

Direct synthesis of H₂O₂ on monometallic and bimetallic catalytic membranes using methanol as reaction medium

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Abstract

Tubular catalytic membranes (TMCs) active in the direct synthesis of hydrogen peroxide were prepared, characterized, and tested using methanol as the reaction medium. Low hydrogen peroxide selectivity was found when only palladium was used as a catalyst, whereas palladium/platinum bimetallic samples gave higher productivity and selectivity, with an optimum molar ratio of 18. The H₂O₂ decomposition rate is influenced by the feed gases. O₂ improves H₂O₂ stability, whereas H₂ causes hydrogen peroxide to decompose at a higher rate. The most likely decomposition pathway should be the reduction of H₂O₂ to water by H₂. Bromide ion was used as a promoter and when used in excess (60 ppm) causes a decrease in overall catalytic activity.

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1. Introduction

The direct synthesis of hydrogen peroxide from hydrogen and oxygen has been known since the beginning of the 20th century [1] and is in principle a more economic and environmentally acceptable alternative to the classic antraquinone route. However, to date it has found no industrial applications, despite a large number of patents filed over the past 30 years [2–15]. This is due to two main reasons: (i) the need to avoid formation of explosive H₂/O₂ mixtures and (ii) the still unacceptably low selectivity of the reaction (whose main product is water). Nonetheless, the interest in the direct synthesis remains very high, as witnessed by Degussa's recent announcement of the constitution of a joint venture with a nanocatalysis firm to develop and commercialize a direct synthesis process [16].

Scientific works in the open literature began appearing only recently [17–23], although Pospelova was a pioneer in the field

during the 1960s [24–26]. Recently, the use of specially designed membranes [27,28] has attracted considerable interest because it provides a promising approach to overcoming, at least in principle, the problems of safety and selectivity [10, 11,27].

Recently [28–30] we reported the use of carbon-coated ceramic membranes containing palladium, which allow the direct synthesis of hydrogen peroxide. These membranes were designed to feed hydrogen from inside the membrane toward the external part, where an oxygen-saturated aqueous solution comes in contact with the Pd active phase. This concept addresses the safety issue, while maintaining interesting productivity, especially if the reaction is carried out under pressure. However, an evaluation of the selectivity of this catalyst design remains crucial. In this paper we address this point and report the use of these catalytic membranes in methanol. This allows reliable measurement of H₂O₂ selectivity with the additional advantage of obtaining H₂O₂ solutions in an organic solvent. In principle, this could lead to an easier concentration step (MeOH instead of H₂O), a factor that can strongly affect the price of hydrogen peroxide given the current production technology.

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2. Experimental

The membranes were 10-cm-long asymmetric α -Al₂O₃ tubular supports externally coated with a synthetic carbon layer. The carbon loading was in the range of 70–80 mg for each tube. The coating was performed by MAST Carbon Ltd., Guildford, UK, and the alumina support was supplied by Hermsdörfer Institut für Technische Keramik-HITK, Hermsdorf, Germany.

2.1. Sample preparation

The metal deposition procedure was as described previously [29]. Carbon-coated membranes (CAMs) were activated in CO₂ at 850 °C and then impregnated by a deposition–precipitation method (a classical method for obtaining eggshell-type catalysts) [31–33]. This technique consists of two steps: (i) basification of the membrane surface by soaking in a NaOH solution (0.1 M) and (ii) deposition of Pd(OH)₂ by precipitation from an acidic PdCl₄²⁻ solution (40 ppm Pd). The pH of the starting Pd(II) solution was 0.7. Bimetallic samples were prepared similarly. In this case the metal salt solution was a PdCl₄²⁻ + PtCl₆²⁻ solution with the appropriate Pd/Pt molar ratio.

