

# The issue of selectivity in the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>: the role of the catalyst in relation to the kinetics of reaction

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The kinetic behavior in the direct synthesis of H<sub>2</sub>O<sub>2</sub> with Pd–Me (Me = Ag, Pt) catalysts prepared by depositing the noble metals by electroless plating deposition (EPD) or deposition–precipitation (DP) methods on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> asymmetric ceramic membrane with or without a further surface coating by a carbon thin layer is 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. Several factors in the preparation of these membranes as well as the reaction conditions (temperature, concentration of Br<sup>−</sup>, pH) determine the selectivity in H<sub>2</sub>O<sub>2</sub> formation, influencing the rate of the consecutive reduction of H<sub>2</sub>O<sub>2</sub> (which is faster with respect to H<sub>2</sub>O<sub>2</sub> decomposition on the metal surface) and/or of direct H<sub>2</sub> + O<sub>2</sub> conversion to H<sub>2</sub>O. Defective Pd sites are indicated to be responsible for the two unselective reactions leading to water formation (parallel and consecutive to H<sub>2</sub>O<sub>2</sub> formation), but the rate constants of the two reactions are differently influenced from the catalytic membrane characteristics. Increasing the noble metal loading on the membrane not only increases the productivity to H<sub>2</sub>O<sub>2</sub>, but also the selectivity, due to the formation of larger, less defective, Pd particles.

**KEY WORDS:** bimetallic catalysts; H<sub>2</sub>; hydrogen peroxide; membrane; Pd–Pt

## 1. Introduction

The development of a new economic process to synthesize H<sub>2</sub>O<sub>2</sub> is a key step towards the introduction of new selective oxidation processes [1,2] for a sustainable production. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a clean and excellent oxidizing reagent for the production of both fine and bulk chemicals (for example, selective hydroxylation and epoxidation of substituted aromatics and alkenes, and propene oxide, caprolactam, and long-chain linear alcohols syntheses, respectively) and find application also in the area of environmental cleanup technologies (water treatment) and “green” technologies (paper and pulp bleaching, for example) [1]. In these processes the cost of H<sub>2</sub>O<sub>2</sub> is often the limiting factor to introduce the cleaner technology. 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 H<sub>2</sub>O<sub>2</sub> with respect to the commercial process based on methyl-anthraquinone route which is largely conditioned also from the monopoly character of the market related to the necessity of having large scale plants for H<sub>2</sub>O<sub>2</sub> production. In addition, the environmental impact of the commercial route is significant, while virtually absent in the case of the direct route. Furthermore, the direct route may be potentially developed economically at a small-medium size scale, allowing a delocalized H<sub>2</sub>O<sub>2</sub> production, which avoids the risks associated to

H<sub>2</sub>O<sub>2</sub> transport and storage. Degussa [3] has recently announced the creation of a joint venture to develop and commercialize a direct synthesis process for H<sub>2</sub>O<sub>2</sub>. Several other companies have similar plans and the research is quite active in this area.

The direct synthesis from H<sub>2</sub> and O<sub>2</sub> was originally developed by Du Pont [4] using Pd-based supported catalysts. However, the process never arrived to commercialization after an explosion of the pilot plant, because the safety aspects of the process related to the wide explosion range of mixtures of H<sub>2</sub> and O<sub>2</sub> critically conditioned the development of the process. Hydrogen has the widest range of flammable concentrations in air among all common gaseous fuels and in addition a high buoyancy and diffusivity in air. Therefore, in confined environments and under pressure such as in autoclave it is possible to have stratification of H<sub>2</sub> in the head of the reactor or in dead zones with the creation of local conditions for an explosion. Even though reactor technologies, which minimize the risks may be adopted, the risk remains high. Therefore in the perspective of development of sustainable technologies it is recommended to develop an intrinsically safe process, e.g. a technology in which there is a separate contact of O<sub>2</sub> and H<sub>2</sub> with the reaction solution in order to avoid the possibility of explosion, even during anomalous operations. This possibility is offered by the use of catalytic membranes [5–8] instead of powder-type catalysts as those used in most of the patents and publications [4, 9–29].

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There is an additional relevant issue related to safety in favor of the use of catalytic membranes instead of powder type catalysts. In fact, not only a physically separated contact between O<sub>2</sub> and H<sub>2</sub> 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 the H<sub>2</sub>O<sub>2</sub> solution and can be extremely dangerous in the downstream process of H<sub>2</sub>O<sub>2</sub> solution concentration, catalyzing fast decomposition and explosion.

Using a catalytic membrane reactor where H<sub>2</sub> is fed through the membrane, one side of which is in contact with a solution saturated with oxygen, it is possible to improve safety of the operations, but selectivity and productivities in the reaction should be improved. With respect to powder-type catalysts, where the O<sub>2</sub> and H<sub>2</sub> concentration at the catalyst surface is determined essentially by the O<sub>2</sub>/H<sub>2</sub> 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 the opportunity to have separate control the O<sub>2</sub> and H<sub>2</sub> gradients in the catalytic zone of the membrane. However, in the most suitable configuration from the safety point of view, e.g. the H<sub>2</sub> which diffuse through the membrane which is in contact with the solution saturated with O<sub>2</sub>, we observed earlier [5–7,30,31] that the membrane show low selectivity due to fast reduction of Pd. We observed also that the nature of Pd particles influences the selectivity and productivity to H<sub>2</sub>O<sub>2</sub>, but a better knowledge of the reaction network and mechanism, and the identification of the role and nature of active sites in the different reactions could allow to further improve the performances. For this reason, the aim of the work reported here is to analyze the influence of the nature of the catalytic membrane on the kinetics of the reaction of direct synthesis of H<sub>2</sub>O<sub>2</sub>.

It should be taken into account that this investigation was made using the cited configuration in which H<sub>2</sub> diffuse through the membrane being in contact with the solution saturated with O<sub>2</sub>, and at ambient temperature and pressure. Higher selectivities, above 80–90%, could be obtained at high pressure (above 50 bar) and operating in conditions of quite large excess of oxygen, even though the latter condition, typically used in the experiments reported in literature, is potentially quite dangerous being inside or quite close to the explosivity region. On the other hand, a simplified kinetic approach can be used in the chosen reaction conditions and reactor (see later) which allow to better relate the kinetics of the various reactions to the catalyst nature and microstructure, therefore separating the intrinsic effect of the catalyst from the effect of the oxygen surface coverage.

Two types of membrane supports have been used:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> asymmetric ceramic membrane (indicated hereinafter as A) and the same type of ceramic membrane, but covered with a surface thin carbon layer (indicated hereinafter as CA). Pd or Pd–Me, where Me = Ag or Pt, have been deposited on these membrane supports by electroless plating deposition (EPD) mostly on A-type membrane and by deposition–precipitation (DP) only on CA-type membrane, because in the latter case the carbon layer is necessary for the dispersion of noble metal. The latter preparation method allows to obtain smaller Pd particles and a better dispersion of Pd, while the former allow to prepare porous thin Pd or Pd–Me films, with thickness of few microns. We will thus refer in the text to dispersed Pd-particles or Pd-thin films in the two cases of catalytic membranes.

## 2. Experimental

### 2.1. Preparation of the catalytic membrane

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 (about 3–5  $\mu\text{m}$  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 sensitization 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  $\alpha$ -alumina asymmetric membrane consists of an  $\alpha$ -alumina macroporous support (3  $\mu\text{m}$  pore size) with an  $\alpha$ -alumina external mesoporous layer (pore size 50–100 nm).

