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Performances of Pd-Me (Me = Ag, Pt) catalysts in the direct synthesis of H_2O_2 on catalytic membranes

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Abstract

The performances in the direct synthesis of hydrogen peroxide (H_2O_2) with Pd-Me (Me = Ag, Pt) catalysts prepared by depositing the noble metals by electroless plating deposition (EPD) or deposition–precipitation (DP) methods on α-Al_2O_3 asymmetric ceramic membrane with or without a further surface coating by a carbon thin layer are reported. The effect of the second metal with respect to Pd-only catalysts considerably depends on the presence of the carbon layer on the membrane support. On ceramic membranes the use of Pd-Ag bimetallic catalysts avoids the formation of β-PdH and improves the catalytic performances, while in the case of Pd-Pt bimetallic catalysts small defective nanoparticles are formed which catalyze the unselective formation of water. Conversely, on carbon-coated membranes the latter effect is not present and good H_2O_2 productivities and selectivities are shown for the Pd-Pt bimetallic systems, in particular those synthesized with the EPD method, although for both types of preparations the Pd-Pt bimetallic catalyst show improved behavior with respect to Pd-only systems.

Keywords: Hydrogen peroxide; H_2; Catalytic membrane; Bimetallic catalysts; Pd-Pt

1. Introduction

Hydrogen peroxide (H_2O_2) is a clean and excellent oxidizing reagent to accomplish processes of sustainable chemistry for fine and large scale (propene oxide, caprolactam, for example) chemicals [1] and also finds application in the area of environmental cleanup technologies (water treatment) and ''green'' technologies (paper and pulp bleaching, for example). The main current limits to its wider application rely on its production and transport costs [2] deriving from the fact that only very large plants are profitable using the current commercial methyl-antraquinone route. The direct synthesis of H_2O_2 from H_2 and O_2 is in principle more economic and eco-friendly, and allows on-site production eliminating problems of H_2O_2 transport. However, till date it has found no industrial application, despite several patents filed during the past 30 years. This is due essentially to two main reasons: (i) safety aspects related to the formation of explosive H_2/O_2 mixtures and (ii) the selectivity of the reaction.

The first issue can be solved using a new technology based on the use of catalytic membranes [3–5] instead of powder-type catalysts as those used in most of the patents and publications. Not only a physically separated contact between O_2 and H_2 with the solution can be realized, but also the formation of fine catalyst particles in the reactor can be avoided. These fine particles, deriving from attrition in the slurry-type of reactor used (larger pellets cannot be used due to severe diffusion limitations), are very difficult to remove from H_2O_2 solution, but can be extremely dangerous in the downstream process of H_2O_2 solution concentration, catalyzing fast decomposition and explosion.

Therefore, the use of catalytic membranes allows intrinsically safe operations, but opens new questions related to the preparation of these catalytic membranes and to the different effect of the reaction conditions. In general, the selectivity in H_2O_2 depends considerably on the reaction conditions: pressure, concentration of O_2 and H_2 in solution at the interface with Pd particles (Pd is the most widely used catalyst in H_2O_2 synthesis, even if some interesting results have been

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also obtained with Au [6,7]), solvent and use of additives [3,8–11]. With respect to powder-type catalysts, where the O_2 and H_2 concentration at the catalyst surface is determined essentially by the O_2/H_2 ratio in the feed and the mass transport of these reactants in solution (which in turn depends on the solvent and pressure), the catalytic membrane offers in addition the opportunity to have separate control the O_2 and H_2 gradients in the catalytic zone of the membrane.

