Direct flow synthesis of $\text{H}_2\text{O}_2$ catalysed by palladium supported on sulfonated polystyrene resins

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1. Background and objectives
Hydrogen peroxide is a versatile and ‘green’ oxidising agent (the only by-product is water) widely used as a bleaching agent in the paper and textile industries. It also finds many applications in the chemical industry, water treatment, semiconductor wafer cleaning and low-cost fuel cell technology. However, it is routinely produced on a large scale by the environmentally unfriendly anthraquinone process. Therefore, direct $\text{H}_2\text{O}_2$ synthesis (from gaseous $\text{H}_2$ and $\text{O}_2$) has emerged as a desirable alternative. Flow chemistry and the microreactor technology have been successfully used for this process by several groups. Our interest lies in developing an integrated microfluidic process for $\text{H}_2\text{O}_2$ direct synthesis, possessing a minimalized ecological footprint while improving the results described in the literature.

2. The catalysts
Catalytic systems based on palladium supported on strongly acidic macrorietical polystyrene resins have been described by several authors. We first used commercial Amberlyst-15 and loaded it with $\text{Pd}^2+$ following the method described by Blanco-Brieva et al. The experimental set-up is shown in case 3 and the results are presented in case 4.

As particle size of Amberlyst-15 is not convenient for microfluidic applications, we decided to prepare our own catalysts which possess a more narrow particle size distribution (40 - 80 µm).

3. Experimental set up

The variation of the amount of palladium on catalysts was next studied. In terms of production, catalysts with 1 % of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results. We obtained similar selectivities using the catalysts with 1% wt of immobilised $\text{Pd}$ led to the best results.

4. Results with Amberlyst-15°

The selectivity $S$ was defined as follows, owing to the existence of side reactions which led to the formation of water:

$$S = \frac{[\text{H}_2\text{O}_2]}{([\text{H}_2\text{O}_2]+[\text{H}_2])}$$

These results revealed the importance of the solvent choice for impregnation. The differences are due to the catalytic species involved in the mechanism of the reaction, and more particularly to the oxidation state of palladium. Indeed, in the presence of methanol, $\text{Pd}^{2+}$ is reduced into $\text{Pd}^0$. We decided to only use acetone for the immobilisation.

5. Influence of impregnation solvent

Increasing the total liquid flow rate (with a total gas flow of 1.25 mL.min$^{-1}$) enabled us to reach a selectivity of 60%, but $\text{H}_2\text{O}_2$ production remained low in these conditions. The efficiency factor $c$ suggests that we should work with higher liquid flow rate to obtain high selectivity. However to reach a satisfactory concentration (2% wt $\text{H}_2\text{O}_2$), we plan to work with moderate liquid flows.

6. Influence of palladium percentage

The improvement of selectivity (at 1.25 scm gas flow and 2*20 µL.min$^{-1}$ liquid flow) could be reached by studying the influence of a gradient of catalyst in the bed, by varying bromide concentration, and phosphoric acid. Further study of the composition of the surface of catalysts should allow us to identify the catalytically relevant species. Finally, optimizing the design of microreactors will be achieved through a kinetic study. Furthermore, we have learned to better master the reaction conditions, rendering the results more reproducible and easier to interpret.

9. Conclusion

We have been able to prepare resin-supported Pd catalysts on beads with small diameters and a narrow particle size distribution which are especially appropriate for microfluidic applications. The assays of direct $\text{H}_2\text{O}_2$ synthesis in flow gave promising results, in many cases superior than those described for similar systems in the literature.

References and Acknowledgments

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