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Preparation, performances and reaction mechanism for the synthesis of H₂O₂ from H₂ and O₂ based on palladium membranes

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Abstract

A series of new tubular catalytic membranes (TCM's) have been prepared and tested in the direct synthesis of H₂O₂. Such TCM's are asymmetric α -alumina mesoporous membranes supported on macroporous α -alumina, either with a subsequent carbon coating (CAM) or without (AAM). Pd was introduced by two different impregnation techniques. Deposition–precipitation (DP) was applied to CAM's to obtain an even Pd particles distribution inside the membrane pore network, whereas electroless plating deposition (EPD) was successfully applied to AAM's to give a 1–10 μ m thick nearly-dense Pd layer. Both type of membranes were active in the direct synthesis of H₂O₂. Catalytic tests were carried out in a semi-batch re-circulating reactor under very mild conditions. Concentrations as high as 250–300 ppm H₂O₂ were commonly achieved with both CAM's and AAM's after 6–7 h time on stream, whereas the decomposition rate was particularly high in the presence of H₂. Important features are the temperature control and pre-activation. In order to slow down the decomposition and favor the synthesis of H₂O₂ a smooth metal surface is needed.

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1. Introduction

Hydrogen peroxide is a commodity which, today, is almost exclusively produced by the anthraquinone process [1]. This process is economically feasible only on large-scale plants. Additionally, the final price of H₂O₂ produced is deeply influenced by the complexity of the process and by the costly separation and concentration steps needed. Direct synthesis, which could be a more economic and “green” alternative, has been known since the beginning of the XXth century [2] and many patents have been filed even during the last 30 years [3–11], however only a few scientific papers have been published in the open literature [12].

To date, no industrial application has ever been accomplished, even if some successful attempts have been

realized at DuPont during 1980's [3]. This is because two severe drawbacks have to be overcome: (i) the formation of explosive H₂/O₂ mixtures that should be avoided and (ii) the selectivity of the reaction (whose main product is water) that should be improved. Recently, the use of especially designed catalytic membranes could have been suggested to overcome both problems [10–12].

2. Experimental

Two types of tubular membranes have been prepared, loaded with Pd and tested in the direct synthesis of H₂O₂.

2.1. α -Alumina asymmetric membranes (AAM)

These were supplied by Hermsdörfer Institut für Technische Keramik (HITK, Hermsdorf, Germany) and

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consist of an α -alumina macroporous support (3 μm pore size) with a α -alumina external mesoporous layer (pore size 50–100 nm). Pd was deposited on these membranes as a thin layer (1–10 μm thick) by electroless plating deposition. This technique consists in subsequent steps of Sn^{2+} sensitizing and Pd^{2+} activations in order to form on the $\alpha\text{-Al}_2\text{O}_3$ membrane surface Pd seeds active in the surface formation of $\text{Pd}(\text{NH}_3)_4^{2+}$ complexes, which could be subsequently decomposed by chemical reduction in order to form on the membrane a homogeneous Pd film. After that, a thermal treatment at 500 or 800 $^\circ\text{C}$ in inert atmosphere gave the final membrane.

2.2. Carbon coated alumina membranes (CAM)

The second type of membrane was a carbon coated α -alumina membrane (CAM) which was impregnated by a deposition–precipitation method (a classical method to obtain egg-shell type catalysts) [13–15]. Carbon coating was accomplished by MAST Carbon Ltd. (Guildford, UK) on the same asymmetric $\alpha\text{-Al}_2\text{O}_3$ membrane used for AAM's preparation. This technique consisted in making the membrane surface alkaline with a NaOH solution (0.1 M) prior to putting in contact with an acidic PdCl_4^{2-} solution (40 ppm Pd^{II} , pH 0.7). During impregnation $\text{Pd}(\text{OH})_2$ deposited into the pore network of the carbon layer. After Pd deposition, membranes were dried at room temperature, reduced in H_2 flow and washed with distilled water to remove the chloride ions. Pd loading was between 1 and 2 wt.% with respect to the total carbon amount.

2.3. Characterization

Both types of membranes were characterized by electron microscopy, physisorption and chemisorption methods either after reduction or subsequent H_2O_2 oxidation treatment. Carbon coated membranes have been broken into small pieces (5–10 mm) before N_2 physisorption. Pre-

treatment was carried out in rotative pump vacuum level by heating at 150 $^\circ\text{C}$ for 2 h.