The selectivity in the synthesis of H_2O_2 is determined not only from the conditions of reaction, but also from the nature of the catalyst. It has been shown clearly that the reduction of Pd leads to a decrease of the selectivity in H_2O_2 formation [4,10]. On the other hand, Lunsford and co-workers [8,9,12,13] indicated metallic Pd particles (in the form of a colloidal solution) as the active species, although passivated by chemisorption of compounds such as acetate, Br^- ions, etc. It should be noted, however, that these studies have been made in the presence of a very large excess of oxygen, i.e. under conditions favorable for the selectivity, but hardly applicable in practice being inside the explosivity region. Therefore, it is interesting to investigate the performances of Pd-based catalysts in oxygen deficient conditions, which could also reveal how the selectivity depends on the catalyst microstructure itself. This is possible in catalytic membranes in which H_2 is flowing through the membrane and the solution is saturated with O_2. In fact, the rate of H_2O_2 decomposition, which in turn affects the selectivity, depends on the microcrystalline structure of the Pd particles [3].

In patent literature, it has been often claimed that the doping of Pd with Pt significantly improves the selectivity [14,15], although no justification is given for this effect. The aim of the present work is therefore to investigate the effect of the modification of Pd-based catalytic membranes with Pt and for comparison with Ag, in order to analyze further the possible relationship between Pd particles microstructure, presence of defects and selectivity in the synthesis of H_2O_2. As pointed out before, the investigation has been made in conditions of low O_2 concentration at the Pd catalyst particles, in order to better evidence the intrinsic effect of the catalyst microstructure and separate this effect from that of the oxygen surface coverage.

Two type of catalytic membranes have been investigated: those prepared by electroless plating deposition (EPD) on α-Al_2O_3 ceramic membrane (indicated hereinafter as AAM) and catalysts prepared by deposition–precipitation (DP) on the same type of ceramic membrane, but covered with a surface thin carbon layer (indicated hereinafter as CAM). The latter preparation method allows obtaining smaller Pd particles and a better dispersion of Pd, but can be applied only for CAM and with a limited noble metal loading.

2. Experimental

2.1. Sample preparation

Membranes in a tubular form were prepared using an asymmetric ceramic support supplied from HITK (Hermsdörfer Institut für Technische Keramik, Germany) on which Pd or Pd-Me (Me = Ag, Pt) thin films (1–10 μm thickness) were deposited by EPD. In this technique, palladium metallic particles are produced by reduction from the plating bath consisting of amine-complexes of the noble metals in the presence of a reducing agent. Metallic particles grow on palladium nuclei which have been pre-seeded on the substrate surface through a successive activation and sensitisation procedure and which also act as a catalyst for the reduction of the noble metal-complexes. The plating procedure may be repeated several times to increase the metallic film thickness. The α-alumina asymmetric membrane consists of an α-alumina macroporous support (3 μm pore size) with an α-alumina external mesoporous layer (pore size 50–100 nm). Further details on the preparation were given elsewhere [3,16,17]. We will define these membranes here as Pd(x)/AMM, when Pd is only present with x indicating the number of plating and Pd-Me(x,y)/AAM, where Me is the second noble metal (Pt, Ag), x indicates the number of plating procedures and y the Pd\Me ratio, and AAM indicates the asymmetric α-Al_2O_3 tubular ceramic membrane support.

The second class of catalytic membranes investigated the use of same AAM support, but covered with a final carbon layer (the final carbon layer was added by MAST Carbon Ltd., Guildford, UK). The thickness of this carbon film is few microns and was activated in CO_2 at 850 °C before depositing the noble metal. The Pd or Pd-Pt is then deposited by DP method. On the carbon layer a base was first deposited by soaking in a NaOH solution (0.1 M), and then the membrane was immersed in an acidic $PdCl_4^{2-}$ or $PdCl_4^{2-} + PtCl_6^{2-}$ solution (40 ppm Pd, Pd/Pt ratio either 10 or 18). The corresponding hydroxides of the noble metals immediately deposit on the carbon layer. After washing and drying, they are reduced at r.t. in H_2 flow. Pd loading was around 1–2 mg. Further details were reported elsewhere [3,16,17]. These membranes are defined here as Pd-Pt(y)-DP/CAM, where y indicates the Pd/Pt molar ratio, DP the preparation by deposition–precipitation and CAM indicates the carbon-coated AAM membrane support.

