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Preparation and characterisation of a Pt/ceramic catalytic membrane

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Abstract

Anionic impregnation was used to depose platinum onto a porous membrane to be used in a gas–liquid contact Catalytic Membrane Reactor. This membrane was a tube made of several layers, with a decreasing pore size in the radial direction to the axis. The top layer was mesoporous (pore diameter ≈ 5 nm), and made of titania. An amount of 5 nm of Pt crystallites were selectively deposited to this porous zone and formed branched-shape particles. Their distribution in the membrane was precisely monitored using electron microscopopy (SEM, TEM and attached analysis methods). The membrane integrity was checked by nitrogen permeation experiments. Other characterisation techniques included XRD (crystallite size) and N_2 adsorption (pore size distribution). © 2001 Elsevier Science B.V. All rights reserved.

Resumé

L'imprégnation anionique a été utilisée pour déposer du platine dans une membrane poreuse destinée à un Réacteur Catalytique Membranaire contacteur gaz-liquide. Ce tube était composé de plusieurs couches possédant une taille de pores décroissante vers l'axe, le long du rayon du cylindre. La couche supérieure, en anatase, était mésoporeuse (diamètre de pore ≈ 5 nm). Des crystallites de Pt de 5 nm environ ont été sélectivement déposés dans cette zone mésoporeuse, et ont formé des particules branchées. Leur distribution spaciale dans la membrane a été précisément controlée par microscopies électroniques (MEB, MET et leurs méthodes d'analyse liées). L'intégrité de la membrane a été vérifiée par perméation d'azote. D'autres méthodes de caractérisation incluaient la diffraction de rayons X (pour la taille des crystallites) et l'adsorption d'azote (pour la distribution de tailles de pores). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the first days of heterogeneous catalysis, the preparation of unsupported then supported powder catalysts has been widely studied and

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mastered. In the case of another support geometry, as with monoliths or membranes, the situation is not so advanced. This paper will focus on a catalyst deposition technique that can be used on a membrane, turning a porous tube into the central element of a catalytic membrane reactor (CMR). CMRs can be defined as reactors drawing a special advantage from the synergy of the catalyst and the membrane when implemented in the same device.

As conventional catalytic reactors are traditionally classified into different types, such as fixed or fluidised bed, batch reactors and many others, CMRs have been divided in previous papers from our group in three categories. Each class can be characterised according to the physical process the membrane is involved in within the reactor.

1.1. Extractor CMRs

Gryaznov and others pioneered the historically first type of CMR [1–3]. It is the well-known extractor type, widely experimented for dehydrogenation reactions for example. In this configuration, the membrane, commonly a palladium-based one, selectively removes hydrogen from the catalyst fixed bed with which it is in contact. This selective extraction brings about the famous equilibrium shift, that will allow much higher conversions than what is limited by thermodynamics in a conventional fixed bed reactor. In this case the synergy advantage described earlier is obvious, it is that equilibrium shift.

1.2. Distributor CMRs

A second type of CMR can be established when the membranes is used as a distributor [4], as illustrated in Fig. 1.

In this situation, the membrane is used to introduce the second reactant all along the length of the catalyst bed, in order to avoid a secondary reaction. This chemical selectivity is indeed an advantage obtained from the coupling of the catalyst and the membrane. These reactors can be applied, for example, to partial oxidation reactions, as shown by Mota and co-workers [5].

1.3. Contactor CMRs

The third physical process in which the membrane may be involved is the triple contact between two different reactant fluid phases and the catalyst. In conventional reactors, one of the reactant is usually favoured by the fact that the catalyst on its support is dispersed in its phase, allowing an easy contact between the two. Nevertheless, the second phase reactant has to suffer access limitations due to the distance between the two-phase interface and the catalyst. Moreover, even in an ideal triphasic reactor, the catalyst is usually deposited in dead-end, or at least in a difficult access, pore of the support. The chemicals must then migrate into the support particle down to the catalyst itself in order to react. This process usually results in some access hindrance for one of the two reactants.