The second class of catalytic membranes investigated use the same support of the first class of membranes, 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<sub>2</sub> 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<sub>4</sub><sup>2-</sup> or PdCl<sub>4</sub><sup>2-</sup> + PtCl<sub>6</sub><sup>2-</sup> 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<sub>2</sub> flow. Pd loading was typically around 2 mg, but using more concentrated solutions of the noble metals, the noble metal loading

could be increased up to 30 mg, even though these membranes show lower stability during the H<sub>2</sub>O<sub>2</sub> direct synthesis. Further details on both the preparation methods were given elsewhere [5,6,30,31].

Table 1 reports a summary of the prepared catalytic membrane and their code, which will be used hereinafter. For further details reference is given to previous papers [5,6,30,31]. Scanning and transmission electron microscopy (SEM and TEM, respectively) characterization of the samples (not reported here for conciseness) indicate that the deposition–precipitation method (DP) on carbon-coated ceramic membrane (CA) leads to Pd or Pd–Me particles with mean dimension of around 8–10 nm which slightly decrease increasing the Pd:Pt ratio. The mean Pd particle dimension increases from 8 to 10 nm for a total loading of around 2 mg on the membrane to around 50–100 nm for the 30 mg loading with the noble metal. In the membranes prepared by EPD, either on A or CA membrane support, a porous thin film of the noble metal is obtained, with a thickness of around 3–5 nm. The TEM characterization of this film reveals that it is an aggregate of particles with broad dispersion in the 100–500 nm range.

## 2.2. Characterization and catalytic tests

Catalytic tests were carried out at r.t. and ambient pressure in a recirculation membrane reactor apparatus with external recirculation and saturation of the solution with O<sub>2</sub>. The membrane is sealed in a tubular holder having transparent walls to monitor the absence of possible leaks in the membrane. From the inner side H<sub>2</sub> is fed at constant pressure (2–3 bar), while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane, e.g. the side where the Pd or Pd–Me active layer was deposited. A pump equipped with special Tygon<sup>®</sup> MH tubing allows the continuous recirculation of the solution which has a

liquid residence time in the membrane reactor of about 3600 h<sup>-1</sup>. This fast circulation allows to maintain nearly constant the O<sub>2</sub> concentration along the axial direction of the reactor, as checked with O<sub>2</sub> sensors, while the absence of leaks in the membrane and its uniform porosity along the axial direction allows to consider nearly constant also the concentration of H<sub>2</sub> along the axial direction of the membrane reactor.

The circulating solution was 100 ml of water or anhydrous methanol containing 6 mg/l KBr and 2.8 g/l H<sub>2</sub>SO<sub>4</sub>, if not otherwise indicated. The pressure at the liquid side was atmospheric pressure, while the reaction temperature 21 °C, if not otherwise indicated. H<sub>2</sub>O<sub>2</sub> concentration was determined by iodometric titration using an automatic titrimetric apparatus, whereas water content was determined by an automatic titrimetric apparatus based on the Karl Fischer method. Selectivity to H<sub>2</sub>O<sub>2</sub> with respect to H<sub>2</sub> was calculated on the basis of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formation. The values of the latter were corrected to consider that in blank experiments in the absence of the catalytic layer, an increase in the water content in anhydrous methanol was observed, probably due to some humidity traces in the O<sub>2</sub> and H<sub>2</sub> gases.

Transmission electron microscopy (TEM) images were taken with a Jeol 3010, operating at 300 kV, equipped with a Gatan slow-scan CCD camera (Mod. 794) and an Oxford Instrument EDS microanalysis detector (Mod. 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

Table 1  
Membrane characteristics and their code used in the text

Code	Membrane characteristic			
	Support <sup>a</sup>	Pd deposition <sup>b</sup>	Composition <sup>c</sup>	Amount, mg <sup>c</sup>
TMC-1	CA	PD	Pd only	2
TMC-1b	CA	PD	Pd:Pt = 10	2
TMC-1b1	CA	PD	Pd:Pt = 10	5
TMC-1b2	CA	PD	Pd:Pt = 10	15
TMC-1b3	CA	PD	Pd:Pt = 10	30
TMC-1c	CA	PD	Pd:Pt = 18	2
TMC-2	A	EPD	Pd only	60
TMC-2b	A	EPD	Pd:Ag = 10	60
TMC-2c	A	EPD	Pd:Pt = 10	60
TMC-2d	CA	EPD	Pd:Pt = 10	60

<sup>a</sup> A =  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> asymmetric ceramic membrane; CA = carbon-coated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> asymmetric ceramic membrane.

<sup>b</sup> PD = Precipitation–deposition; EPD = Electroless plating deposition.

<sup>c</sup> Composition of the active layer and approximated amount (mg) deposited on the whole membrane.

electron microscope. The tubular membrane were cut for this characterization.

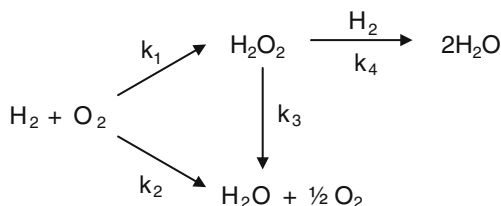
### 3. Results and discussion

#### 3.1. Kinetic reaction network

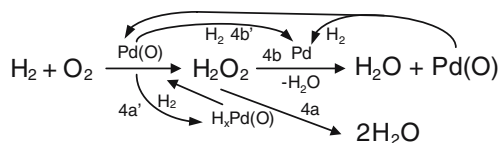
The kinetic reaction network in H<sub>2</sub>O<sub>2</sub> direct synthesis is reported in Scheme 1 which, respect to the usual triangular reaction scheme considered in literature, reports also the possibility of H<sub>2</sub>O<sub>2</sub> further conversion along two pathways, the first (reaction 3) of catalyzed decomposition (the homogeneous decomposition in the reaction conditions investigated is negligible) and the second (reaction 4) of catalyzed reduction of H<sub>2</sub>O<sub>2</sub> to two molecules of H<sub>2</sub>O. This second pathway can be either the effective reduction of H<sub>2</sub>O<sub>2</sub> by activated H species on the surface of the Pd catalyst (reaction 4a in Scheme 2) or instead the first reduction of oxidized Pd particles (schematically indicated as Pd(O)) to metallic Pd and then the decomposition of H<sub>2</sub>O<sub>2</sub> on the reduced Pd surface (reaction 4b in Scheme 2). In fact, the surface oxidation state of Pd is important in determine the amount of H<sub>2</sub>O<sub>2</sub> formed [5,6,26] and is known that metallic Pd is highly active in H<sub>2</sub>O<sub>2</sub> decomposition [32].

On the other hand, if the reduction of oxidized Pd surface (reaction 4b' in Scheme 2) is faster than the decomposition of H<sub>2</sub>O<sub>2</sub> on the metallic Pd (reaction 4b) and similarly the H<sub>2</sub> activation (dissociation) on the Pd surface (reaction 4a') is faster than the reaction of H<sub>2</sub>O<sub>2</sub> with activated H atoms on the surface of Pd (schematically indicated as H<sub>x</sub>Pd(O) in Scheme 2) (reaction 4a) it is possible to lump the two reactions 4a and 4b in a single reaction. Both assumption seems reasonable, taking into account that (i) temperature programmed reduction tests with H<sub>2</sub> evidence that the reduction of oxidized Pd particles (Pd(O)) is quite fast already at room temperature [30] and (ii) dissociative chemisorption of H<sub>2</sub> on Pd is also a fast reaction at room temperature [33]. But, as far as we known, there are no evidences in literature whether these reactions are effectively faster than the H<sub>2</sub>O<sub>2</sub> decomposition under the experimental conditions of H<sub>2</sub>O<sub>2</sub> synthesis.

