

Hydrogen Peroxide Direct Synthesis: from Catalyst Preparation to Continuous Reactors

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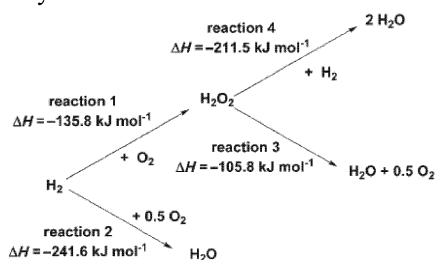
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Bimetallic Pd-Au catalysts supported on sulphated zirconia (ZS) were prepared by different methods and used for hydrogen peroxide direct. The effect of the addition of gold to Pd enhance the selectivity and the yield of H₂O₂. Activity was tested at both atmospheric and high pressure, batch and semi-batch wise. Decomposition, hydrogenation and direct synthesis of H₂O₂ were assessed on the PdAu-ZS catalyst. Catalysts have been tested also in a trickle bed reactor for the continuous direct synthesis. The H₂/Pd mol ratio was investigated to enhance both H₂O₂ concentration and selectivity in batch and TBR. H₂O₂ concentration was successfully compared between batch and TBR. The TBR shows an enhancement in selectivity towards H₂O₂ compared to the batch synthesis. A H₂O₂ selectivity of 90% was achieved with the TBR.

1. Introduction

Hydrogen peroxide (H₂O₂) 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 H₂O₂ 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 H₂O₂ manufacturing process (e.g. AO process). 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. One of the main issues is the catalyst: it promotes both hydrogen peroxide formation and the unwanted side reactions (Scheme 1). Further

to selectivity, safety issues require the identification a suitable reactor and operating policy.



Scheme 1: Reactions involved in the direct synthesis of H_2O_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. H_2O_2 synthesis) and can be integrated to already existent processes.

A promising catalyst based on palladium and gold, supported on sulphated zirconia (ZS) (Menegazzo et al., 2008) was compared in batch and continuous reactors. The effect of H_2/Pd molar ratio is manipulated to affect the conversion and selectivity.

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 H_2PdCl_4 and HAuCl_4 aqueous solutions, followed by calcination at 500°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 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. O_2 and 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 H_2SO_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. An autoclave with an internal volume of 100 ml (Autoclave Engineers), made of Hastelloy C. Stirring was realized with a magnetically coupled electric engine (MagneDrive, Autoclave Engineers) and a radial turbine. Pressure and temperature are continuously monitored

and logged during the experiments. Gases were loaded in the reactor directly from gas cylinders: H₂, O₂, CO₂, and N₂. A high pressure pump was employed to feed the liquid inside the reactor at the beginning of the experiments. The standard operating procedure loaded the gases first (CO₂ and O₂), and then the given amount of liquid solvent (39.5 gr of CH₃OH) with an HPLC pump, H₂ (the limiting reactant) is fed after the vapor liquid equilibrium between CO₂, O₂ and CH₃OH is reached. The reactor operated at 20 bar and -10°C.

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: N₂, CO₂/ H₂ 97.5/2.5% (or 95/5%), and O₂. 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 H₂/O₂/CO₂ 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 H₂O₂ (iodometric titration) concentrations were measured. The water content was also measured prior to each experiment, before feeding H₂ (batch reactor) or O₂ (TBR). H₂O₂ concentration is defined as [(H₂O₂ mg) / (CH₃OH 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 H₂O₂ produced, divided by the moles of H₂ consumed.

3. Results and Discussion

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.

3.1 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 H₂ and O₂ (Fig. 1 a). Hydrogenation of H₂O₂ with the catalyst causes a significant loss of H₂O₂ (Fig. 1 b) in a time frame comparable to the synthesis. The amount of catalyst increases the rate of loss.

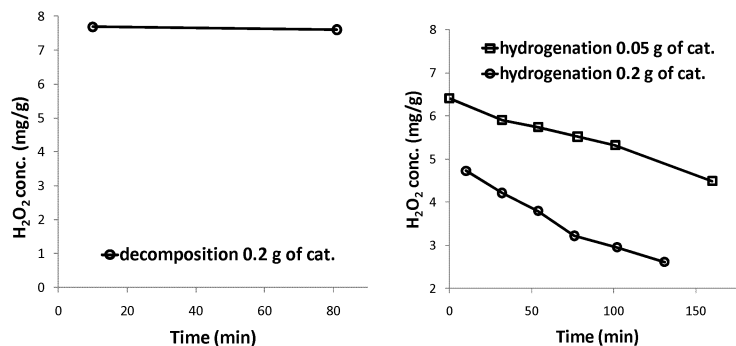


Figure 1 a) decomposition (left) and b) hydrogenation (right) of H₂O₂ on PdAu-ZS catalyst.