2.4. Catalytic tests

These were carried out in a semi-batch recirculation reactor (Fig. 1), where the membrane was sealed in a tubular holder. From the inner side H_2 was fed at constant pressure (2–3 bar) whereas an oxygen-saturated acidic solution continuously circulated (25 ml/min, 1 bar) on the outer side of the membrane (where Pd was deposited). The circulating solution was 100 ml of 0.03 M H_2SO_4 containing 6 ppm NaBr as a promoter. H_2O_2 concentration was determined by permanganometric titration.

3. Results and discussion

3.1. α -Alumina asymmetric membranes (AAM)

A dense Pd film was deposited on such supports by EPD, as stated in the Section 2.

After thermal treatment in inert atmosphere at different temperatures, two kind of surfaces could be obtained: (i) a rough and disordered surface after a thermal treatment in inert gas at 800 $^\circ\text{C}$, as shown in Fig. 2(a) and (ii) a surface formed of well developed crystallites after a thermal treatment at 500 $^\circ\text{C}$ (Fig. 2(b)). A notable difference in reactivity was observed for these two different surfaces (Fig. 3): large, ordered crystallites on the surface showed a very high ability to produce H_2O_2 compared to the disordered, microcrystalline surface. The presence of regular metal surfaces seems therefore to be mandatory to obtain a high rate of reaction in H_2O_2 synthesis and a low decomposition rate.

3.2. Carbon coated alumina membranes (CAM)

The carbon layer of these membranes possesses a high surface area as shown by N_2 physisorption measurements, summarized in Table 1, and are micro- to meso-porous. HRTEM analysis shows that the Pd particles deposited are evenly distributed and the dimensions range is between 5 and 10 nm (Fig. 4) for almost all the membranes prepared. Most of them possess 7–8 nm-sized Pd particles. Correlation between catalytic activity and average particle diameter determined by CO chemisorption shows that 8 nm-sized particles are more active than smaller ones. These membranes were highly reproducible and fairly active.

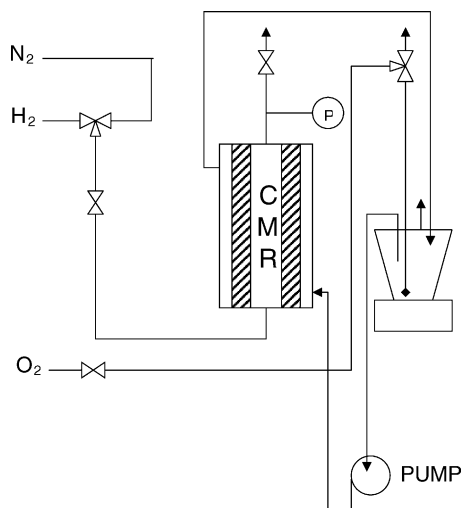


Fig. 1. Scheme of the experimental apparatus used for the catalytic tests.

Table 1
Surface characterization data on support, CAM and AAM

Membrane	Specific surface area (m^2/g)	Pore size range
Bare α -alumina support	<1	3 μm
AAM's	<1	50–100 nm
CAM's	700–800	1–3 nm