The contactor type CMRs offer an improvement for that unfavoured reactant, with two handling possibilities. The first alternative is the flow-through contactor, in which a solution of the two reactants is forced through the membrane, constraining both reactants to come close to the catalyst particle. As a matter of fact, the catalyst particle is here deposited in a membrane double-ended pore, through which the pumped flux imposes the triple contact explained above [6–8].

The second alternative can be called the interfacial contactor. In this case also, the catalyst particles are included into the pores of the membrane, but this time each fluid phase is located on one side of the membrane. The operational conditions allow a proper location of the interface, which is in the catalysed zone of the membrane.

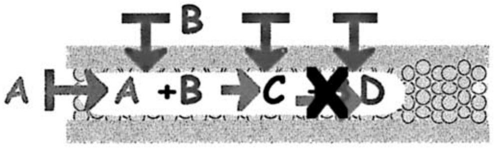

Fig. 1. Principle of the CMR of the extractor type. Packed particles of catalyst can be seen in a tubular membrane in which is introduced the first reactant, A, and through which permeates the second reactant B, to lead to product C, without the secondary reaction to D.

Such a system has been studied thoroughly through the model reaction of nitrobenzene hydrogenation [9]. In this case, nitrobenzene was in solution in ethanol on one side of the membrane, and hydrogen was placed on the other side. The membrane consisted of a multilayer alumina tube, with the internal surface coated with γ-alumina of about 10 nm pore size. In this layer was deposited platinum particles used as catalyst for the reaction. Operational conditions allowed us to maintain the interface located into that γ-alumina top layer, showing a kinetic order of zero relative to the gaseous reactant, hydrogen, whereas this order has been observed to be one in a conventional triphasic batch reactor. It was then demonstrated that the reactor design in itself favoured the access of the gas to the catalytic zone.

In order to achieve such a result, a need to prepare the catalytic membrane in a suitable way, i.e. to locate the catalyst right in the mesoporous top layer zone. This paper presents the results of the preparation of a catalytic membrane where the mesoporous interface zone is not made of γ-alumina, but of titanium dioxide. As a matter of fact, γ-alumina is not adapted for all applications as it is a very sensitive to corrosion. Titanium dioxide is much more resistant, which could give the prospect for the use of the interfacial contactor type CMR in other applications, where the liquid phase might be corrosive.

2. Experimental

2.1. Materials

The membranes used in this work are provided by TAMI. They are made of four layers. The largest layer is a mixture of α-alumina, zirconia and titania with a 10-μm pore size and a 2-mm thickness. The two subsequent layers are made of titania and titania/zirconia and the top layer of pure rutile titania (Fig. 2). The membrane is tubular and has an internal diameter of 6 mm, an external diameter of 10 mm, a total length of 10 cm.

The platinum precursor used to prepare the catalytic membranes was a H_2PtCl_6 solution from Aldrich Chemical.

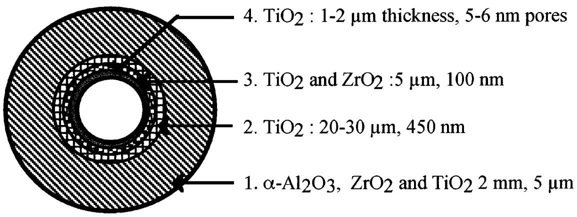

Fig. 2. Schematic cross-section of the membrane showing the four layers, their thickness and pore sizes.

2.2. Membrane preparation

The technique used here is inspired by a similar protocol widely practised on powder supported dispersed catalysts, and is referred to as anionic impregnation. This method has proved to be efficient in obtaining well-dispersed Pt metal particles [10] in order to reach the highest active surface.