During impregnation, Pd(OH)₂ (with or without Pt(OH)₄) was deposited into the pore network of the external membrane layer. After metal(s) deposition, membranes were dried, reduced at room temperature in H₂ flow, and eventually washed with distilled water to remove chloride ions. Pd loading was around 2.5 wt% with respect to carbon loading. The Pd/Pt ratio was either 10 or 18. Hereafter, the different samples are denoted as tubular membrane catalysts (TCMs).

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained with a Jeol JSM 5600 LV (low-vacuum) microscope. The membrane was gently broken into several chips (10–20 mm) that were subsequently attached on a support with conductive glue and put in the microscope chamber.

Transmission electron microscopy (TEM) images were obtained with a Jeol 3010, operating at 300 kV, equipped with a Gatan slow-scan CCD camera (model 794) and an Oxford Instrument EDS microanalysis detector (model 6636). Each membrane surface was scratched, and the resulting powder was dispersed in isopropyl alcohol, ultrasonicated for 5–10 min so that particles would not settle down, and then deposited onto a holey carbon film.

CO chemisorption measurements were carried out at 25 °C with a pulse technique on a homemade apparatus equipped with a thermostatted reactor and a ESS Genesys quadrupole mass spectrometer interfaced to a computer for data collection and analysis. CO⁺ fragment ($m/z = 28$) was used for quantitative measurements. A 2/1 chemisorption stoichiometry was assumed for both CO/Pd [34] and CO/Pt [35].

Calibrations were carried out after each measurement by injecting a known amount of CO from a calibrated loop. A specially shaped sample holder was used to analyze the TCM as a

whole. Because CO is strongly chemisorbed on Pd and Pt, all samples were characterized after the catalytic tests. Before each measurement, samples were reduced in situ by passing a 5% H₂/He mixture at 25 °C, and then thoroughly evacuated with He.

Metal loading was determined by atomic absorption spectroscopy from the solutions used for metal deposition on the membranes. Differences between metal concentration before and after impregnation gave the amount of loaded metal. The efficiency of this method has been proven previously [30].

2.3. Catalytic tests

Tests were carried out in a semibatch recirculation reactor as described previously [29], in which the membrane was sealed in a tubular holder. From the inner side, H₂ was fed at constant pressure (3 bar) while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane (on which Pd was deposited) by a peristaltic pump (25 ml/min) equipped with special Tygon[®] MH tubing. The circulating solution was 100 ml of anhydrous methanol containing 6 ppm Br⁻ and 2.8 g/l H₂SO₄. Before the catalytic experiments were begun, the catalyst surface was activated by circulating an oxygen-saturated solution on the membrane already placed in the reactor and pressurized with N₂ from the inner side. Hydrogen peroxide concentration was determined by iodometric titration, whereas water content was determined by the Karl Fischer volumetric method. All kinetic runs were carried out at room temperature.

Selectivity toward H₂O₂ at any time was calculated as follows:

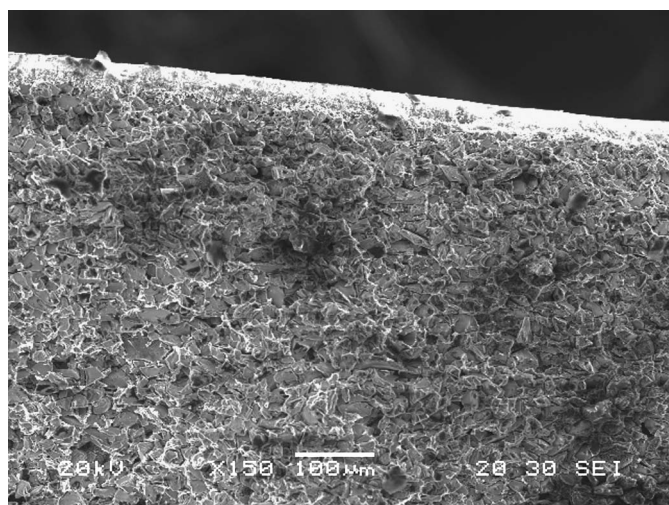
$$S_{\text{H}_2\text{O}_2} = \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2] + [\text{H}_2\text{O}]}$$

