catal. Commun. 8 (2006) 73–79.
[14] M. Piccinini, N.E. Ntainjua, J.K. Edwards, A.F. Carley, J.A. Moulijn, G.J. Hutchings, Phys. Chem. Chem. Phys. 12 (2010) 2488–2492.
[15] A. Pashkova, K. Svajda, R. Dittmeyer, Chem. Eng. J. 139 (2008) 165–171.
[16] A. Pashkova, R. Dittmeyer, N. Kaltenborn, H. Richter, Chem. Eng. J. 165 (2010) 924–933.
[17] T. Inoue, Y. Kikutani, S. Hamakawa, K. Mawatari, F. Mizukami, T. Kitamori, Chem. Eng. J. 160 (2010) 909–914.
[18] T. Inoue, M.A. Schmidt, K.F. Jensen, Ind. Eng. Chem. Res. 46 (2007) 1153–1160.
[19] Y. Voloshin, R. Halder, A. Lawal, Catal. Today 125 (2007) 40–47.
[20] Y. Voloshin, A. Lawal, Chem. Eng. Sci. 65 (2009) 1028–1036.
[21] T. Inoue, K. Ohtaki, Y. Kikutani, K. Sato, M. Nishioka, S. Hamakawa, K. Mawatari, F. Mizukami, T. Kitamori, Chem. Lett. 38 (2009) 820–821.
[22] T. Inoue, Y. Tanaka, T.D.A. Pacheco, T.M. Suzuki, K. Sato, M. Nishioka, S. Hamakawa, F. Mizukami, Chem. Eng. Sci. 65 (2009) 436–440.
[23] G. Blanco-Brieva, d.F.E.M. Pilar, J.M. Campos-Martin, J.L.G. Fierro, Green Chem. 12 (2010) 1163–1166.
[24] F. Menegazzo, M. Signoretto, M. Manzoli, F. Boccuzzi, G. Cruciani, F. Pinna, G. Strukul, J. Catal. 268 (2009) 122–130.
[25] G. Mary, J. Chaouki, F. Luck, IJCRE 7 (R2) (2009).
[26] P.A. Ramachandran, R.V. Chaudhari, Three-Phase Catalytic Reactors, Gordon and Breach, New York, 1983.
[27] P.G. Jessop, B. Subramaniam, Chem. Rev. 107 (2007) 2666–2694.
[28] V.R. Choudhary, A.G. Gaikwad, S.D. Sansare, US Patent 6,534,440, (A1), 2003.
[29] V.R. Choudhary, P. Jana, Appl. Catal., A 352 (2009) 35–42.
[30] J.H. Lunsford, J. Catal. 216 (2003) 455–460.
[31] Q. Liu, K.K. Gath, J.C. Bauer, R.E. Schaak, J.H. Lunsford, Catal. Lett. 132 (2009) 342–348.
[32] G. Paparatto, F. Rivetti, P. Andrigo, G. De Alberti, (Eni S.p.A.), US Patent 6,649,140, 2003.
[33] S. Melada, R. Rioda, F. Menegazzo, F. Pinna, G. Strukul, J. Catal. 239 (2006) 422–430.
[34] V.R. Choudhary, P. Jana, Appl. Catal., A 329 (2007) 79–85.
[35] C. Burato, S. Campestrini, Y.-F. Han, P. Canton, P. Centomo, P. Canu, B. Corain, Appl. Catal., A 358 (2009) 224–231.