After testing in H_2O_2 synthesis, some of these membranes were further processed by adding a Pd-Pt thin film by the EPD method described above. These membrane are indicated as Pd-Pt(x,y)-EPD/Pd-DP/CAM, where x indicates the number of plating procedures and y the Pd/Me ratio, Pd-DP indicates that the starting membrane was one in which Pd (about 1 mg) was already deposited with the DP method, and CAM indicates the carbon-coated AAM membrane support. For comparison, Pd-Pt was deposited by EPD method also directly on the CAM membrane. These samples are indicated here as Pd-Pt(x,y)-EPD/CAM.

Before the catalytic tests, each membrane was checked to determine that the bubbling point, e.g. the pressure at which start the detection of bubbles of H_2 in anhydrous methanol, was higher than 5 bar, e.g. at least 3 bar higher than the pressure used during the catalytic tests. This allows indicating the absence of leak of H_2 through crack or hole of the Pd-Me membrane.

2.2. Characterization and catalytic tests

Catalytic tests were carried out at r.t. and ambient pressure in a semi-batch recirculation reactor already described [3], where the membrane was sealed in a tubular holder. The geometrical surface area of the Pd-M membrane was 8 cm^2, while the total surface area of the Pd, estimated by CO chemisorption, was typically in the 0.05–0.1 m^2 range. From the inner side H_2 was fed at constant pressure (2 bar), while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane (where Pd was deposited) by means of 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 H_2SO_4. H_2O_2 concentration was determined by iodometric titration, whereas water content was determined by an automatic titrimetric apparatus based on the Karl Fischer method. The experimental values of the amount of H_2O formed were corrected for water which may be adsorbed from external or associated to traces of humidity in the flow of H_2 and O_2 by making blank tests in the absence of the Pd coating on the membrane. All tests were carried out at room temperature. Selectivity towards H_2O_2 was calculated based on H_2O_2 and H_2O formation.

Transmission electron microscopy (TEM) images were taken 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 should not be settled down and then deposited on a holey carbon film.

EDX-SEM characterization studies of the membranes were made with a scanning electron microscope Jeol 5600 LV. Elemental analysis was carried out via energy dispersion analysis using an X-ray analytical system EDX OXFORD, coupled to the scanning electron microscope. The tubular membrane was cut for this characterization.

Temperature programmed reduction (TPR) tests were measured using a Micromeritics Autochem II apparatus after r.t. helium pre-treatment. The rate of temperature increase was 10 °C/min in a flow of 5% H_2/Ar. A cryostat was used to reach temperatures below r.t.

3. Results and discussion

3.1. Pd-Me supported on ceramic membrane (AAM)

Fig. 1a reports the comparison of the catalytic performances in H_2O_2 formation and selectivity between a Pd supported on ceramic membrane (AAM) sample and of bimetallic systems having Pd/Me molar ratio of 10, close to that indicated as optimal in several patents on H_2O_2 direct synthesis. These three samples were prepared with the same procedure (EPD) using three plating steps. The amount of noble metals is similar (around 5–6 mg) in the three samples.

Operating in a semi-continuous reactor, where H_2 is continuously feed through the membrane and the circulating solution (anhydrous methanol) is continuously saturated with O_2, the amount of H_2O_2 formed should linearly increases with time, if there is no change in catalyst reactivity. Therefore, the clear deviation from linearity in Pd(3)/AAM and even more evident in Pd-Pt(3,10)/AAM indicates a catalyst modification during the direct synthesis of H_2O_2. This modification is instead less significant in the sample modified with Ag [Pd-Ag(3,10)/AAM]. Temperature programmed reduction data (see Fig. 2) show that the presence of Ag reduces or inhibits the formation of β-PdH during the catalytic reaction, pointing out that the decrease of catalyst reactivity is probably associated to an easier reduction of Pd with formation of β-PdH phase. In fact, after the main reduction peak near 70 °C