The support membrane was sunk into a stirred solution of hexachloroplatinic acid ($pH = 2.5$, $[Pt] = 2.5\ 10^{-4}$ mol/l) for 4 h after soaking in distilled water. It was then washed three times 20 min in 0.1 N nitric acid, until the concentration of Pt species in the wash-water were negligible. Then, the membrane was dried under nitrogen atmosphere at 100°C for 1 h, and the temperature was increased slowly to 200°C to decompose the impregnated Pt precursor (activation step). The gas flux was then switched to hydrogen for 12 h, in order to reduce the Pt(II) species to metal particles.

2.2.1. Characterisations

Chemical analyses by ICP (inducted coupled plasma) of the impregnation solutions were carried out before and after catalyst deposition, in order to estimate the amount of deposited Pt.

The mass uptake of the membrane was also carefully controlled, after sufficient drying, in order to avoid water condensation in the mesopores.

Nitrogen permeation measurements allowed us to follow any structure degradation of the permeance-limiting top layer. It was measured using a home-made apparatus, with an overpressure on the tube side and the atmosphere on the shell side. No sweep gas was used and the flux was measured at the inlet of the device.

XRD spectra of powder scratched from the top layer of the membrane gave information on the deposited platinum crystallite size. This was obtained on the (111) Pt peak, situated at $2\theta = 39.7°$, after careful calculations, due to a close TiO_2 peak at 39.2°. Carried out on the same powder, nitrogen adsorption experiments were interpreted according to the DFT (density function theory), and provided data on pore size distribution of the membrane.

Scanning Electron Microscopy (SEM), in backscattering electron (BSE) mode was used for imaging. Electron probe micro-analysis–wavelength dispersive X-ray spectroscopy (EPMA-WDS) was then used to have a fist estimate of the Pt location along the cross-section of the membrane. The samples were prepared by cutting and polishing.

Transmission Electron Microscopy (TEM) was more precise for the determination of the catalyst location, using imaging and energy dispersive spectroscopy (EDS). The sample preparation was more difficult as it implied reducing the thickness of a porous solid to less than 100 nm. The membrane tube was first cut in four quarters, along the axis of the cylinder. Two quarters were then glued together. The resulting stack of material (mainly porous ceramic filled up with epoxy glue) was then ground to cylindrical rod of 3 mm diameter. Then, this rod was sliced into a disk of low thickness (less than a mm). The disk thickness was reduced by mechanical means down to about 30 μm in the centre. Further thinning to the final thickness was obtained by argon ion milling in a Gatan PIPS ion mill.

3. Results

3.1. Characterisation of anionic impregnation membranes

3.1.1. Mass, gas permeation and pore size distribution

The weight difference was similar to the value determined from the analysis of the impregnation solutions. The membranes were found to contain about 3 mg ± 0.1 of Pt.

Nitrogen permeation was in the range of 20–35 $\mu mol/(m^2/s/Pa)$ before deposition, depending on the sample. Out of the nine samples prepared, none shown a change of more than 15%. Therefore, the structure of the membrane seems to have not been modified.

The DFT pore size measurement shown a distribution between 4 and 6 nm with a maximum of 5 nm diameters.

3.1.2. DRX

X-ray diffractogram on powder scratched off from the inside of the tubes provided a Pt crystallite size of about 5 nm, as shown in Fig. 3.

3.1.3. SEM-BSE and EPMA-WDS

Fig. 4 shows the SEM-BSE image and the EPMA-WDS platinum analysis for the same zone. The adjacent images show the three last layers of the membrane, with Pt dispersed in the mesoporous top layer on the left-hand side. Note the thickness of the platinum-loaded zone is in the order of a micrometre, which corresponds to that of the mesoporous top layer. This means an important part of the platinum is deposited in that layer.