Therefore, it is reasonable to assume the simplified kinetic reaction network reported in Scheme 1, although better studies would be necessary to clarify which of the



Scheme 1. Reaction network in H<sub>2</sub>O<sub>2</sub> synthesis.



Scheme 2. Different pathways of conversion of H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>.

two reaction pathways reported in Scheme 2 is the effective one dominating the catalyst reactivity.

#### 3.2. Decomposition versus reductive pathway in H<sub>2</sub>O<sub>2</sub> conversion

A further simplification in the kinetic reaction network reported in Scheme 1 could derive from the identification of which of the two reactions of H<sub>2</sub>O<sub>2</sub> further conversion, e.g. the decomposition pathway (reaction 3 in Scheme 1) or the reductive pathway (reaction 4), is the dominating (faster) reaction. In order to clarify this point, specific experiments were made to investigate the conversion of H<sub>2</sub>O<sub>2</sub> when an inert gas (N<sub>2</sub>) or instead H<sub>2</sub> are feed through the membrane, while maintaining all other reaction conditions equal to those for H<sub>2</sub>O<sub>2</sub> synthesis, e.g. use of an acidic solution containing Br<sup>-</sup> anions which continuously circulated from the membrane reactor to the service vessel for O<sub>2</sub> saturation, expect that for the initial concentration of H<sub>2</sub>O<sub>2</sub> (about 2000 mg/l).

The results are shown in figure 1 in terms of dependence of the kinetic constant of H<sub>2</sub>O<sub>2</sub> decomposition from the time of reaction when N<sub>2</sub> or H<sub>2</sub> is feed through the membrane, either having dispersed Pd particles (TMC-1) or a thin Pd film (TMC-2). The kinetic constant has been estimated assuming a pseudo first-order reaction, e.g. that H<sub>2</sub> concentration is constant and the rate depends only on H<sub>2</sub>O<sub>2</sub> concentration. This kinetic assumption is reasonable on the basis of experiments on the dependence on H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> concentration (see below). The rate has been corrected considering the formation H<sub>2</sub>O<sub>2</sub>, determined in separate experiments where the initial H<sub>2</sub>O<sub>2</sub> concentration was zero.

On both type of membrane the rate constant of H<sub>2</sub>O<sub>2</sub> decomposition (tests flowing N<sub>2</sub> through the membrane) is significantly higher than that when H<sub>2</sub> is flowing through the membrane. This indicates that in a simplified kinetic approach it may be assumed that the reaction of H<sub>2</sub>O<sub>2</sub> reduction (reaction 4 in Scheme 1) is the dominating pathway of H<sub>2</sub>O<sub>2</sub> conversion to H<sub>2</sub>O with respect to the pathway of decomposition (reaction 3). This is in agreement with the results of Han and Lunsford [34] that also indicated, although not clearly demonstrated, that the reduction of H<sub>2</sub>O<sub>2</sub>, rather than its simple decomposition, is primarily responsible for further conversion of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O.

It may be also noted that in the Pd thin film membrane (TMC-2) the rate of decomposition is similar to

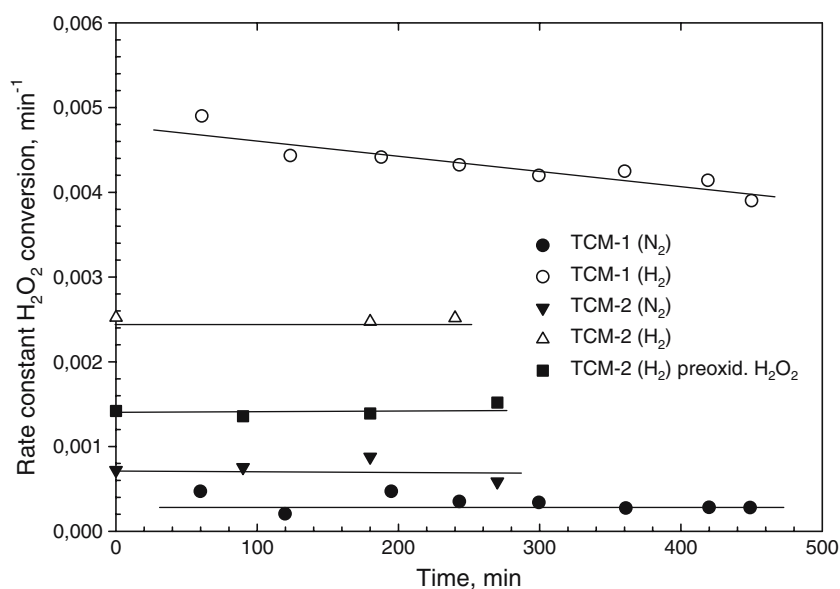
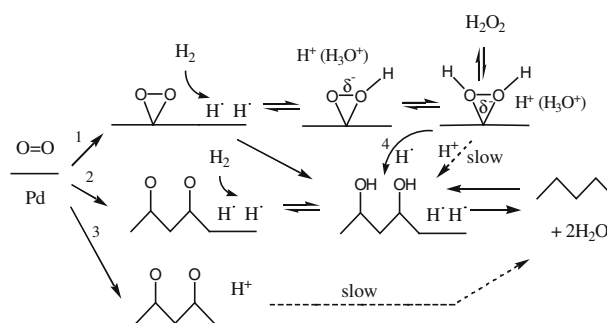


Figure 1. Dependence of the rate constant of H<sub>2</sub>O<sub>2</sub> conversion from the time of reaction for TCM-1 and TMC-2 membranes when N<sub>2</sub> or H<sub>2</sub> was flowing through them. The effect of a preoxidation treatment of the TMC-2 membrane with a 1% H<sub>2</sub>O<sub>2</sub> aqueous solution is also reported.

that of the membrane having dispersed Pd particles (TMC-1), notwithstanding the ratio of the amount of Pd in the two samples is about 30 (table 1). This indicates that no direct relationship exists between amount of Pd and rate of H<sub>2</sub>O<sub>2</sub> decomposition. No relationship between the rate of H<sub>2</sub>O<sub>2</sub> reduction (tests in the presence of H<sub>2</sub> flowing through the membrane) and amount of Pd was also observed, but instead the rate of the membrane having dispersed Pd particles and the lower amount of Pd is about twice that of the membrane with a Pd thin film and about 30 times higher Pd loading. The total metallic surface area of the two membrane is similar (about 0.1 m<sup>2</sup>), because TMC-1 in comparison with TMC-2 has smaller size particles (around 8–10 nm instead of particles in the 100–500 nm range), but lower amount of Pd (about 1/30).