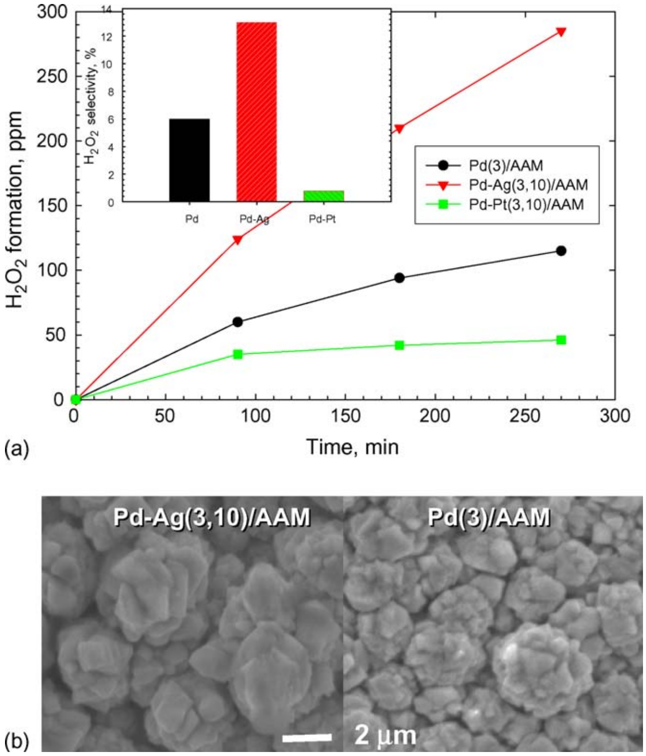

Fig. 1. (a) Formation of H_2O_2 and selectivity to H_2O_2 (in the inset) of three catalysts on α-Al_2O_3 ceramic membrane (AAM): Pd(3)/AAM, Pd-Ag(3,10)/AAM and Pd-Pt(3,10)/AAM and (b) Scanning electron micrographs of Pd(3)/AAM and Pd-Ag(3,10)/AAM.

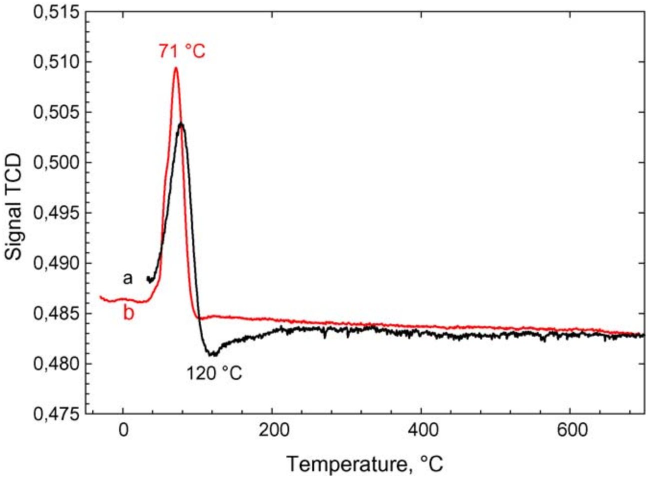

Fig. 2. Comparison of the TPR curves of: (a) Pd(3)/AAM and (b) Pd-Ag(3,10)/AAM after the catalytic tests in the synthesis of H_2O_2.

associated to PdO reduction to metallic Pd [18], a negative peak is observed near 120 °C in Pd-Ag(3,10)/AAM, but not in Pd(3)/AAM (Fig. 2). This negative peak is due to the presence of β-PdH phase [18,19]. Note, however, that the reduction peak near 70 °C (PdO → Pd) does not indicates that the catalyst works in the oxidized forms during the synthesis of H_2O_2, because metallic palladium easy reoxidize upon exposition at air at r.t.

The fact that the initial rate of H_2O_2 formation is significantly lower in Pd(3)/AAM and Pd-Pt(3,10)/AAM samples in comparison with the silver-containing sample indicates that there is probably an additional factor determining the catalytic performances, in addition to the inhibition of the β-PdH phase formation.