3. Results and discussion

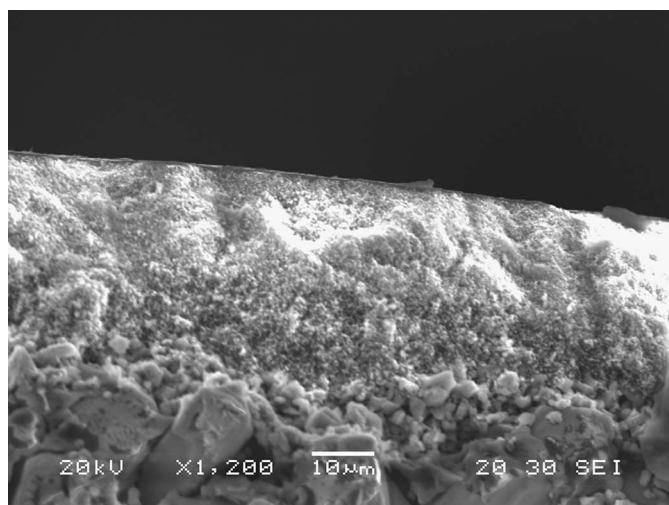
3.1. Catalyst characterization

SEM images given in Fig. 1 show the asymmetric structure of the α -Al₂O₃ support. The inside macroporous structure has mean pore size of 3 μm , whereas the external thin layer mean pore size is around 100 nm. Carbon coating is hardly visible in Fig. 1, because carbon did not form an external thick layer, but rather penetrated into the pore structure of the alumina support. Carbon is spread all over the TCM, but mostly deposited in the 100-nm α -Al₂O₃ external layer, where it generates a microporous fine structure. During impregnation and catalytic tests, this microporous structure was filled by capillarity with the solvent.

TEM images of the different samples are shown in Figs. 2a–f. TCM1, containing only Pd, is shown in Figs. 2a and b. In this sample the metal particles are roundish and evenly spread on the amorphous carbon layer. In presence of Pt (TCM3 and TCM4), particles are smaller, irregularly shaped, and grouped in clusters. TCM4 (Figs. 2c, d) shows small particles on carbon and bigger ones near the alumina crystallites. EDS analysis confirmed the presence of both Pd and Pt on



(a)



(b)

Fig. 1. SEM images of TCM's: (a) section at low magnification (TCM2), (b) external asymmetric carbon coated layer at high magnification (TCM2).

Table 1
CO chemisorption and particle size data

Sample label	Pd/Pt molar ratio	CO adsorption [mmol _{CO} /g _{metal}]	Metal particle size (nm)
TCM1		0.51	8.2
TCM2		0.52	8.3
TCM3	10	0.59	8.0
TCM4	18	0.81	6.4

the analyzed samples. Moreover, alumina crystallites were also identified as the regularly shaped darker regions appearing in the micrographs. TCM3, which has the highest amount of Pt, shows two types of particles: (i) clusters of 8- to 10-nm particles and (ii) very small and evenly spread particles (Figs. 2e, f).

CO chemisorption data are collected in Table 1. These data indicate improved chemisorption for the most active sample (TCM4). This is in agreement with TEM observations showing smaller particles for this sample with respect to those samples containing Pd only (TCM1 and TCM2). TCM3 shows slightly improved chemisorption, which gives rise to a smaller mean

particle diameter, whereas TEM observation shows two types of particles, as stated earlier. The mean diameter calculated by chemisorption is clearly an average.

3.2. Catalytic activity in methanol

The catalytic activity of TCMs is to a large extent influenced by the gas concentration in solution. Solvents capable of dissolving H₂ and O₂ in amounts higher than water could help improve TCM performance. This is clearly shown by the different reactivities resulting from replacing water with methanol (Fig. 3). The higher H₂ and O₂ solubilities [36] gave a higher H₂O₂ productivity in methanol with respect to that found in water. As can be seen from Fig. 3, using a 1:1 water/methanol mixture did not improve catalytic activity. The effect of improved gas solubility was probably not the only factor to be considered in this case.

