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COMPARISON OF DIFFERENT SUPPORT TYPES FOR THE PREPARATION OF NANOSTRUCTURED CATALYTIC MEMBRANES

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Abstract. Different nanostructured catalytic membranes have been prepared by platinum deposition (evaporation-crystallisation and ionic impregnation) within the porous framework of different tubular porous supports of a few nanometer pore size. The aim of the work is to investigate the influence of preparation methods and the influence of the type of support on the properties of the obtained catalytic membranes. Some parameters of the preparation procedure, controlling the deposition performance, have been explored. Various types of supports made of different types of oxides and carbon with different layer distribution and pore diameters have been investigated. The catalytic membranes have then been characterised by hydrodynamic measurements as well as by electron microscopy. An attempt of correlation between the platinum distribution within the thickness of the membrane wall and the preparation parameters and support material was carried out.

1. INTRODUCTION

The preparation of unsupported and supported powder catalysts has been widely studied and mastered. However, the study of other support geometries, as monoliths or membranes, is not so advanced. This paper will focus on a catalyst deposition technique that can be used on a membrane being the central element of a catalytic membrane reactor. These reactors show a special advantage with respect to the synergy of the catalyst and the membrane when implemented in the same device. The catalytic membrane reactors have been divided in previous papers from our group in three categories: extractor, distributor and contactor [1,2]. Among these different types of catalytic membrane reactors, only the contactor-mode necessitates a catalytically active membrane. The two other types, extractors and distributors, generally combine a fixed-bed catalyst and a membrane that only controls transfers.

Our group has developed the use of catalytic membrane contactors for gas-liquid applications [3,4], with the idea of benefitting from the unique structure of a porous catalytic membrane, when compared to a conventional catalyst. As a matter of fact, the membrane pore, contrary to pores of conventional porous solids, presents two distinct ways of access, corresponding to the two sides of the membrane. In the interfacial contactor mode, the reactants are separately introduced from each side of the membrane, and meet in the catalyst zone [5]. Such configuration has been used in the case of non-miscible reactants, as in gas-liquid catalytic reactions. Contrarily to what is generally observed in conventional reactors, the gaseous reactant is no more limiting [3], its access to the catalyst being facilitated by the specific implementation of the in-

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terfacial contactor. In order to achieve such a result, the catalyst should be conveniently located, the position and loading of the active phase playing a major role with respect to the final reactor performance [6].

In this paper, we report on different possibilities for a controlled deposition of an active metal (platinum) in the pores of different types of oxide membranes as well as of carbon membrane. The influence of the preparation methods and the influence of the type of support on the properties of the obtained nanostructured catalytic membranes have been investigated.

2. EXPERIMENTAL

2.1. Support materials

The oxide membrane supports used in this work, provided by PALL EXEKIA, have a tubular geometry (external diameter 10 mm, internal 7 mm). They are made of 4 concentric layers. The first three layers are made of alpha-alumina surface coated with titania, showing an average pore size decreasing from the outside to the internal surface of the tube. The final mesoporous top-layer is located inside the tube. Two types of mesoporous layers have been used, made either of titania (10 nm average pore size) or zirconia particles (20 nm pore size). The samples have a total length of 100 or 250 mm.

Carbon tubular supports, provided by MAST, have been also tested. Contrary to the previous multilayered structures, the MAST supports present a single uniform layer. The porous structure is made of connected macropores combined with a secondary internal microporosity.

2.2. Catalytic membrane preparation

Two different methods, anionic impregnation and an evaporation-crystallisation technique, have been investigated for the platinum deposition in the porous framework of the oxide and carbon membranes. H_2PtCl_6 (Strem Chemicals, 39.85% Pt) has been used as a platinum precursor. All the tubes used during this work were firstly dried under air at 170 °C overnight. In several cases (for samples series PE1 and PE2), the support tubes were soaked in distilled water prior to catalyst deposition. In order to provide a more homogenous contact of the solution of hexachloroplatinic acid with the support, the magnetic stirring (used for sample series PE1, PE2 and PE3) was replaced by a mechanical stirring (for all other sample series). Details concerning the preparation of catalytic membranes are summarised in Table 1.