Fig. 1b reports the scanning electron microscopy (SEM) images of Pd(3)/AAM and Pd-Ag(3,10)/AAM samples. The thin noble metal film is characterized by grains of 1–5 nm, coalesced in irregularly shaped Pd crystals whose dimensions range from about 100 to 500 nm. The presence of silver leads to a more regular structure of the noble metal crystals and grains, which become characterized by a rose-like morphology. The enhanced properties of the Pd-Ag thin metallic membrane catalyst in comparison with the analogous Pd-only sample could be thus attributed to this morphological difference in the noble metals crystals leading not only to a different preferential crystal planes exposition on the surface, but also to a lower presence of surface defects. We have already suggested that O_2 chemisorbs on large, non defective Pd particles without dissociation, while on more energetic sites (defects, edges, corners, etc.) it will dissociatively chemisorb. The latter is the first step towards H_2O formation [3]. These defective sites can also readsorb H_2O_2 catalyzing its decomposition. Therefore, the selectivity in H_2O_2 formation decreases on increasing the amount of these defective sites. In agreement with this view, the selectivity of Pd-Ag(3,10)/AAM is significantly higher than that of Pd(3)/AAM, although in general the selectivity is low due to the low surface coverage with oxygen, a consequence of the chosen reaction conditions, as pointed out above.

In order to confirm this idea on the role of defects, it is interesting to compare Pd(3)/AAM with Pd-Pt(3,10)/AAM which gives quite low H_2O_2 productivity and selectivity (Fig. 1). SEM data do not evidence significant changes in the morphology which could be identified, in high resolution transmission microscopy (TEM) images. In fact, Pd(3)/AAM is characterized by round shape and large metal particles, with dimension ranging from about 100 to 500 nm. Pd-Pt(3,10)/AAM is characterized by the evident presence on the surface of the Pd macrocrystals (nearly unchanged with respect to those present in the Pd-only sample) of very small (5–20 nm) and highly defective Pd-Pt nanoparticles (Fig. 3). These are reasonably responsible for the lowering of both selectivity and productivity, catalyzing parallel and consecutive reactions of H_2O formation.

Notably, no promotion, but instead lowering of the catalytic performance is observed by modification of the catalyst with Pt, at variance from what could be expected from literature data, although on different type of support, typically carbon. We will see in the following section that indeed the effect of Pt is very dependent on the type of support for the Pd active component.