Krause and Hermann [32] already several years ago observed that etched Pd foils show significantly higher rate of H<sub>2</sub>O<sub>2</sub> decomposition than Pd polished foil, introducing therefore the concept of the role of defect sites in H<sub>2</sub>O<sub>2</sub> decomposition. There is a general agreement in literature that the synthesis of H<sub>2</sub>O<sub>2</sub> requires an undissociative chemisorption of O<sub>2</sub> [5,6,28,34–38]. Subsequent protonation of chemisorbed O<sub>2</sub>, possibly in the form of a surface peroxy species, by H<sup>+</sup> or H<sub>3</sub>O<sup>+</sup> (hydronium) [39] leads first to HO<sub>2</sub> as a surface intermediate and then by the addition of a second hydrogen atom to H<sub>2</sub>O<sub>2</sub>, which desorb from the catalyst. On the other hand, on defect Pd sites (steps and kinks), the dissociative chemisorption of O<sub>2</sub> and the further reaction with chemisorbed hydrogen will lead to the formation of water via intermediate formation of OH surface species. It is reasonably that H<sub>2</sub>O<sub>2</sub> will competitively chemisorb with O<sub>2</sub> and therefore that the

same defect sites are also responsible for H<sub>2</sub>O<sub>2</sub> decomposition. However, the large enhancement of the rate of H<sub>2</sub>O<sub>2</sub> conversion in the presence of H<sub>2</sub> could be interpreted considering that the chemisorption O<sub>2</sub> on these defect sites leads to a strong chemisorption, which inhibits the dissociative chemisorption of H<sub>2</sub>O<sub>2</sub> on these defect sites (Scheme 3). The reaction of proton or hydronium with the oxygen atoms produced by dissociative chemisorption of O<sub>2</sub> is slow, but faster in the presence of spillover hydrogen. For this reason, there is a significant increase in the rate of H<sub>2</sub>O<sub>2</sub> dissociation when H<sub>2</sub> is present. It is therefore reasonable that the rate of H<sub>2</sub>O<sub>2</sub> dissociation for TMC-1 and TMC-2 is similar in absence of H<sub>2</sub>, but higher in the former in the presence of H<sub>2</sub>, because the smaller diameter of the Pd particles in this samples leads to an increase in the presence of more energetically crystalline planes and therefore of defect sites.



Scheme 3. Model of the possible surface pathways for the synthesis of H<sub>2</sub>O<sub>2</sub> on Pd catalysts.

In agreement with this interpretation, we could observe that an oxidative pretreatment of the catalyst with a concentrated solution of H<sub>2</sub>O<sub>2</sub> significantly decreases the rate of H<sub>2</sub>O<sub>2</sub> conversion (figure 1). This explains also why in TMC-1 a slightly decrease of the rate constant is observed with the time on stream (figure 1). Due to the faster rate of H<sub>2</sub>O<sub>2</sub> conversion in this sample, the rate of further conversion by spillover hydrogen of the dissociatively chemisorbed oxygen is lower than that of formation, leading to a progressive decrease in the rate of reaction.

The effect of the reaction conditions on the rate of H<sub>2</sub>O<sub>2</sub> conversion is reported in the figures 2 and 3. Figure 2 shows the dependence of the rate constant from the amount of KBr and H<sub>2</sub>SO<sub>4</sub> in solution, the latter also influencing the pH of reaction which is also shown in figure 2, and from the reaction temperature. Figure 3 shows instead the dependence of the initial rate of H<sub>2</sub>O<sub>2</sub> conversion from the H<sub>2</sub>O<sub>2</sub> initial concentration and from the H<sub>2</sub> concentration in solution, the latter changed increasing the total liquid pressure, while maintaining constant the pressure differential across the membrane.

The increase of the concentration of Br<sup>-</sup> anions significantly decrease the rate of H<sub>2</sub>O<sub>2</sub> conversion, in agreement with literature results [4,27,36,40]. The

exponential-type decrease of the rate constant on increasing Br<sup>-</sup> concentration is more consistent with the indication that Br<sup>-</sup> on the surface may block the sites for the dissociation of O<sub>2</sub> [36,40] rather than the interaction of bromide anions with palladium change its electronic properties [27], because in the latter case a linear or volcano-type dependence should be expected. Alternative explanation is that Br<sup>-</sup> anions, which can act as electron scavenger, will inhibit radical-type decomposition pathways [5]. Also this interpretation is consistent with the observed trend. It is interesting to note that the trend of the rate constant of H<sub>2</sub>O<sub>2</sub> conversion is quite similar to that observed on increasing the H<sub>2</sub>SO<sub>4</sub> concentration, although the scale is different and in the case of H<sub>2</sub>SO<sub>4</sub> there is also the additional effect of a change in the pH of the solution.

Han and Lunsford [25] observed that the sulfate ion is a non-coordinating ligand and would not be expected to block Pd ensembles that promote the dissociation of O<sub>2</sub>, which results in the direct formation of water, differently from bromide and chloride anions. It may be noted that these authors have studied the reaction using a high O<sub>2</sub>/H<sub>2</sub> ratio and therefore in conditions where already a large part of the Pd defective sites would be blocked from the strong chemisorption of O<sub>2</sub>, as discussed above. Data in figure 2 show that there is a significant

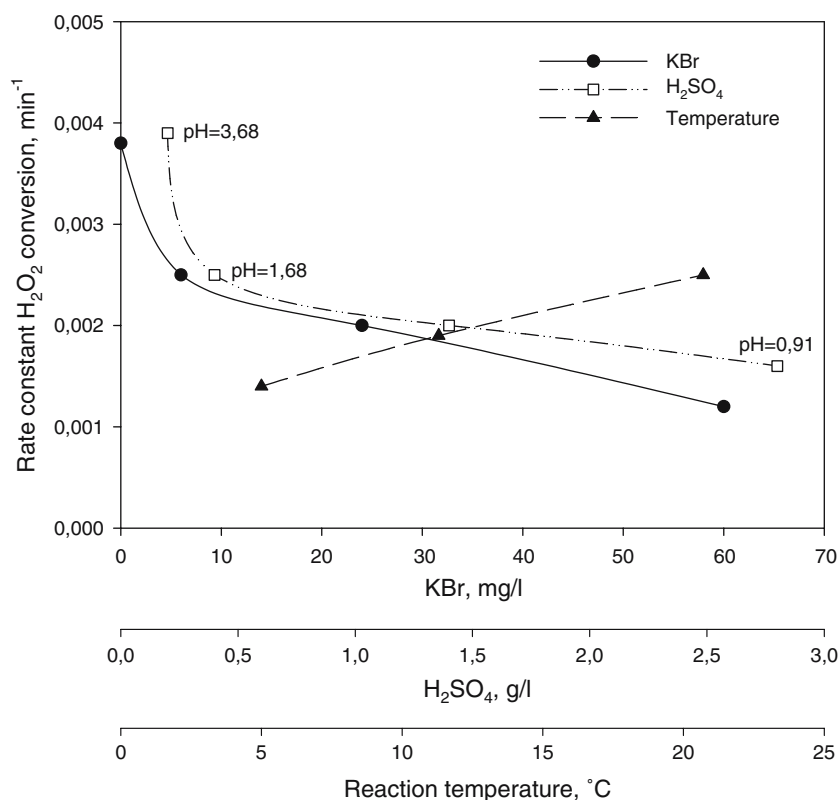


Figure 2. Dependence of the rate constant of H<sub>2</sub>O<sub>2</sub> conversion from the KBr and H<sub>2</sub>SO<sub>4</sub> concentrations and from the reaction temperature for TMC-2 membrane. The experimental conditions were 6 mg KBr, 2.8 g H<sub>2</sub>SO<sub>4</sub> (pH = 0.91) and 20.7 °C, if not the related parameter was changed. Initial concentration of H<sub>2</sub>O<sub>2</sub> was 2000 mg/l, the liquid pressure was 1 bar and the pressure differential across the membrane was 2.5 bar. Solvent was distilled water.

effect of the concentration of sulphate ions, although it would be difficult to discriminate between the effect due to sulphate ions itself and that associated to the change of the pH of the solution. Chemisorbed H<sub>2</sub>O<sub>2</sub> species are probably stabilized from proton or hydronium (Scheme 3) reducing thus the rate of breaking the O–O bond and therefore it is reasonable that the increase of pH leads to a decrease in the rate constant of H<sub>2</sub>O<sub>2</sub> conversion, although a direct effect of sulphate ions in blocking Pd defect sites could be not excluded.