Anionic impregnation. For this type of deposition (denoted as AI), the tubes were soaked for 4 h in a 0.5 gPt/l H_2PtCl_6 aqueous solution and then washed three times for 20 minutes in 0.1 N HNO_3, until the concentration of Pt species in the wash-water was negligible. The impregnated membranes were then dried in nitrogen flow (60 ml/min) at 100 °C for 1h (heating rate of 1 °C/min.) and then calcined at 200 °C in nitrogen flow (60 ml/min) for 2h (heating rate of 1 °C/min.) in order to decompose the Pt precursor, introduced within the membrane wall. The gas flux

Table 1. Characteristics of the oxide and carbon impregnated membranes (each sample from a sample series being identified with an additional subscript letter).

Sample series	*Delivered by*	*Top layer*	*Length,* mm	*Method of deposition*	*Absorbed* H_2PtCl_6, ml	*Pt amount,* mg
PE1$_a$		10 nm TiO_2	100	Evap. A*	–	3.9 [1]
PE2$_{a\text{-}b}$		10 nm TiO_2	100	AI*	–	0.5 ± 0.2 [2]
PE3$_a$		10 nm TiO_2	100	Evap. A	1.0	10 [1]
PE4$_{a\text{-}c}$	PALL	10 nm TiO_2	250	Evap. A	2.9-3.3	24-34 [1]
PE5$_{a\text{-}e}$	EXEKIA	20 nm ZrO_2	250	Evap. A	3.2-3.7	32-39 [1]
PE6$_a$		20 nm ZrO_2	250	Evap. B	3.7	41 [1]
PE7$_{a\text{-}b}$		20 nm ZrO_2	250	Evap. C	3.7-3.8	33-38[1]
M1$_{a\text{-}b}$	MAST	carbon	100	AI	2.7-2.9	10 ± 0.1 [2]
M2$_a$		carbon	100	Evap. A	2.7	85 [1]

* – the sample has been pre-soaked in distilled water for 2 h before impregnation

[1] – calculated by mass uptake; [2] – measured by ICP

was then switched to hydrogen for 12 h, the platinum species being then reduced to metal particles [1].

Evaporation-crystallisation deposition. Different techniques, based on the so-called "reservoir" method [7-9], have been investigated. Using the standard technique (Evap. A), the tube was soaked overnight in a 10 g Pt/l H_2PtCl_6 aqueous solution. The sample was then kept at room temperature under air and rotated, in order to allow the evaporation and uniform distribution of the precursor solution. Two alternative ways of deposition based on this technique have been used. In the first one (Evap. B), the tubular support was soaked in the 10 gPt/l H_2PtCl_6 precursor solution, as for method A, but during the evaporation step the ends of the tube were tightly capped to allow evaporation only through the larger pore (external) side of the support. In the second one (Evap. C), the external side of the tube was covered with PTFE foil in order to allow the penetration of the platinum precursor only from the mesoporous top-layer (internal side of the support) to the larger pore (external) side of membrane. Contrarily to the previous method, the evaporation step occurs only through the pores of the internal side of the tube.

2.3. Characterisation

Gas permeation measurements were performed before and after Pt deposition using a conventional set-up [9]. The estimation of the amount of platinum deposited within the wall of the membrane was based on one hand on the mass uptake during the deposition and on the other hand on the quantity of precursor solution which was absorbed within the pores during the soaking step, in the case of the evaporation-crystallisation procedure. Chemical analyses by ICP (Inductive Coupled Plasma) of the impregnation solutions was also carried out, before and after catalyst deposition, in order to estimate the amount of deposited Pt after of anionic impregnation. The results obtained through these three methods were found to be in good agreement.