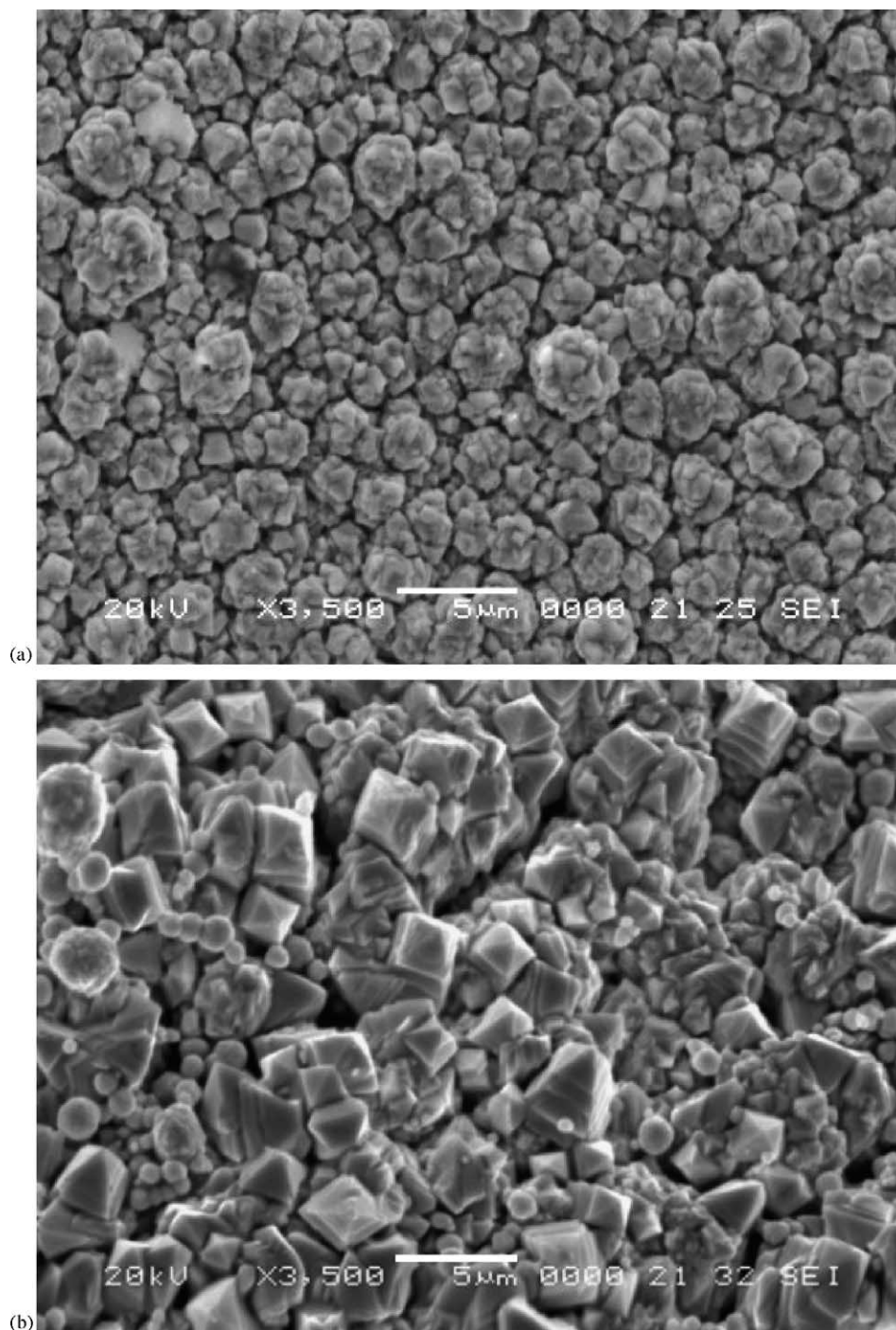


Fig. 2. (a and b) SEM cross-section and surface images of the nearly-dense Pd film on an AAM.

3.3. Catalytic activity

The following features are described for CAM's, but similar results were obtained also for AAM's.

An important observation was that a preliminary oxidation treatment is mandatory for the membrane to be catalytically efficient. Non-oxidized membranes show lower catalytic activity than oxidized ones (Fig. 5). Oxidation pre-

treatment was carried out either by soaking the membrane in a concentrated H_2O_2 solution (AAM's), or by circulating an oxygen-saturated solution on the membrane (CAM's) which is mounted in the CMR holder and pressurized with N_2 from the inner side (Fig. 1). Similar results were obtained with both activations.

H_2O_2 decomposition tests were carried out by circulating a solution containing 2000 ppm H_2O_2 . Either pure H_2 or

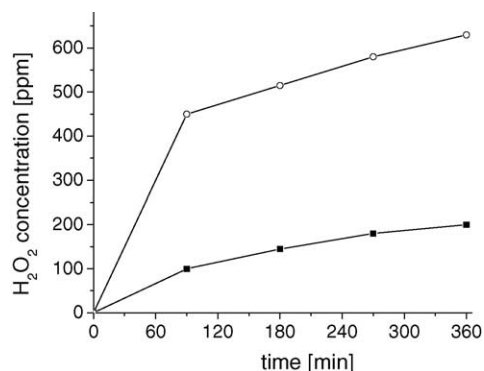


Fig. 3. Comparison between catalytic activity of commonly encountered disordered Pd film (black squares) surface and well-developed Pd crystallites (hollow circles).

pure N₂ were fed inside the membrane at constant pressure in order to evaluate the effect on the decomposition rate. The presence of H₂ improves the ability of the membrane to decompose H₂O₂ as evidenced in Fig. 6, whereas in the absence of H₂ only a small amount of H₂O₂ was decomposed. This seems to indicate that the preferential

decomposition pathway was the reduction of H₂O₂ by H₂ and that an oxygen-saturated acidic solution (from H₂SO₄) prevents spontaneous H₂O₂ disproportionation. Therefore the presence of surface oxygen on Pd seems to be necessary to promote the synthesis of H₂O₂ and minimize its decomposition.