Using a solvent other than water is also mandatory for determining H₂O₂ selectivity. In fact, measurement of the consumed H₂ is not reliable with our reactor design; the analysis of water by titration and calculation of the selectivity based on the amount of H₂O₂ and H₂O formed are much easier tasks that yield reliable data. Fig. 4 shows the concentration profiles for H₂O₂ and H₂O during a kinetic run. As can be seen, water forms at a much higher rate because its overall formation is a combination of direct synthesis (reaction b in Scheme 1) and H₂O₂ decomposition (reactions c and d). The observed selectivity ranges from 2.5 to 3.0% throughout the experiment.

3.3. H₂O₂ decomposition

Independent tests for H₂O₂ decomposition were carried out by placing the catalytic membrane in contact with a slightly concentrated H₂O₂ solution (about 0.2%) in the same reactor used for synthesis (Fig. 5). In this case a decrease in the concentration of H₂O₂ with time was recorded. The kinetic data can be fit by a simple first-order decomposition rate equation, and the value obtained for the kinetic constant (Table 2) can be used as an indication of the catalyst's ability to favor H₂O₂ decomposition.

These tests were carried out as follows. Either H₂ or O₂ was replaced by N₂, as appropriate. The upper curve of Fig. 5 reports the results in the absence of H₂ and clearly indicates that H₂O₂ is rather stable in contact with the catalyst in the presence of O₂. This gives an indication of the intrinsic properties of the catalyst to decompose H₂O₂ by dismutation, which are almost negligible. In contrast, the lower curve represents the results in absence of O₂. In this case there is a clear indication that H₂O₂ is poorly stable in the presence of H₂ only. In the case of an aqueous solution, the decomposition rate in the presence of H₂ is even higher (Table 2). Finally, when both H₂ and O₂ were fed, there was a sort of intermediate situation. This demonstrates that the presence of H₂ in the gas feed, although necessary for H₂O₂ synthesis, also improves the undesired H₂O₂ decomposition.

On the basis of the *k* values reported in Table 2, it appears that H₂O₂ reduction (reaction c) is about one order of magni-