The impregnated membranes were characterised by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Electron Probe Micro-Analysis (EPMA), Energy Dispersive x-ray Spectroscopy (EDS) as well BackScattered Electron (BSE) imaging. The EDS analysis was performed using a stationary probe of approximately 0.5 μm in diameter at three positions in the inner surface top layer. Measurements were made at the very inner surface, the middle of the layer and close to the interface with the substrate. The samples for EPMA analysis were prepared by standard metallographic procedures, mounting in resin, grinding on silicon carbide paper, followed by a final polish using diamond paste. EMPA composition line profiles were performed at 100x magnification with an accelerating voltage of 10 kV and a step size of one micron. EPMA composition line scans were recorded, running from a few microns inside the mounting resin, through the inner top layer and into the support layer. Normalised Pt levels were measured for each sample. The BSE images were recorded at low magnification, to give an overview of the whole tube structure, and at intermediate and higher magnification to show the structure of the inner surface of the top layer and its support.

3. RESULTS AND DISCUSSION

Oxide membranes. In the case of anionic impregnation, the structure of the oxide membranes does not seem to be modified after Pt deposition, since only negligible changes with respect to the nitrogen permeance were found. For the sample series PE2, only a very low amount of ca. 0.5 mg Pt was obtained by ICP. The TEM analysis, recorded on the sample $PE2_a$, showed that the TiO_2 top layer is approximately 3 microns thick. EDS showed no significant Pt signal from this sample, above the level that can reliably be quantified by the EDS technique. The very low amount of platinum deposited using this technique can be attributed to the lack of chemical interactions between the anionic precursor and the surface species of the support.

In the case of the *evaporation-crystallisation*, the oxide impregnated membranes showed nitrogen permeances in the range of 15-30 $\mu mol/m^2 \cdot s \cdot Pa$ depending on the sample. Since a decrease of less than 15% was observed with respect to the permeance values before and after deposition, it can be assumed that the structure of the membrane has not been modified. The deposited platinum amount, depending on the length and type of the tube, is presented in Table 1.

It can be mentioned that the pre-soaking in distilled water leads to a much lower amount of deposited platinum, as on sample $PE1_a$, when compared to sample $PE3_a$. Normalised Pt levels of ~0,8 at% and 3.2 at% were measured for the sample $PE1_a$ and $PE3_a$, respectively. The visual appearance of sample $PE1_a$ showed clear inhomogeneity in coverage of the inner surface layer that was not observed for the other analysed samples. In the case of sample $PE1_a$ the dissolved precursor reaches the support porous framework by diffusion within an aqueous phase, while in the case of sample PE3$_a$, when no pre-soaking in H_2O was used, the whole precursor solution is soaked in the pore system by convection, due to capillary forces.

Keeping in mind the difference in tube length between sample series PE3 and PE4, the amount of platinum deposited was similar. However, stronger and more homogeneous catalyst particle distribution is visible in sample PE4$_a$ relative to sample PE3$_a$. This can be related to the more homogenous stirring during the impregnation provided by the mechanical system that replaced the magnetic stirring used for sample PE3$_a$. The TiO_2 top layer was found to be about 3 microns thick for both sample series. Platinum particles of approximately 3 to 5 nanometres have been detected. EDS confirmed the presence of a significant level of Pt in the TiO2 top layer. A significantly lower Pt concentration was measured immediately below the mesoporous layer. Pt was also detected in the alumina titania surface coated sublayer in intergranular location with particle dimensions between 10 and 50 nm.

Different alternatives based on the *evaporation-crystallisation* technique (Evap. A, B and C) have been used on 20 nm pore top layered ZrO_2 supports (sample series PE5-7) in order to investigate their influence with respect to the location of platinum within the membrane structure. The BSE images of the samples in series PE5-7 showed the structure of the material with the first three macroporous layers made of alumina covered by titania and the Pt/ZrO_2 top layer. This was confirmed by EPMA observations. The top layer showed bright contrast in the inner layer, consistent with it being of relatively high average atomic number. The Pt/ZrO_2 inner top layer is slightly less than 3 microns thick. The EPMA scans illustrate clearly the location of the Pt within the mesoporous top layer. Concerning the TEM analysis, it must be mentioned that the difference in atomic number between Pt and Zr is not as large as with Ti. Consequently, the relative image contrast of the Pt particles is not so strong in a ZrO_2 support. Based on the TEM analysis, Pt was found to be concentrated in the ZrO_2 top layer. As experienced previously, some Pt was found between the alumina grains in the macroporous sublayer, generally in the form of larger particles, mixed with the titania surface modification material. Comparing the impregnated 20 nm top layered zirconia (sample series PE5) with impregnated 10 nm top layered titania (sample series PE4), the type of support seems to have no significant influence with respect to the deposition of platinum when using the evaporation-crystallisation method.