3.1.4. TEM and EDS

Fig. 5 shows transmission electron microscopy (TEM-EDS) of the membrane. Black dots can be seen in the mesoporous top layer, which were identified as platinum particles. More precisely, the distribution of the particle is concentrated in the first half of the top layer depth. A higher magnification shows that the particles are

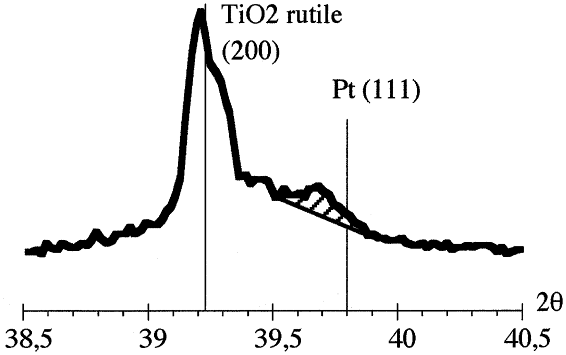

Fig. 3. XRD spectrum of scratched powder, showing the integration of the (111) Pt peak used to determine the crystallite size.

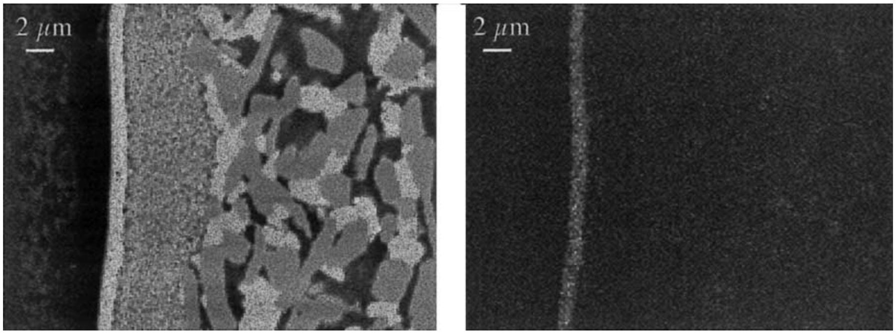

Fig. 4. SEM-BSE image (left) and platinum EPMA-WDS cartography (right) of the last layers of the catalytic membrane.

branched-shaped, and seem to be made of joined 5-nm components.

Pt/Ti EDS analysis of the top layer confirmed that the black dots are made of platinum, as shown in Fig. 6.

4. Discussion

According to the SEM characterisation results, the platinum loading was mainly located in the mesoporous top layer (Fig. 4). To explain this, the mechanism of anionic impregnation needs to be taken into account. In this case, the precursor solution pH (2.5) was below the isoelectric point of the support (≈ 6). As stated by many authors on conventional powder supports [11,12], the equation involved in the impregnation can then be written as (with S figuring the support):

$$\mathrm{S{-}OH} + \mathrm{HPtCl_6^-\,H^+} \leftrightarrow \mathrm{S{-}OH_2} + \mathrm{HPtCl_6^-}$$

In our system, when the membrane was rinsed, it retained as much precursor as its surface contained surface groups. Then, during activation under nitrogen, the impregnated species were degraded and reduced under hydrogen to form particles.

Of course, the amount of surface groups increases with the surface area. As the mesoporous TiO_2 layer, due to its small pore size, exhibited most of the surface area of the whole membrane, most of the groups were located in that layer, therefore most of the platinum was also deposited in that zone.

The results of the TEM studies first corroborated the small Pt crystallite size obtained from XRD studies (5 nm). Even if this could be considered quite large, it is actually larger than the particles obtained on a γ-alumina membrane [13]. Nevertheless, it is a well-known phenomenon that the Pt particle size on titania is larger than on alumina on powder support.

TEM studies were also more precise regarding the particle location. It can clearly be seen on the images (Fig. 5), that Pt was located mainly in the first half of the top layer. This was confirmed by the Pt/Ti EDS analysis (Fig. 6). This is not in contradiction with the SEM EPMA-WDS results, as the accuracy of this technique is noticeably lower.