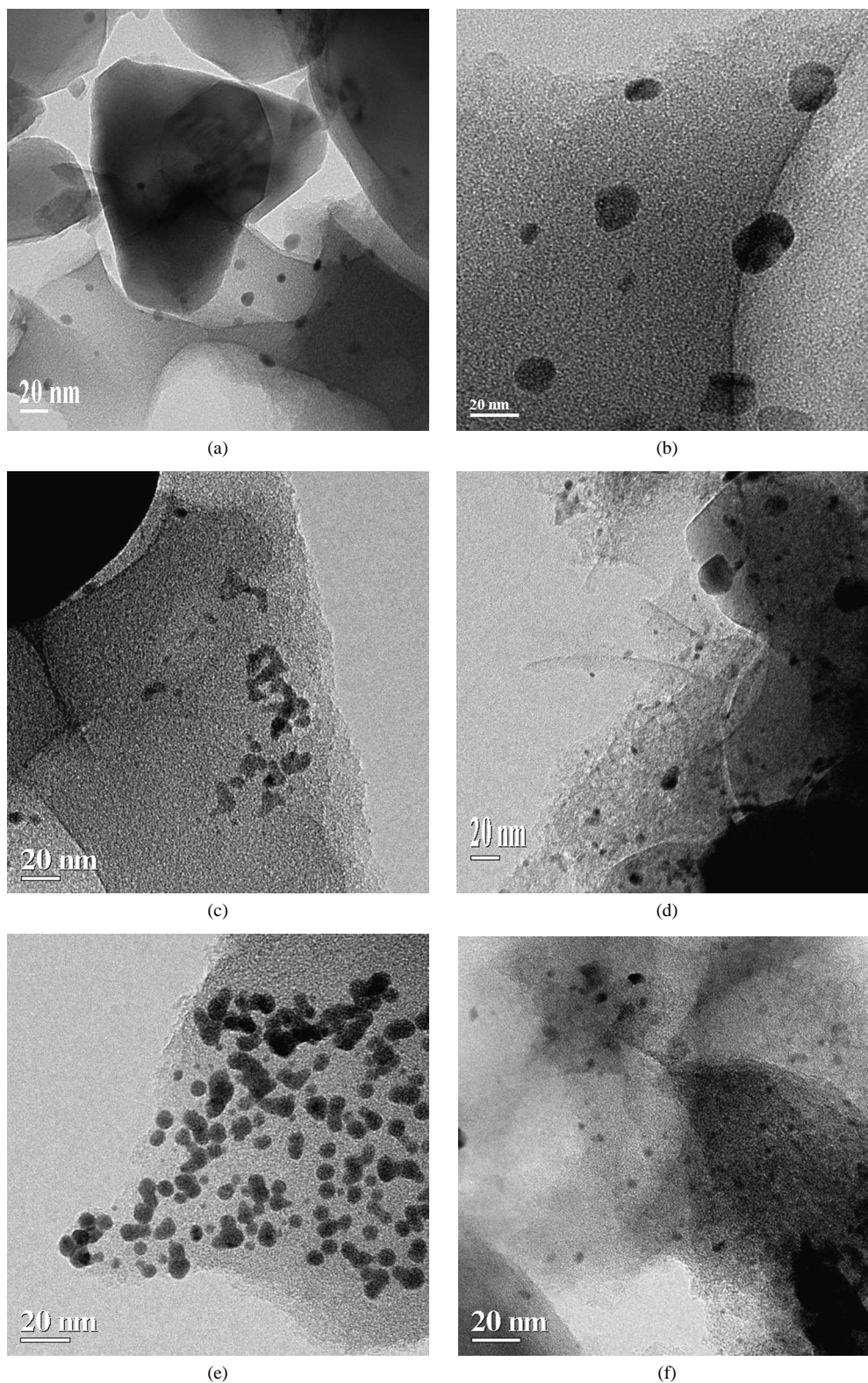


Fig. 2. (a and b) TEM pictures of TCM1, (c and d) TEM pictures of TCM4 (Pd:Pt = 18:1), (e and f) TEM pictures of TCM3 (Pd:Pt = 10:1).

tude higher than H_2O_2 dismutation (reaction d). Hence it can be concluded that the former, caused by H_2 , is the most likely decomposition mechanism. Other authors have reached the same conclusions working with powder catalysts [19,37].

The k values reported in Table 2 merit some further comment to justify why hydrogen peroxide decomposition under H_2 is faster in water than in methanol, despite the higher solubility of hydrogen in methanol. Keep in mind that the Pd surface is

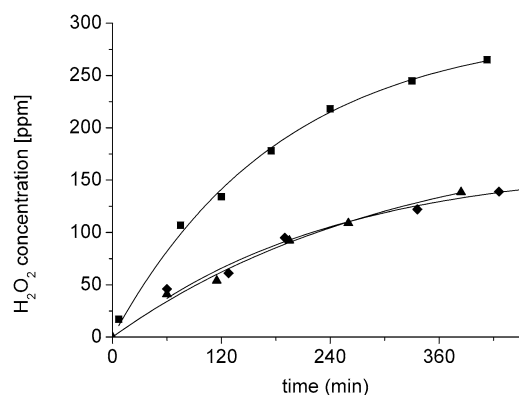


Fig. 3. H_2O_2 concentration profiles in different reaction media for TCM1. ■, 100% methanol; ◆, 100% water; ▲, 50% water and 50% methanol.

