

## Direct synthesis of H<sub>2</sub>O<sub>2</sub> on palladium-based membranes. Results from a EU founded project.

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Developing a new economic process to synthesize H<sub>2</sub>O<sub>2</sub> (alternative to the commercial anthraquinone process) is a key objective for developing clean selective oxidation processes. In fact, both for large petrochemical productions such as propylene oxide and caprolactame, and for smaller scale production processes of interest for fine and specialty chemicals (by epoxidation and hydroxylation) the cost of H<sub>2</sub>O<sub>2</sub> is often the limiting factor. These new processes are all characterized by a significant reduction of the environmental impact.

The direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> may potentially half the cost of hydrogen peroxide with respect to the commercial anthraquinone process which is largely conditioned also by the monopoly character of the market related to the necessity of large scale plants. Direct synthesis of H<sub>2</sub>O<sub>2</sub> offers the additional advantage of being less sensitive to scale-up factor, and to allow in principle the use in small scale plants. Moreover H<sub>2</sub>O<sub>2</sub> could be produced "in situ" and immediately used for the desired oxidation reaction, avoiding the production, storage and transportation costs.

The direct synthesis from H<sub>2</sub> and O<sub>2</sub> was originally developed by Dupont using Pd-based supported catalysts, but has some drawbacks related to (i) safety aspects (mixtures of H<sub>2</sub> and O<sub>2</sub> are explosive over a wide range of composition), (ii) productivity (rate of reaction and concentration of H<sub>2</sub>O<sub>2</sub> that can be achieved) and (iii) selectivity (competition with the direct combination of H<sub>2</sub> and O<sub>2</sub> to form water).

The safety aspects could be significantly reduced to a level compatible with practical applications (especially on a medium-low scale) by carrying out the reaction in a catalytic membrane reactor where H<sub>2</sub> is fed through one side of the membrane, the other one being in contact with a solution saturated with oxygen<sup>1</sup>. In addition, the process could be scalable and applicable also to small productions. This was the objective of the EU project NEOPS (Contract No: G5RD-CT2002-00678). Selectivity of H<sub>2</sub> towards H<sub>2</sub>O<sub>2</sub> formation is a main issue which should be solved for the application. This requires a better knowledge of the reaction network and mechanism, and the identification of the role and nature of active sites in the different reactions. The relationships among preparation method, nature of the active components, and catalytic reactivity should also be better identified.

In the literature, the information on these aspects in relation to powder-type catalysts is scarce, while nearly negligible regarding catalytic membranes<sup>2</sup>. The aim of this contribution is to discuss the reaction network and mechanism in the synthesis of H<sub>2</sub>O<sub>2</sub> on catalytic membranes based on thin Pd or Pd/C catalytic films on ceramic tubular membranes. The specific aspects that will be analyzed concern: (i) the role of the oxidation state of palladium and the presence of a second metal in determining the rate of synthesis and decomposition of H<sub>2</sub>O<sub>2</sub>, and (ii) the role of the preparation method of these catalytic membranes and the relationship with the performances in the synthesis or decomposition of H<sub>2</sub>O<sub>2</sub>.

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### References

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