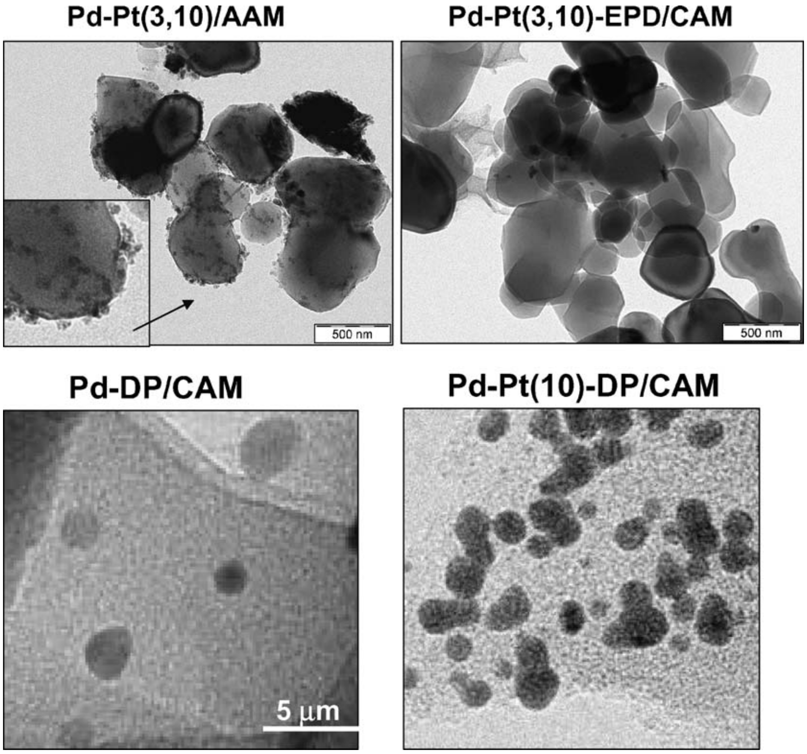

Fig. 3. *Top images*: Transmission electron micrographs of Pd-Pt(3,10)/AAM and Pd-Pt(3,10)-EPD/CAM samples. *Bottom images*: Transmission electron micrographs of Pd-DP/CAM and Pd-Pt(10)-DP/CAM samples.

3.2. Pd-Me supported on carbon-coated ceramic membrane (CAM)

Fig. 4 reports the behavior of a series of catalysts prepared using carbon-coated membranes (CAM). Two general observations are immediate: (i) up to three times higher productivities in H_2O_2 formation can be obtained on these materials with respect to those obtained using AAM-based catalysts and (ii) a positive effect of Pt addition is present in this case. Also, the selectivity in H_2O_2 formation is higher and is promoted by Pt addition.

It may be evidenced that in all cases the rate of formation of H_2O_2 (the slope of the curve of H_2O_2 formation versus time) tends to decline and also the selectivity in the formation of H_2O_2 slight decrease during the catalytic reaction. In Fig. 4 as well as in Fig. 1, the selectivity after 2 h of reaction is given. For the most selective sample d [Pd-Pt(3,10)-EPD/CAM], the selectivity slightly decreases from 29% after 1 h to 26% after 5 h of reaction. At the same time, the TON (turnover number, moles H_2O_2 h^{-1} per mol Pd) halves from about 0.50 to 0.24 h^{-1}. This indicates that the variation in the formation of H_2O_2 is mainly due to a lowering in the rate of formation of H_2O_2 rather than to an increase in the rate of the consecutive or parallel reactions leading to water, although still present. This suggests that for the most selective catalysts the change in performance with time on stream is only moderately due to a change in the catalyst during the catalyst reaction such as the reduction of Pd surface which is expected to lead to a drastic loss of selectivity. Therefore, the change of the surface reactivity is probably associated to the decrease of the surface coverage with chemisorbed oxygen. In fact, initially (when H_2 starts to be fed through the membrane) the surface coverage should be the equilibrium one with respect to O_2 solubility in the solvent (methanol) at the given reaction conditions (room temperature, atmospheric pressure). During the catalytic reaction, however, the O_2 chemisorbed surface coverage will be progressively determined from the rate of O_2 mass transfer to the catalyst surface, being H_2, fed directly through the membrane, probably in excess.