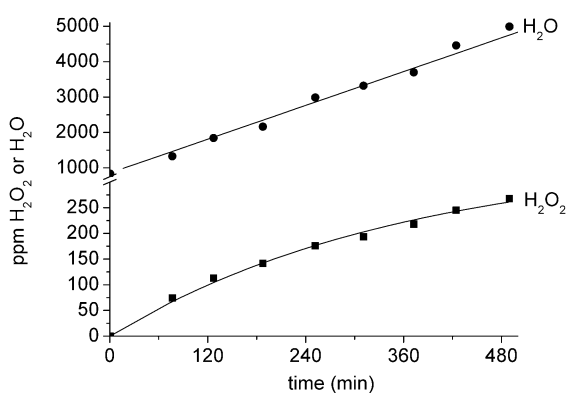


Fig. 4. H_2O_2 (■) and H_2O (●) concentration profiles for a kinetic run on TCM2.



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

preoxidized before each catalytic experiment, because this pretreatment improves the catalytic performance [29]. With MeOH as the solvent, this may lead to the formation of surface formate species, blocking the most reactive Pd sites responsible for HO–OH bond breaking, similar to what was observed by Han and Lunsford [38] in ethanol as the solvent.

3.4. Effect of the Br^- ions on H_2O_2 productivity

It is well known that productivity and selectivity toward H_2O_2 are improved by promoters, such as acids and bromide ion [15]. In the absence of H^+ , little H_2O_2 was produced. Moreover, the addition of small amount of Br^- reportedly improved selectivity toward H_2O_2 [4,20]. Bromide ion is a known poison for Pd, blocking the active sites on the catalyst particle surface. Under these circumstances, the improved catalyst performance observed in the presence of bromide ions could well be due to

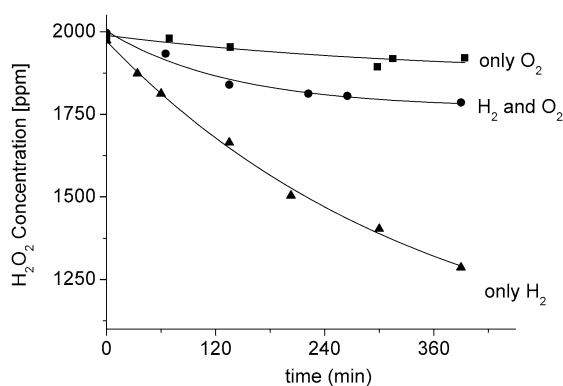


Fig. 5. Influence of different feeds on H_2O_2 decomposition rate for TCM1.

Table 2

Apparent first order rate decomposition constants and H_2O_2 (mol%) decomposed after 7 h for the sample showed in Fig. 5 (TCM1)

Fed gases	k_{dec} (min^{-1})	H_2O_2 decomposed after 7 h (%)
Only H_2	0.00112	34.8
H_2 and O_2	0.00032	11.6
Only O_2	0.00011	3.0
Only H_2 , in water	0.00428	83.0

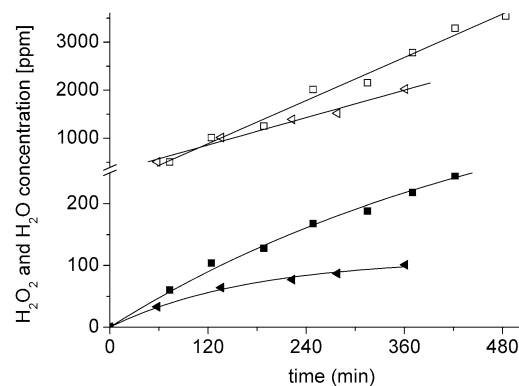


Fig. 6. Effect of the Br^- concentration on the catalytic activity of TCM2. Squares, 6 ppm Br^- ; triangles, 60 ppm Br^- (filled symbols, H_2O_2 concentration; open symbols, H_2O concentration).