The effect of the reaction temperature on the rate constant of H<sub>2</sub>O<sub>2</sub> conversion is also reported in figure 2. The activation energy for the reaction, which can be estimated from these data is 24.7 KJ/mol which is in agreement with that earlier reported on Pd catalysts [41–43]. This value is close that the value observed by DFT calculations for the H<sub>2</sub>O<sub>2</sub> desorption or for HO<sub>2</sub> hydrogenation and desorption from Au cluster, supporting the indication in Scheme 3 of the presence of reversible chemisorption and dissociation reactions.

The effect on the rate of reaction of the initial concentration of H<sub>2</sub>O<sub>2</sub> and of the H<sub>2</sub> concentration are shown in figure 3. Data indicate a linear dependence of the rate of H<sub>2</sub>O<sub>2</sub> decomposition from its concentration at least up to a value of about 2000 mg/l. In addition, a very low dependence of the rate of H<sub>2</sub>O<sub>2</sub> conversion from the H<sub>2</sub> concentration in solution can be observed. The H<sub>2</sub> concentration in solution was increased by increasing the liquid phase total pressure at a constant pressure differential through the membrane. Therefore, the minimal change of the rate of H<sub>2</sub>O<sub>2</sub> decomposition from the liquid pressure pointed out that the reaction

rate is not influenced from the H<sub>2</sub> chemisorption and/or dissociation, in agreement with the assumptions previously discussed. Therefore, within the experimental range investigated, the assumption of pseudo-first order reaction is valid.

### 3.3. Kinetics modeling of the H<sub>2</sub>O<sub>2</sub> synthesis

In a semi-batch reactor, the material balance for H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formation for the reaction network reported in Scheme 1 can be written as follows:

$$\frac{dc_{\text{H}_2\text{O}_2}}{dt} = k_1 c_{\text{H}_2}^\alpha c_{\text{O}_2}^\beta - k_3 c_{\text{H}_2\text{O}_2} - k_4 c_{\text{H}_2\text{O}_2} c_{\text{H}_2}^\delta \quad (1)$$

$$\frac{dc_{\text{H}_2\text{O}}}{dt} = k_2 c_{\text{H}_2}^\alpha c_{\text{O}_2}^\beta + k_3 c_{\text{H}_2\text{O}_2} + 2k_4 c_{\text{H}_2\text{O}_2} c_{\text{H}_2}^\delta \quad (2)$$

As pointed out before, it is possible to consider in our reactor constant the H<sub>2</sub> and O<sub>2</sub> concentration along the axial direction of the membrane reactor. In addition, on the basis of the above discussion, it is possible to simplify the kinetic reaction network reported in Scheme 1 considering negligible the reaction 3 (decomposition) and assuming therefore that the consecutive conversion of H<sub>2</sub>O<sub>2</sub> derives only on the reduction by H<sub>2</sub>. This means that the above equations can be simplified as:

$$\frac{dc_{\text{H}_2\text{O}_2}}{dt} = k'_1 - k_4 c_{\text{H}_2\text{O}_2} \quad (3)$$

$$\frac{dc_{\text{H}_2\text{O}}}{dt} = k'_2 + 2k'_4 c_{\text{H}_2\text{O}_2} \quad (4)$$

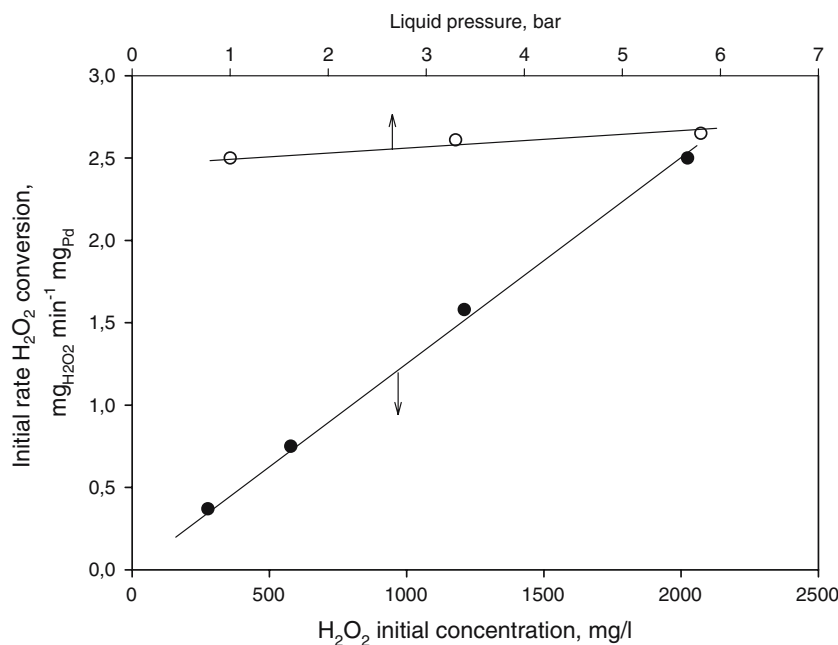


Figure 3. Effect on the initial rate of H<sub>2</sub>O<sub>2</sub> conversion of the initial H<sub>2</sub>O<sub>2</sub> concentration and the H<sub>2</sub> partial pressure modified by increasing the liquid pressure, while maintaining constant the pressure differential across the membrane, for TMC-2 membrane. Other conditions as in figure 2.



This equation can be solved analytically. For an initial concentration of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O equal to zero:

$$c_{\text{H}_2\text{O}_2} = \frac{k'_1}{k'_4} \left(1 - e^{-k'_4 t}\right) \quad (5)$$

$$c_{\text{H}_2\text{O}} = \left[ k'_2 + 2k'_1 \left(1 - e^{-k'_4 t}\right) \right] \cdot t \quad (6)$$

The fitting of the data of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O synthesis as a function of the time of reaction allows to determine the kinetic constants of the reaction and analyze their dependence from the characteristics of the catalytic membrane. We prefer to make a balance on the formation of H<sub>2</sub>O instead of H<sub>2</sub>, because the fast diffusivity of H<sub>2</sub> could introduce a significant analytical error. However, this implies the necessity of using a non-aqueous solvent if the full kinetic network should be analyzed, while the model could be applied to water as solvent limiting the analysis to the determination of the rate constants of direct H<sub>2</sub>O<sub>2</sub> formation ( $k_1$ ) and of its consecutive conversion ( $k_4$ ) (see Scheme 1).

Han and Lunsford [25,34] observed that the use of an organic solvent such as ethanol instead of water leads to differences in the reaction mechanism and surface reactivity, but on the other hand it was both patented and reported also in literature [6,25,28,44] that the use of methanol or ethanol as solvents improve the catalytic performances and could be the preferable choice both when the same solvent can be used in further syntheses (for example, epoxidation reactions) or when the H<sub>2</sub>O<sub>2</sub> solution should be concentrated by distillation. Even if the solvent influences the rate constants, as will be

shown later, the overall results are consistent with those observed using water as solvent. This suggests that the conclusions about the relation between catalytic membrane characteristics and kinetics of reaction could be valid also for water as the solvent.