The question remains why the catalyst was not homogeneously distributed over the whole mesoporous top layer. Two hypotheses can be considered. On one hand, the top layer material may have been heterogeneous itself, i.e. the surface groups may have been less frequent in the deeper zone. One the other hand, the precursor might have faced access limitations during the impregnation step, which prevented it reaching the deepest part of the top layer. Or, the result might be explained from a contribution of both phenomena. Further investigations will be necessary in order to clarify this point.

One has to notice, however, that the catalyst location corresponded to a zone that is quite thin. As a matter of fact, when the membrane is used in a biphasic catalytic membrane reactor, the 2-phase interface will have to be maintained in the catalytic zone, and only the catalyst in that zone

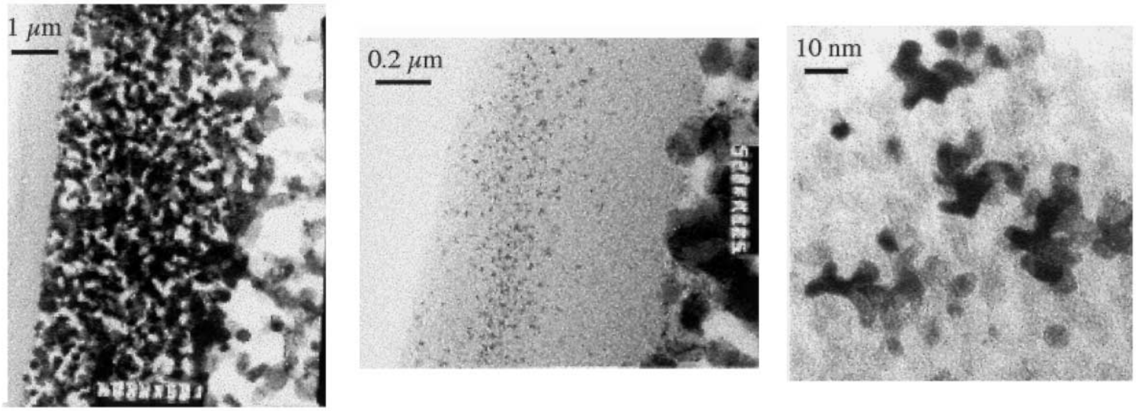

Fig. 5. TEM last layers of the catalytic membrane (growing magnification from left to right). One can distinguish the platinum particles located into the first half of the mesoporous top layer.

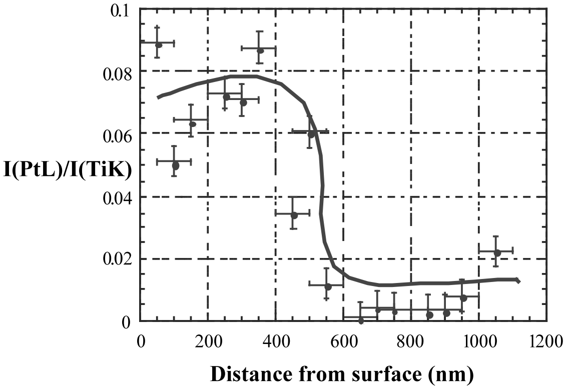

Fig. 6. EDS ratios of Pt over Ti according to the depth in the membrane top layer after catalyst deposition.

will be used. Therefore, any precious metal dispersed out of the interface zone would be lost, and it favours a higher economic efficiency to be able to limit the distribution to such a tight zone. Of course, the catalytic region must not be too thin, in order to allow some flexibility in the operating conditions of the reactor, and thereafter in the location of the interface.

5. Conclusion

The deposition of platinum on a ceramic porous multilayer membrane was controlled in order to be limited to the mesoporous top layer that is used as an interface zone in a biphasic catalytic membrane reactor. To achieve this goal, anionic impregnation was used.

The result was checked thoroughly by physical characterisation techniques, and particularly by electron microscopy. The platinum was located in the first half of the depth of the mesoporous top layer. The platinum crystallites were about 5 nm in diameter, forming branched-shaped aggregates of about 10 to 20 nm.

The membrane is to be tested in a biphasic gas–liquid catalytic membrane reactor.

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