a selective poisoning of certain sites. A test was carried out increasing the Br^- concentration from 6 to 60 ppm, values within the optimum range in aqueous medium, as indicated in the cited literature. As can be seen from Fig. 6, an increase of Br^- concentration in MeOH from 6 to 60 ppm was detrimental to overall catalytic activity. In fact, the overall formation rates for both H_2O_2 and H_2O were smaller for the higher Br^- concentration (although, in relative terms, H_2O_2 decreased much more than H_2O). Thus, because Br^- acts as a poison for catalytic sites, the proper concentration could be associated with selective blocking of the sites responsible for H_2O_2 decomposition. An increase above this critical value causes an indiscriminate poisoning of the catalytic sites, including those active for the synthesis of H_2O_2 . As suggested in previous work [29], H_2O_2 formation likely requires a smooth metal surface. Highly energetic sites are able to break both the O_2 and the H_2O_2 molecules

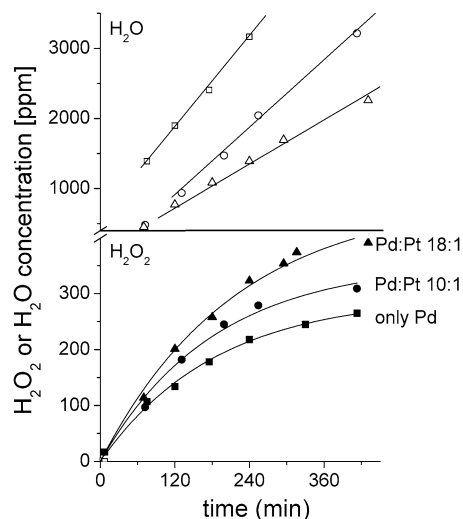


Fig. 7. Catalytic performance of bimetallic samples (TCM3 and TCM4) compared to a monometallic sample (TCM1). Filled symbols, H_2O_2 concentration; open symbols, H_2O concentration.

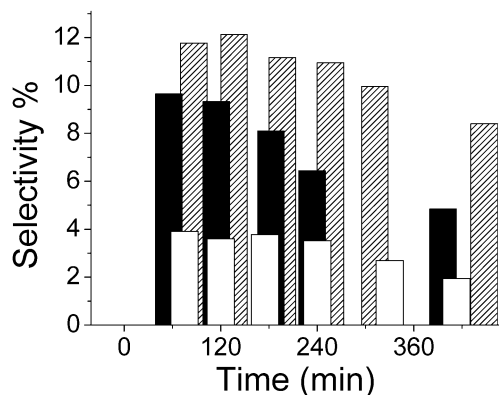


Fig. 8. Selectivity comparison for bimetallic and monometallic samples. White, Pd only (TCM1); black, Pd/Pt = 10 (TCM3); dashed, Pd/Pt = 18 (TCM4).

to give adsorbed hydroxyl species that eventually give water. The results reported herein seem to support this view and indicate that the presence of Br^- ions, which bind first to the more energetic sites, could be necessary to expose a smooth Pd particle surface. As these sites become occupied, excess Br^- also adsorbs on the other sites, inhibiting overall catalytic activity.

3.5. Bimetallic catalysts: effect of the addition of Pt

The addition of a second metal to Pd has been claimed in several patents [4,5,7,39] and in the open literature [19,40,41] to improve catalyst selectivity in the direct synthesis of H_2O_2 . Platinum was chosen, because it was used successfully in patent examples. For our purposes, Pd/Pt molar ratios of 10 and 18 were selected.