#### 3.4. H<sub>2</sub>O<sub>2</sub> synthesis in water as the solvent

Reported in figure 4 is the comparison of formation of H<sub>2</sub>O<sub>2</sub> on TCM-1 and TMC-2 membranes. The symbols reports the experimental values, while the lines are calculated on the basis of the equation (5) and the rate constants reported in table 2. The formation of H<sub>2</sub>O<sub>2</sub> on the two type of membranes having dispersed Pd particles (TMC-1) or a thin Pd film (TMC-2) is apparently similar, but a closer inspection of the rate constants (table 2) obtained from the fitting of the data indicates that TMC-1 shows a higher rate of H<sub>2</sub>O<sub>2</sub> formation, but also of H<sub>2</sub>O<sub>2</sub> decomposition with respect to TMC-2, confirming the indications obtained studying the rate of H<sub>2</sub>O<sub>2</sub> decomposition (figure 1). The ratio between the  $k_4$  and  $k_1$  rate constants is higher in TMC-2 than in TMC-1 (table 2).

Reported in figure 4 and table 2 are also the results obtained for a Pd:Ag (10:1) thin film catalytic membrane (TMC-2b) which shows higher formation of H<sub>2</sub>O<sub>2</sub>. The formation of an alloy of Pd with Ag has been indicated in some patents [19,45] to promote the performances in H<sub>2</sub>O<sub>2</sub> direct synthesis and it is known [33] that reduces the formation of  $\beta$ -hydride palladium phase [46,47] which could be an index that may be reduced the activity in H<sub>2</sub>O<sub>2</sub> conversion. We observed

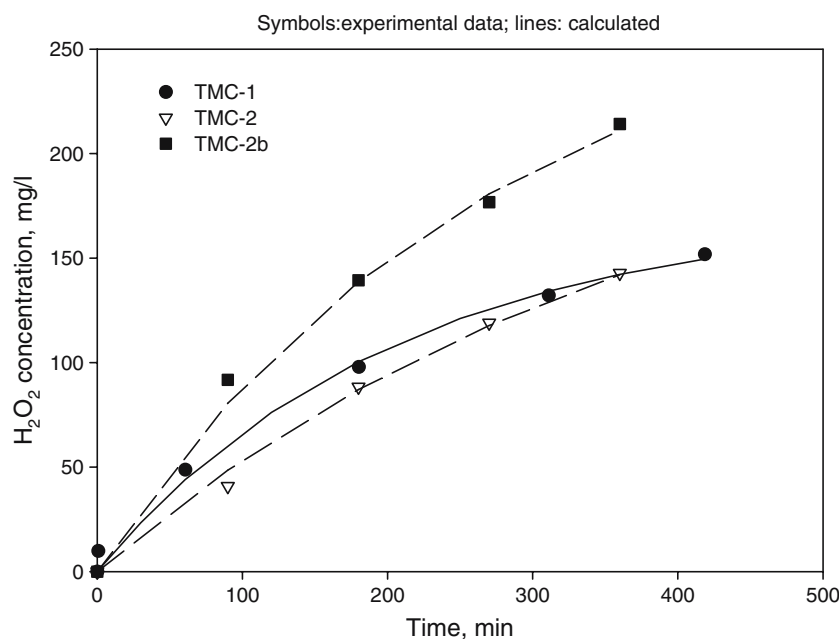


Figure 4. Dependence of the amount of H<sub>2</sub>O<sub>2</sub> formed from the time of reaction for TMC-1, TMC-2 and TMC-2b membranes. Reaction conditions as in figure 2. The symbols represent the experimental values, while the lines were calculated from the equation (5) using the rate constants reported in table 2.



Table 2

Rate constant of direct H<sub>2</sub>O<sub>2</sub> formation ( $k_1$ ) and consecutive H<sub>2</sub>O<sub>2</sub> conversion to water ( $k_4$ ) for TMC-1, TMC-2 and TMC-2b membranes

Membrane	$k_1$ , mol l <sup>-1</sup> min <sup>-1</sup>	$k_4$ , min <sup>-1</sup>	100*k <sub>1</sub> /k <sub>4</sub>
TMC-1	4.19E-05	4.88E-03	0.86
TMC-2	3.02E-05	2.56E-03	1.18
TMC-2b	5.24E-05	3.62E-03	1.45

Tests in water. Reaction conditions as in figure 4. The rate constants were determined by fitting of the data reported in figures 2–4 using equation (5).

[30] that the presence of silver leads to a more regular structure of the noble metal crystals and grains, that become characterized by a rose-like morphology, with respect to the irregularly shaped Pd crystals with dimension ranging from about 100–500 nm observed in thin Pd-only films.

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 exposition of the crystal planes on the surface, e.g. more flat surfaces, but also to a lower presence of surface defects. The analysis of the rate constants reported in table 2 confirm that there is an increase in the  $k_4/k_1$  ratio of the rate constants of synthesis and further conversion of H<sub>2</sub>O<sub>2</sub>.

### 3.5. H<sub>2</sub>O<sub>2</sub> synthesis in anhydrous methanol as the solvent

As indicated above, the investigation of the synthesis of H<sub>2</sub>O<sub>2</sub> in anhydrous methanol allows to determine also the formation of water and therefore to obtain information on the rate of parallel conversion of H<sub>2</sub> and O<sub>2</sub> to water. Reported in figure 5 are the results

obtained for TMC-11 and TMC-2b membranes: formation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O as a function of time on stream and selectivity to H<sub>2</sub>O<sub>2</sub> with respect to H<sub>2</sub>. The symbols reports the experimental values, while the lines are calculated on the basis of the equations (5) and (6) and the rate constants reported in table 3. This table reports also the rate constants determined for TMC-2 membrane which results were omitted from figure 5 for clarity.

With respect to the rate constants determined using water as the solvent (table 2), the  $k_4/k_1$  ratio of the rate constants of synthesis and further conversion of H<sub>2</sub>O<sub>2</sub> is slightly higher in anhydrous methanol, but the trend is similar: TMC-2b > TMC-2b > TMC-1. The presence of a Pd thin film with respect to dispersed Pd particles reduces not only the rate of consecutive H<sub>2</sub>O<sub>2</sub> conversion, as noted using water as solvent, but also the rate of the parallel conversion of H<sub>2</sub>/O<sub>2</sub> to H<sub>2</sub>O, in agreement with the basic analogy of the sites involved in the two reactions discussed before and summarized in Scheme 3. As a consequence, the selectivity in Pd thin film membrane results higher than that of dispersed Pd particles.

The selectivity to H<sub>2</sub>O<sub>2</sub> decreases with time of reaction due to the increasing rate of H<sub>2</sub>O<sub>2</sub> reduction on increasing its concentration in solution.

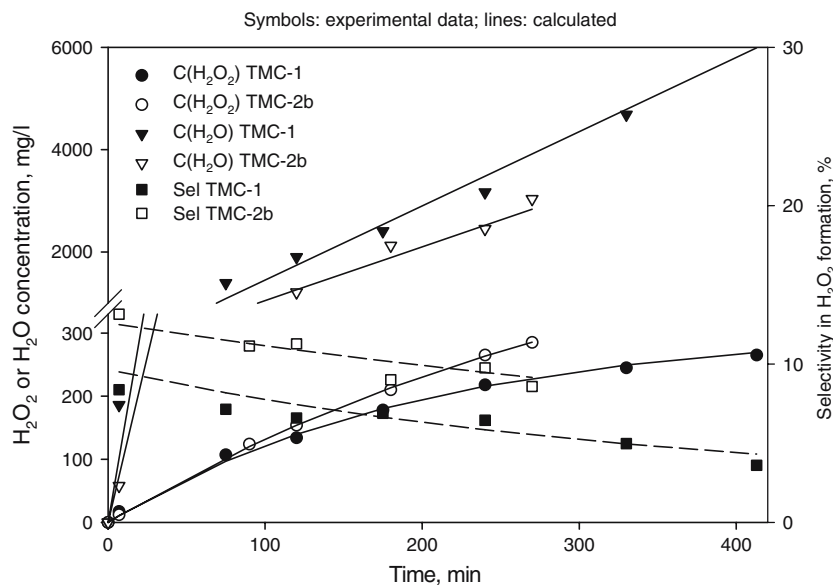


Figure 5. Dependence of the amount of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formed and of the selectivity to H<sub>2</sub>O<sub>2</sub> from the time of reaction for TMC-1 and TMC-2b membranes. Reaction conditions as in figure 2, except that anhydrous methanol was used as the solvent. The symbols represent the experimental values, while the lines were calculated from the equation (5) (for H<sub>2</sub>O<sub>2</sub>) and equation (6) (for H<sub>2</sub>O) using the rate constants reported in table 3.