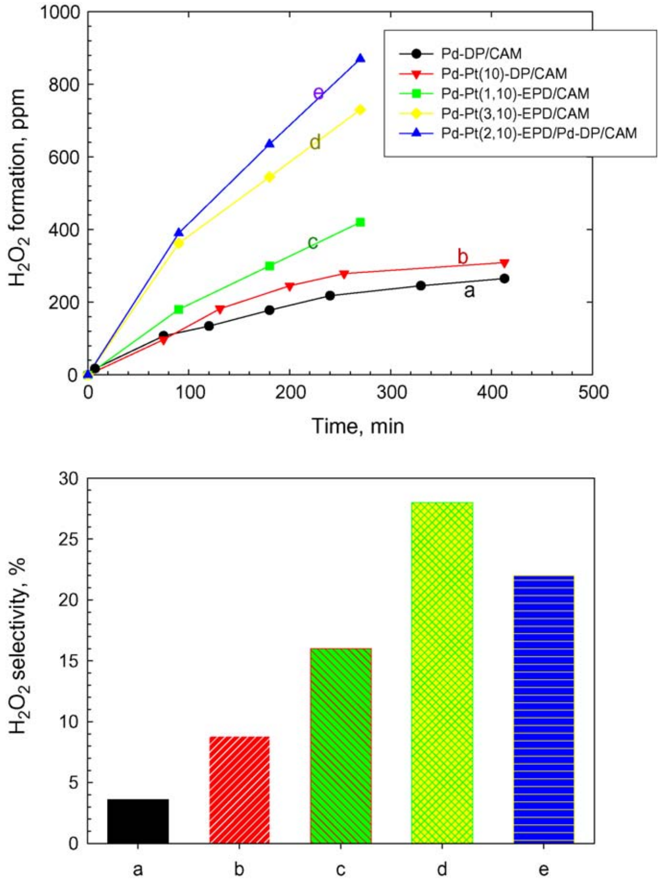

Fig. 4. Formation of H_2O_2 (top graph) and selectivity to H_2O_2 (bottom graph) of the following catalysts on carbon-coated α-Al_2O_3 ceramic membrane (CAM): (a) Pd-DP/CAM, (b) Pd-Pt(10)-DP/CAM, (c) Pd-Pt(1,10)-EPD/CAM, (d) Pd-Pt(1,10)-EPD/CAM and (e) Pd-Pt(2,10)-EPD/Pd-DP/CAM.

Fig. 4 summarizes the performance of catalysts prepared with different procedures. The reference behavior is the Pd-only catalyst prepared by deposition–precipitation [sample a, Pd-DP/CAM] which forms about 250 ppm H_2O_2 in 5 h and which show a selectivity of about 3–4%. The preparation of a bimetallic Pd-Pt (Pd/Pt molar ratio of 10) catalyst using the same procedure of preparation by deposition–precipitation [sample b, Pd-Pt(10)-DP/CAM] leads to a slight increase in the productivity to H_2O_2 and a twice higher selectivity (8–9%). The TEM characterization of these samples (Fig. 3, bottom images) show that in this case the introduction of Pt does not change significantly the morphology and size of the noble metal particles, although they appear slightly smaller, better round-shaped and grouped in clusters.

No evidences are observed for the formation of very small and highly defective Pt-Pd bimetallic particles either using DP method or EPD method (Fig. 3), but using the carbon-coated support (CAM) instead of directly the ceramic support (AAM). See the direct comparison reported in Fig. 3 (top images). It should be mentioned that good performances are observed only with Pd-Pt bimetallic systems, while Pd-Ag bimetallic or Pd-only thin films give much lower performances and are not reported here for the sake of conciseness.

The use of only one plating step [sample c, Pd-Pt(1,10)-EPD/CAM] results in the formation of about 450 ppm H_2O_2 in 5 h and the selectivity increases to 16–18% (Fig. 4). Using three plating steps [sample d, Pd-Pt(3,10)-EPD/CAM] about 800 ppm H_2O_2 are formed in 5 h and the selectivity increases to 26–28%. In addition, if sample a after catalytic tests is further treated to deposit the Pd-Pt thin film by EPD method (two plating steps), a drastic promotion of the catalytic performances is observed. In this case, about 900 ppm H_2O_2 are formed after 5 h, but the selectivity is slightly lower (22–24%). Therefore, depositing a thin Pd-Pt film on carbon-coated membranes leads to good catalytic performance that may be further improved operating under reaction conditions allowing a sufficient supply of O_2 to the surface of the catalyst, such as operating under pressure. TEM micrographs evidence that large and regular crystallites are present without the presence of the defective nanoparticles observed using AAM as support (Fig. 3).

The reasons of the considerable effect of the support, e.g. of the presence of a thin carbon-layer on the surface, should be further investigated, as well as the reasons of the considerable promotion of the catalytic performances by Pd-Pt bimetallic systems. In this respect, it should be pointed out that X-ray diffraction (XRD) analysis of the tested catalytic membranes do not give any evidence for the formation of a Pd-Me alloy. The latter can be revealed only after a heat treatment at 700 °C in inert gas, with a consequent drop of the catalytic performance. These observations do not completely exclude a possible involvement of an amorphous alloy in improving the catalytic performance, but would rather suggest a more significant role for the catalyst microstructure and/or reducibility.

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