Fig. 7 and Table 3 shows the effect of the presence of the second metal on the catalytic activity. The best results were obtained with the highest Pd/Pt ratio (lowest Pt amount). As can be seen, both productivity and selectivity increased (Fig. 8). As a general trend, Fig. 8 shows that selectivity decreased with time as a consequence of increased H_2O_2 reduction as H_2O_2

Table 3

Metal loading and catalytic performance of mono- and bimetallic samples. TOF is expressed as mol H_2O_2 formed per mol Pd loaded per hour

Sample label	Pd loading (wt%)	Pd/Pt molar ratio	Final H_2O_2 conc. after 7 h (ppm)	TOF after 7 h (h^{-1})
TCM1	2.4		265	6.4
TCM2	2.4		245	5.5
TCM3	2.5	10	309	7.6
TCM4	2.4	18	395	10.5

itself builds up in the system. Pd-only TCMs showed a very low selectivity (4% maximum). The bimetallic samples were generally better, particularly TCM4 (Pd/Pt 18), which had 3 times the selectivity (12% maximum) with respect to TCM1 (Pd only).

Bimetallic Pd/Pt catalysts were successfully used in several epoxidation reactions, mainly propene epoxidation, with in situ-generated H_2O_2 from H_2 and O_2 [42–46]. Both metals were needed to ensure proper epoxide productivity. The Pd/Pt ratio was found to affect both Pd oxidation state and particle features. Hölderich et al. [43,44] found that adding Pt to Pd/TS-1 catalysts stabilized a surface Pd^{2+} oxidation state and, over certain compositions and under specific reduction conditions, influenced the metal particle shape. The optimum level of Pt was found to be a balance between the desirable increase of Pd^{2+} concentration and the undesirable changes in the surface morphology of the Pd aggregates, from needle-shaped to spherical [43,45]. This is in agreement with our TEM observations reported above. Pd-only samples had well-developed spherical particles, whereas bimetallic samples had irregularly shaped particles. Moreover, the most active sample (TCM4) showed the smallest particles and a spread in the size distribution (see Figs. 2c, d).

In our case the effect of Pt addition should not be limited to the evident Pd particle morphology change (Fig. 2), but also should also play a role in the overall catalytic cycle. On the basis of the observations reported by Meiers et al. [43] we believe that Pt would mainly stabilize an oxidized Pd surface, a condition known to favor the formation of hydrogen peroxide, and reduce the formation of HO-chemisorbed species favored on Pd^0 highly energetic sites. In this way there should be a synergistic effect between the presence of both the second metal and the anion in the proper proportion, which could explain the improved catalytic performance.

4. Conclusions

In this work, tubular catalytic membranes that are active and fairly selective for the direct synthesis of hydrogen peroxide under very mild and safe conditions have been prepared and suitably characterized. Their use in methanol as solvent allows accurate determination of their selectivity in the formation of hydrogen peroxide, a factor that is of foremost importance in the evaluation of their overall catalytic performance.

A careful analysis of the H_2O_2 decomposition reaction indicates that the preferred decomposition pathway is H_2O_2 reduction caused by H_2 . H_2O_2 is stable in contact with the catalyst

in the presence of only O₂. The presence of promoters like Br⁻ is necessary, because these promoters adsorb on sites that are able to decompose H₂O₂ or dissociatively chemisorb O₂. An analysis of their concentration effect indicates that an optimum value is needed to achieve this goal and supports the idea that a smooth metal surface is needed to improve productivity and selectivity. An excess of Br⁻ leads to indiscriminate poisoning of the surface and is detrimental to overall catalytic activity.

The use of Pd/Pt bimetallic catalysts in the direct synthesis of hydrogen peroxide was shown to yield higher activity and selectivity, with 3 times the selectivity than that of monometallic Pd catalysts when a Pd/Pt ratio of 18 was used.

The selectivities obtained so far by bimetallic catalysts are well below those of industrial interest (selectivity > 60%), but it must be emphasized that our tests have been carried out at 1 bar pressure. Higher pressure generally improves H₂O₂ selectivity and productivity to a large extent, because H₂O₂ synthesis (reaction a in Scheme 1) is favored over H₂O synthesis (reaction b). In fact, tests carried out at ≥65 bar gave very good productivity and selectivity results. These data are preliminary [47] and will be published elsewhere.

Acknowledgments

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