Table 3

Rate constant of direct H<sub>2</sub>O<sub>2</sub> formation ( $k_1$ ) and of water formation (parallel and consecutive reactions to the H<sub>2</sub>O<sub>2</sub> formation;  $k_2$  and  $k_4$ , respectively) for all the used membranes

Code	$k_1$ , mol l <sup>-1</sup> min <sup>-1</sup>	$k_2$ , min <sup>-1</sup>	$k_4$ , min <sup>-1</sup>	100*k <sub>1</sub> /k <sub>4</sub>
TMC-1	7.75E-05	14.5	5.04E-3	1.53
TMC-1b	9.69E-5	7.7	5.43E-3	1.78
TMC-1 b1	11.4E-5	14.1	0.43E-3	26.4
TMC-1 b2	18.4E-5	15.4	1.24E-3	14.9
TMC-1 b3	18.9E-5	13.4	1.03E-3	18.3
TMC-1c	12.7E-5	5.7	5.88E-3	2.15
TMC-2	6.95E-5	11.3	3.64E-3	1.91
TMC-2b	7.57E-05	10.5	2.84E-3	2.67
TMC-2c	3.27E-5	21.7	3.83E-3	0.85
TMC-2d	0.24E-3	12.4	3.50E-3	7.02

Tests in anhydrous methanol. Reaction conditions as in figure 4. The rate constants were determined by fitting of the data reported in figures 5–7 using equations (5) and (6).

A =  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic membrane; CA = carbon-coated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic membrane.

PD = Precipitation–deposition ; EPD = Electroless plating deposition.

Composition of the active layer and approximated amount deposited on the membrane.

### 3.6. Effect of the second metal on the H<sub>2</sub>O<sub>2</sub> synthesis

The addition of a second metal to Pd was claimed in several patents [11,12,14] and in a scientific paper [22] to improve catalyst selectivity in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. The effect of the doping of Pd with a second metal (Pt or Ag) is summarized in figure 6 which reports the dependence of the selectivity to H<sub>2</sub>O<sub>2</sub> from the time on a series of catalytic membranes, either characterized from dispersed Pd–Me (Me = Pt) particles on carbon-coated ceramic membrane (TMC-1, TMC-1b, TMC-1c) or from a Pd–Me (Me = Ag, Pt) thin film on alumina ceramic membrane (TMC-2, TMC-2b, TMC-2c). Table 1 summarizes the characteristics of these membrane.

The effect of the doping with the second metal, which could form an alloy with Pd depends on the type of support, the method of Pd–Me deposition and the doping metal. In the membrane having dispersed Pd particles (TMC-1x series) the doping with Pt promotes the selectivity, with a maximum for a Pd:Pt ratio of 18, while the further increase of Pt decreases the selectivity. Hölderlich *et al.* [48,49] found that addition of Pt to Pd/TS-1 catalysts, stabilized a surface Pd<sup>2+</sup> oxidation state. The optimum level of Pt was found to be a balance between the desirable increase of Pd<sup>2+</sup> concentration and an undesirable change in the surface morphology of the Pd aggregates, from needle-shaped to spherical [48,50]. This is in agreement with our TEM observations

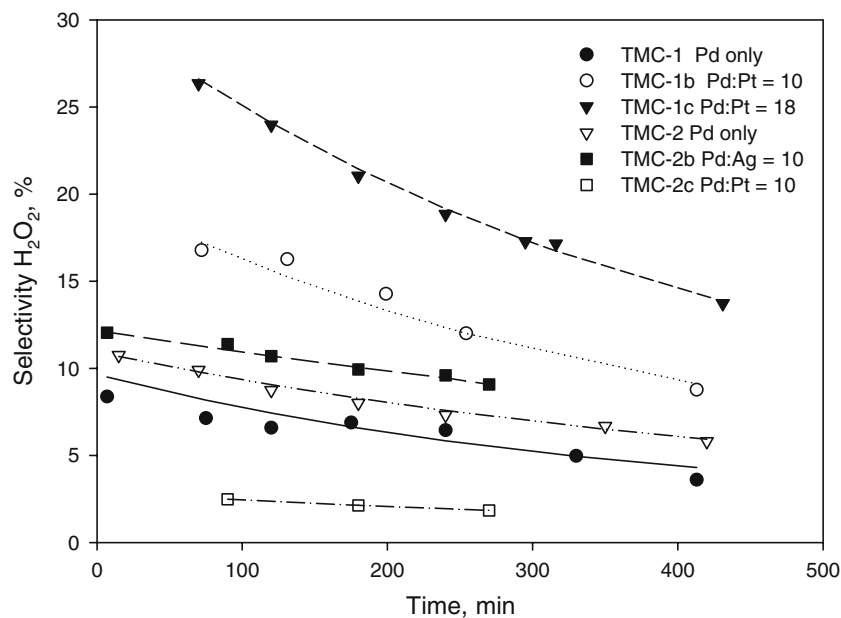


Figure 6. Dependence of the selectivity to H<sub>2</sub>O<sub>2</sub> from the time of reaction for TMC-1, TMC-1b, TMC-1c, TMC-2, TMC-2b and TMC-2c membranes. Reaction conditions as in figure 5. The symbols represent the experimental values, while the lines were calculated from the equations (5) and (6) using the rate constants reported in table 3.

[6b]. Pd-only samples possessed well-developed spherical particles, whereas bimetallic samples showed irregularly shaped particles. Moreover, the most active sample showed the smallest particles and a spread in the size distribution [6b]. Probably the effect of Pt addition is not be limited to the Pd particle morphology change, but for low levels of doping Pt would also block the surface Pd defects sites reducing the formation of HO<sup>-</sup> chemisorbed species that are favored on Pd<sup>0</sup> high energetic sites. In fact, the analysis of the kinetic constants (table 3) evidences that the effect of Pt is minimal on the  $k_4$  rate constant, e.g. on the rate of H<sub>2</sub>O<sub>2</sub> conversion, but very drastically depress the rate constant of the parallel reaction of H<sub>2</sub>O formation and increase the rate the rate of H<sub>2</sub>O<sub>2</sub> formation for the lowest amount of Pt doping (Pd:Pt = 18). A further increase of Pt (Pd:Pt = 10) instead causes a lowering of the selectivity which, however, still remains higher of that of the Pd-only sample.

The effect, however, is different in the case of thin film membrane catalysts. TMC-2c sample having a Pd:Pt ratio of 10 show significantly worsen selectivity with respect to TMC-2 (figure 6), due to a drastic increase in the rate of the parallel reaction of H<sub>2</sub>O formation (table 3). SEM data do not evidence significant changes in the morphology between these two samples, which could be instead identified in high-resolution transmission microscopy (TEM) images [30]. In fact, while TMC-2 is characterized by round shape and large metal particles, with dimension ranging from about 100–500 nm, the TMC-2c 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. These are reasonably responsible for the lowering of the selectivity significantly increasing the rate of the parallel reaction of H<sub>2</sub>O formation, while the effect is reduced on the consecutive reaction of H<sub>2</sub>O<sub>2</sub> conversion (table 3). Using Ag as second metal (TMC-2b), this morphological effect is instead not present and the membrane show better selectivity than the Pd-only thin film membrane (TMC-2). This suggests that the main role of the second metal is to influence the defective state of surface Pd particles more than an influence on the electronic and redox properties.