The samples in series PE5 showed a homogenous distribution of Pt within the mesoporous top-layer. On sample PE6$_a$, some inhomogeneity, showed by a light grey/brown coverage that became darker moving into the tube from the impregnated end, was revealed by visual evaluation. However, the EPMA analysis demonstrated that the platinum was mainly deposited within the top-layer. Pt typical particle size may have been slightly larger (>10nm) in sample series PE7 than in the others sample series (PE5 and 6). The TEM showed also a higher Pt/Zr ratio in sample series PE7. In the case of this sample series, the EPMA scans illustrate the location of Pt mainly in the top-layer, but it was clearly shown that some significant amount of platinum is concentrated around the interface between the top-layer and the substrate and further into the substrate as well (Fig. 1). A strong “darker” band of contrast that was observed immediately adjacent to the titania modified alumina substrate in sample PE7$_a$ in TEM observation (Fig. 2), was found to contain a higher level of Pt and some of the Pt particles appeared larger than in the rest of the ZrO_2 layer.

Carbon membranes. In the case of the anionic impregnated carbon membrane (M1) the whole amount of platinum contained into the precursor solution (10 mg Pt in 20 ml of solution used for the contact with the support) has been introduced into the structure. The support structure provides a high exchange capacity due to the surface species characteristic of the carbon material. The sample M2,

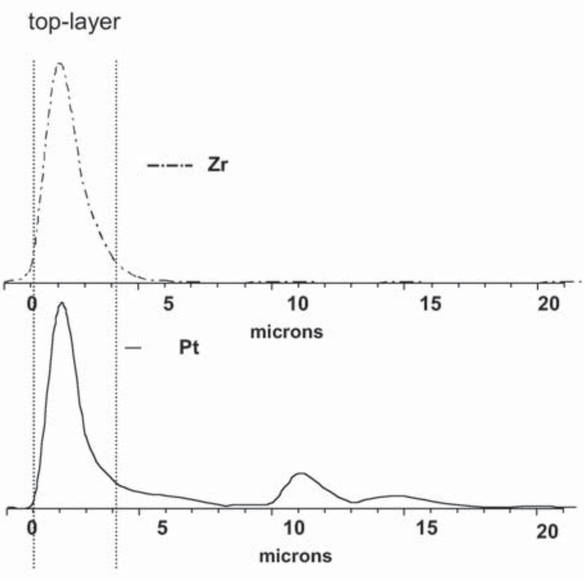

Fig. 1. EPMA line-scans of Pt and Zr levels from a cross-section of sample PE7$_a$.