The catalytic activity of the membranes depends on the reaction temperature, due to the different solubilities of the reactant gases (bottom of Fig. 7): lower temperatures tests (5 °C) showed a higher H₂O₂ overall production rate with respect to those performed at room temperature (25 °C). In fact, with reference to Fig. 7, it is clear that at 25 °C the decomposition rate is higher than the synthesis rate. On the contrary, if the temperature is reduced to 5 °C, all the kinetics are slowed down, but to a larger extent that of H₂O₂ decomposition. The final effect is an increase in the overall selectivity towards H₂O₂.

On the basis of the results observed with both types of catalytic membranes, we suggest the following possible reaction pathway (see Scheme 1) for the formation of hydrogen peroxide: O₂ chemisorbs on large, non defective (and hence less energetic) Pd particles without dissociation,

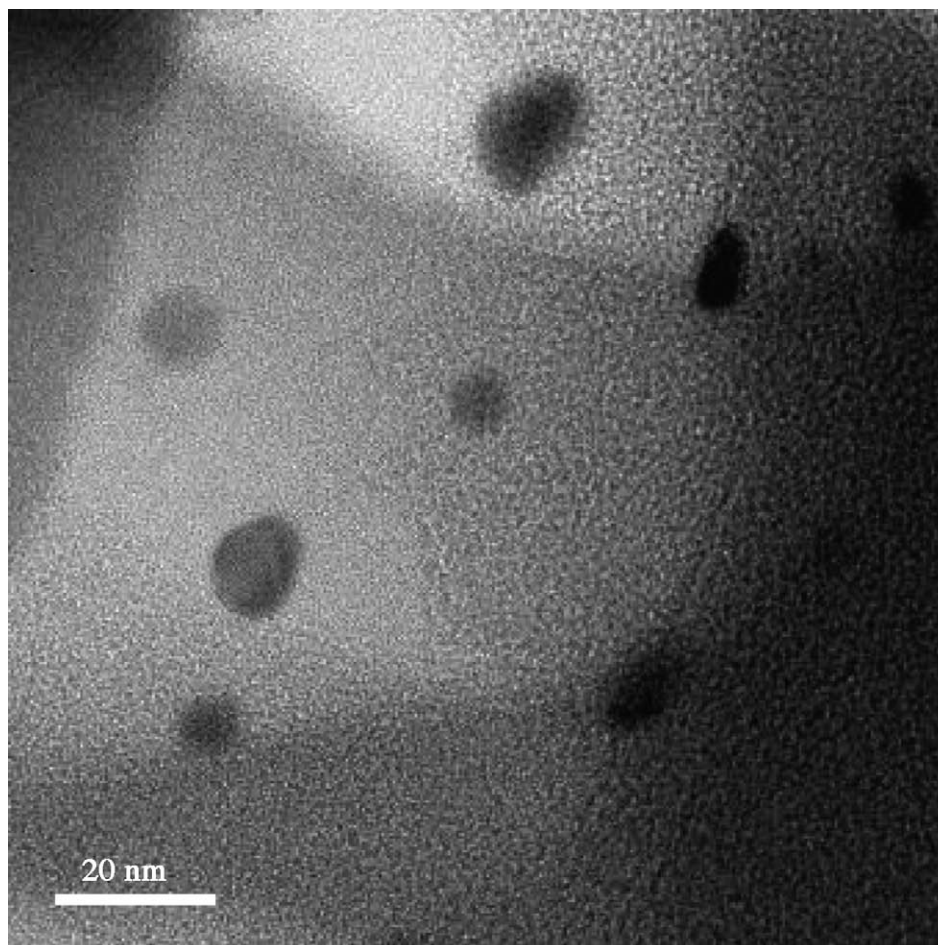


Fig. 4. HRTEM images of Pd particles on a CAM.