This concept is further supported from the analysis of the effect of the noble metal loading on the performances of the membranes in H<sub>2</sub>O<sub>2</sub> synthesis. Reported in figure 7 are the amount of H<sub>2</sub>O<sub>2</sub> formed after 270 min of reaction and the corresponding selectivity for a series of carbon-coated membranes having increasing loading with the noble metal doped with Pt (Pd:Pt = 10). Most of these membranes were prepared by precipitation–deposition, but TMC-2d was prepared by EPD on carbon-coated membrane and is thus characterized from the presence of a porous Pd/Pt thin film. Note that differently from the use of alumina as support (TMC-2c), the doping with Pt in the case of carbon-coated alumina membrane (TMC-2d) promotes the performances also in the case of the porous thin film samples.

Increasing the noble metal loading, there is an increase in both productivity and selectivity in H<sub>2</sub>O<sub>2</sub> formation, which then remains nearly constant above a loading of about 30 mg, independently on the method of noble metal deposition. Increasing the loading, there is a significant increase in the rate of H<sub>2</sub>O<sub>2</sub> synthesis and a decrease in the rate of the parallel reaction of H<sub>2</sub>O

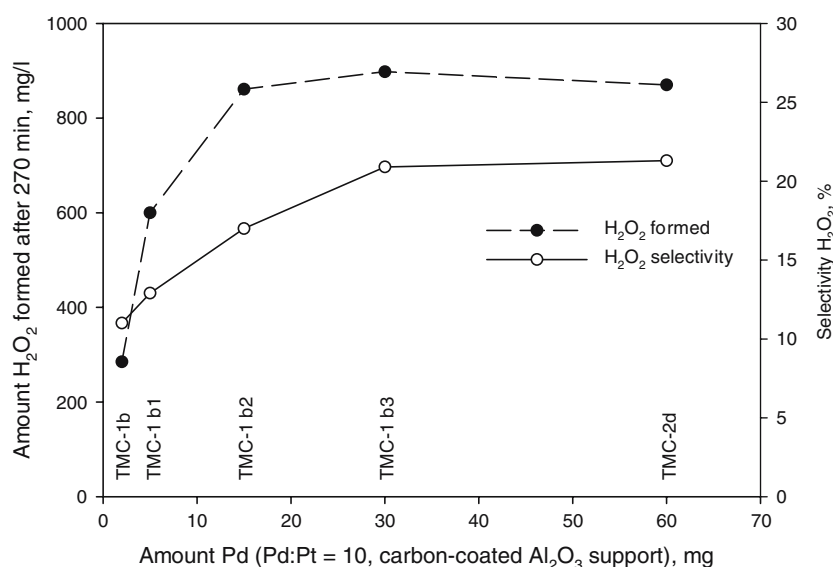


Figure 7. Dependence of the amount of H<sub>2</sub>O<sub>2</sub> formed after 270 min of reaction and of the corresponding selectivity to H<sub>2</sub>O<sub>2</sub> from the loading of the Pd for membranes having a Pd–Pt ratio of 10 and a carbon-coated alumina support. The figure also reports the corresponding codes for the samples.

formation, while the effect is reduced on the rate of consecutive H<sub>2</sub>O<sub>2</sub> conversion. Increasing the noble metal loading, progressively larger Pd particles are obtained thus reducing the presence of the higher energetic sites responsible of the O<sub>2</sub> dissociative chemisorption.

#### 4. Conclusions

The analysis of the dependence of the rate constants from both the nature of the catalyst membrane and the reaction conditions using a simplified kinetic approach provides some useful indication regarding the reaction network and mechanism of the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub>. Several factors in the preparation of these membranes as well as the reaction conditions (temperature, concentration of Br<sup>-</sup>, pH) determine the selectivity in H<sub>2</sub>O<sub>2</sub> formation, influencing the rate of the consecutive reduction of H<sub>2</sub>O<sub>2</sub> (which is faster with respect to H<sub>2</sub>O<sub>2</sub> decomposition on the metal surface) and/or of direct H<sub>2</sub> + O<sub>2</sub> conversion to H<sub>2</sub>O.

The same type of defective Pd sites are indicated to be responsible for the two unselective reactions leading to water formation (parallel and consecutive to H<sub>2</sub>O<sub>2</sub> formation), but the kinetic analysis shows that the rate constants of the two reactions are differently influenced from the catalytic membrane characteristics. This could be explained considering the stronger competitive dissociative chemisorption of O<sub>2</sub> with respect to H<sub>2</sub>O<sub>2</sub> and the presence of a pathway of breaking of the O–O bond in the chemisorbed peroxo species. This reaction is slow in the presence of proton or hydronium (which stabilize the peroxo adsorbed species), but faster in the presence of spillover hydrogen (Scheme 3).

The presence of dispersed Pd particles or of a porous thin film influences the membrane performances. The former show higher specific activity (turnover) in H<sub>2</sub>O<sub>2</sub> synthesis, but show also a higher presence of surface defects, which enhance the unselective transformation to water and therefore lower the selectivity. The doping with low amounts of Pt significantly decrease the rate of these unselective reactions, especially the parallel formation of water.

Increasing the noble metal loading on the membrane not only increases the productivity to H<sub>2</sub>O<sub>2</sub>, but also the selectivity, due to the formation of larger, less defective, Pd particles. The performances reach those observed for a membrane prepared by EPD method, which show, however, a very different behavior with respect to the doping with Pt. In fact, negative or positive effect was observed depending if alumina or carbon-coated alumina was used as the membrane support.

In conclusion, the analysis of the kinetic behavior of Pd-based catalytic membrane prepared by different methods and doped or not with a second metal (Pt, Ag) gives some useful indication regarding the reaction

network and mechanism, pointing out the possible role of defect sites, but also of the changes on the surface microstructure during the catalytic reaction. The better identification of the reaction mechanism requires the development of suitable methods for *in situ* characterization of the surface of Pd or Pd–Me particles during the catalytic reaction of H<sub>2</sub>O<sub>2</sub> synthesis. It may be also noted that the nature of the catalyst influences the selectivity in H<sub>2</sub>O<sub>2</sub> formation, but in a more limited range with respect to the effect of using a high O<sub>2</sub> partial pressure, which allows to increase the selectivity above 80%. This is consistent with the above discussion regarding the strong chemisorption of O<sub>2</sub> and the reactivity of surface species with spillover hydrogen (Scheme 3). Operations at high pressure (above 50 bars) are therefore necessary to combine a good selectivity with a good productivity.

#### Acknowledgments

Financial support from EU (NEOPS Project, contract No. G5RD-CT2002-00678) and MIUR (PRIN04 project “New eco-sustainable catalytic processes based on the synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub> and its integrated use in selective oxidation and depuration of emission processes”) is gratefully acknowledged. The authors are indebted to Dr. H. Richter (HITK e.V.) and Dr. S. Tennison (Mast Carbon Ltd.) for kindly providing respectively the  $\alpha$ -alumina tubular membranes and the carbon coating. Finally the author would thank P.D. Dr. Ing. Roland Dittmeyer and Mr. Karel Svajda from DECHEMA e.V. for the useful discussions regarding the kinetic modeling of the reaction.

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