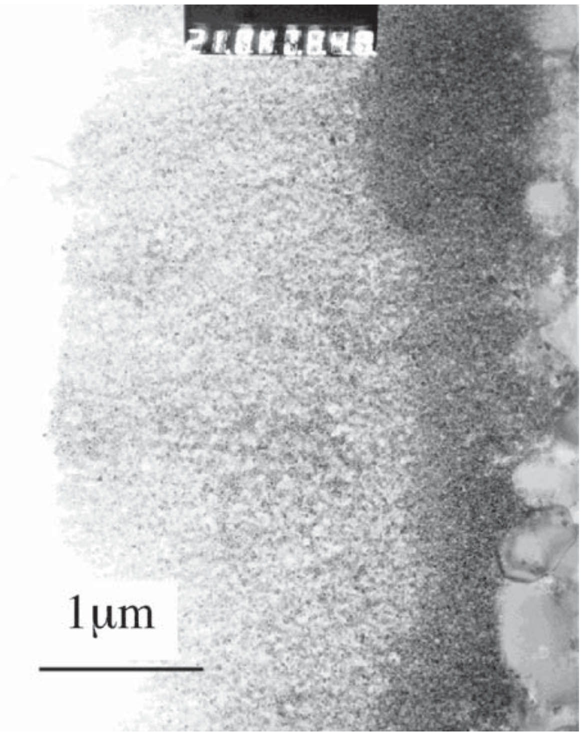

Fig. 2. TEM micrograph of sample PE7$_a$ showing the microstructure of the ZrO_2/Pt top-layer and substrate.

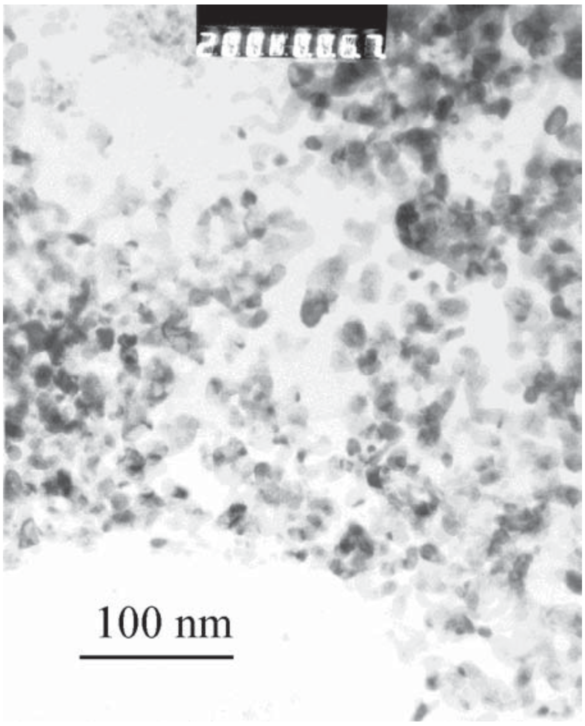

Fig. 3. TEM micrograph of sample M2 showing the morphology of the individual particles in a Pt cluster.

prepared using the standard evaporation technique (Evap. A), was found to contain 85 mg Pt. Taking into account that ca. 2.8 ml of absorbed precursor solution was measured (corresponding to ca. 28 mg of Pt), the Pt deposited can be attributed mainly to the ionic exchange during the contact of support with the precursor solution. The permeance was found to be for both samples series in the range of 30-35 μmol/m^2·s·Pa, with a decrease lower than 15% after the platinum deposition, that suggested no structure degradation.

On both membranes, Pt is distributed throughout the whole wall, as particles on carbon grain surfaces and between grains. In the case of the sample series M2, the TEM and SEM examination show a bimodal distribution of particles. The distribution was quite inhomogeneous. The SEM images show globules with diameters up to several hundred nanometers. On TEM micrographs, clusters including individual particles with size from 10 up to 50 nm (Fig. 3) were observed. The clustering can be attributed to defects in the porous system that lead to local accumulation of precursor solution. For sample M2$_a$, SEM and TEM examination showed that individual globules and clusters of globules were present on the internal grain surfaces in the material. EPMA measured low levels of Pt throughout the material, with no special concentration at the tube inner surface. Keeping in mind that the carbon supports possess a symmetric structure, the absence of the enrichment at the inner surface can be explained by the fact that no capillary forces are present in order to force the precursor solution to move.

4. CONCLUSION

Various deposition techniques have been applied to different nanometer-pore sized membrane support structures. As a function of the support characteristics, e.g. chemical nature, pore size and layer structure, the approaches used gave different results.

Chemical interactions between platinum precursor and surface species is an important parameter for the choice of the deposition method. The intensity and localization of the interaction sites will determine the amount and distribution of platinum particles. In the case of the evaporation-crystallisation technique, the deposition of platinum is mainly controlled by physical parameters.

Metallic platinum nanoparticles are generated in all cases. Nevertheless, the anionic impregnation approach generally led to better dispersion.

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