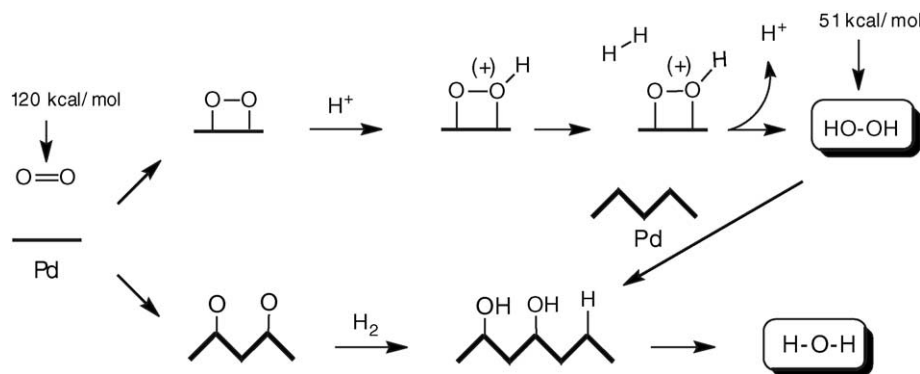
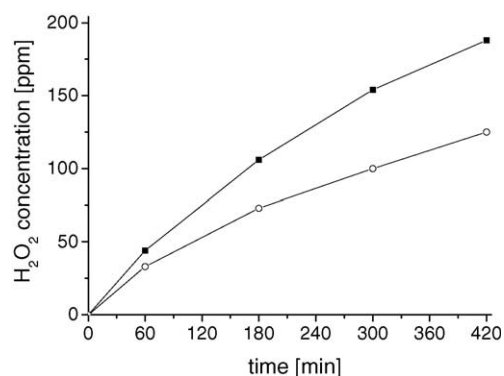
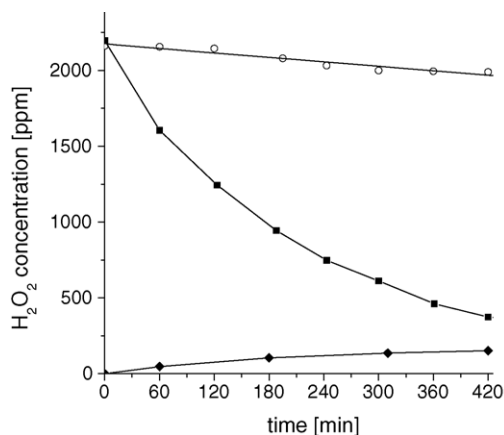
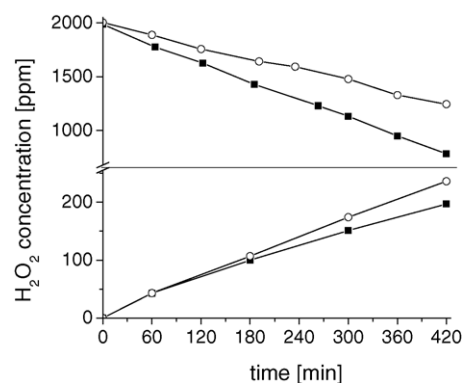
Scheme 1. Probable pathway for the synthesis of H_2O_2 on Pd catalysts.

Fig. 5. Effect of the oxidation treatment on catalytic activity for CAM's. Legend – black square: pre-oxidized sample, hollow circle: non-oxidized sample.

a necessary condition to give the desired H_2O_2 product. Then, protonation from external H^+ takes place, followed by reaction with non-chemisorbed H_2 which leads to the formation of H_2O_2 and restores H^+ . This is in agreement with the observation that a fully oxidized surface maximizes H_2O_2 formation. At the same time, more energetic sites

Fig. 6. Decomposition of H_2O_2 in presence and in absence of H_2 . Legend – black square: decomposition test in the presence of H_2 , hollow circle: decomposition test in the absence of H_2 , diamond: synthesis test at 25°C .Fig. 7. Catalytic tests at different temperatures (5 and 25°C) for CAM's. Legend – black square: test at 25°C , hollow circle: test at 5°C .

(defects, edges, corners, etc.) will dissociatively chemisorb O_2 (or readsorb H_2O_2). The presence of chemisorbed hydrogen will lead to the formation of water either directly by reaction with oxygen atoms or by reaction with OH fragments coming from H_2O_2 . The need for promoters like Br^- , which can act as electron scavenger, will inhibit radical-type decomposition pathways.

4. Conclusions

Tubular catalytic membranes are able to catalyze H_2O_2 synthesis under mild conditions ($2\text{--}3$ bar H_2 , $5\text{--}25^\circ\text{C}$) with a fair productivity (~ 2 mmol H_2O_2 $\text{g}_{\text{Pd}}^{-1}$ min^{-1}). Regardless of the type of membrane, catalytic activity depends on: (i) the oxidation state of surface Pd atoms (a pre-oxidation step is needed); (ii) the temperature (temperatures as low as $2\text{--}5^\circ\text{C}$ favor H_2O_2 synthesis over decomposition). In addition, the decomposition of H_2O_2 on tested catalysts mainly proceeds via its reduction by H_2 .

Specific features were observed for the two different types of membrane:

CAM's catalytic activity depended strongly on the Pd particle size, whereas well developed crystallites was necessary to improve catalytic activity of AAM's. These

features seem to indicate that a smooth metallic surface was necessary to improve catalytic activity.

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