In the direct synthesis, H₂O₂ 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) H₂O₂ 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.

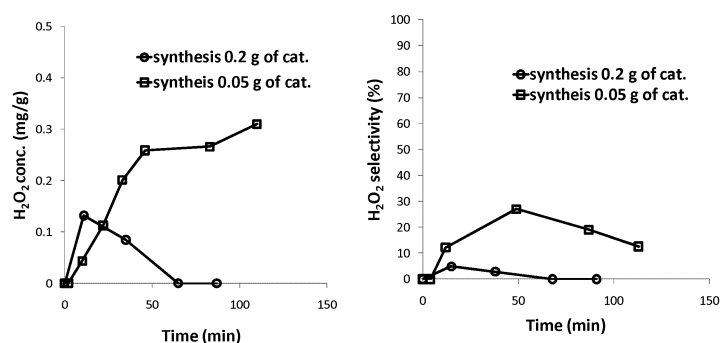


Figure 2 a) concentration (left) and b) selectivity (right) of H₂O₂

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, H₂O₂ is not present anymore in the reaction medium. Clearly, hydrogenation and water formation largely prevailed on the H₂O₂ synthesis. Further, all these reactions competes for the same H₂. Hydrogen peroxide decomposition and hydrogenation further accelerate owing to the increase of the H₂O₂ 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.

3.2 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 3 and 4. At 0.5 ml/min liquid flow rate and 4% H_2 in the inlet, PdAu-ZS catalyst showed the highest production rate, Figure 4a, while at the highest liquid flow rate, there was no significant variation between the experiments with different concentration of H_2 in the feed, in terms of H_2O_2 production rates. 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.

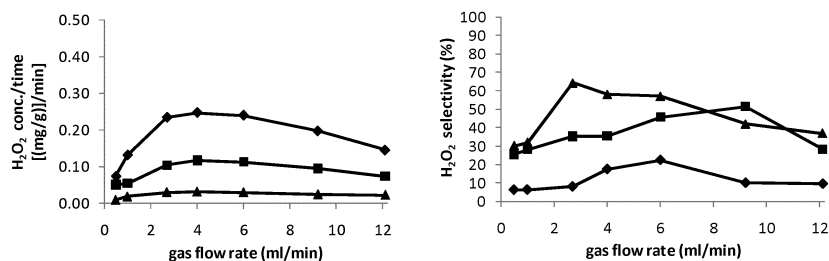


Figure 3a (left) and Figure 3b (right): concentration rate and selectivity of H_2O_2 over PdAu-ZS catalyst. Combined effect of gas and liquid flow rates at 10 bar and $-10^\circ C$. Gas composition H_2 (2%), O_2 (18%) and CO_2 (80%) Methanol flow rate: 0.5 ml/min (diamonds), 1 ml/min (squares), 2 ml/min (triangles).

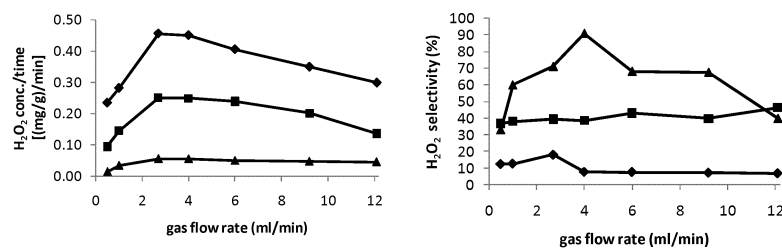


Figure 4a (left) and Figure 4b (right): concentration rate and selectivity of H₂O₂ over PdAu-ZS catalyst. Same conditions and symbols as in Figure 3, except for gas composition: H₂ (4%), O₂ (16%) and CO₂ (80%).

4. Conclusions

Bimetallic catalysts confirmed to be promising for the H₂O₂ 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 H₂/Pd mol ratio there is an enhancement of both H₂O₂ maximum concentration achievable and selectivity. The H₂O₂ 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.

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