

Catalysis in membrane reactors: what about the catalyst?

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Catalytic membrane reactors (CMRs) combine a membrane that controls transfers and a catalyst that provides conversion. This paper focuses on the catalyst itself. Depending on the application, the environment of the catalyst in the CMR may be quite different from that existing in conventional reactors. This could originate changes of the catalyst properties. In some cases, catalysts for CMRs might require a specific design.

KEY WORDS: membrane catalysis; catalysts for membrane reactors.

1. Introduction

Since the early days of membrane catalysis, most of the attention has been devoted to the membrane, its role, characteristics and performance. This is probably due to various facts. A large part of the groups involved in the development of membrane catalysis had a membrane science background, and mainly focussed on this material. Also, many analyses of the potential of catalytic membrane reactors (CMRs) used a modelling approach, and the membrane separative property rapidly appeared as the key parameter of the reactor performance. In most of these initial studies, the catalyst was considered as a “black box”, with intrinsic characteristics and properties deduced from those observed in conventional reactors.

In this paper, the attention will be focused on the other partner of membrane catalysis, i.e., on the catalyst itself. We will see how the specific conditions prevailing in membrane reactors may modify the catalyst state and properties in comparison to conventional systems. Some examples from the literature that illustrate the subject will be given.

Let us underline that this contribution is not a revue describing all types of catalysts that have been used in combination with membranes. Its goal is more to show that sometimes, beside a proper membrane, CMRs may need a proper catalyst.

2. How to classify CMRs?

There are numerous ways of combining a catalyst and a membrane. Moreover, depending on the membrane role, the catalyst may be placed in a very different situation. All this makes a global analysis almost impossible.

A classification of CMRs has been proposed according to the way of combining catalyst and membrane [1].

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The main criterion is based on the presence in the CMR of a catalytic membrane (the same material acts as catalyst and membrane) or of an association of a conventional catalyst (packed or fluidized bed) and a membrane that just rules transfers. Another classification is based on the membrane role [2]. As a matter of fact, as schematized in figure 1, the membrane can have 3 very different functions according to the CMR type:

(i) The membrane can be used to remove a reaction product from the reaction zone. This type of CMR, called *extractor*, is certainly the most studied. An extractor can be used to increase reaction yields. This is obtained either by improving the conversion in equilibrium-restricted reactions or, in consecutive reactions, by improving the selectivity towards a primary product *via* its selective extraction through the membrane [1].

(ii) The membrane can control the introduction of one of the reactants in the reaction zone. This type of CMR, called *distributor*, is used to spread a reactant all along the catalytic zone, in which the other reactant is introduced as usually. In this way, when compared to conventional reactors, though the same (or even larger) amounts of the distributed reactant can be introduced, its concentration is kept at a low level in the entire reaction zone. This low concentration may increase the selectivity of reactions when the distributed reactant can undergo successive additions. Selective oxidations (hydrogenations) can be improved in distributor-type CMR if a membrane distributes oxygen [3,4] (hydrogen [5]). Another advantage of such reactor is related to flammable mixtures [6]. Due to the low O₂ concentration in the catalyst bed, the local reactants composition can be kept outside the flammability region, though the total amount of reactants introduced corresponds to a ratio that is forbidden in conventional reactors.

(iii) A membrane may be used to facilitate the contact between reactants and catalyst. This CMR type, called *contactor*, takes advantage of the very unique configuration of the membrane pore, which contrary to pores of

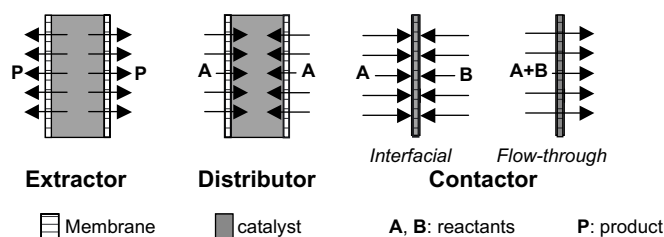


Figure 1. Sketch of the different CMRs.

conventional solids, presents two distinct ways of access, corresponding to the two sides of the membrane. In contactors, the membrane generally also acts as catalyst support (or is intrinsically active). A contactor can be used following two modes (figure 1). In the *interfacial contactor* mode, the reactants are separately introduced from each side of the membrane, and meet in the catalyst zone. Such configuration has been used in the case of non-miscible reactants, as in gas-liquid catalytic reactions [7–9]. It has been pointed out that, contrary to what is generally observed in conventional reactors, the gaseous reactant is no more limiting [8]. Dense polymeric membranes containing metal catalyst encaged in zeolites have also been used as interfacial contactors in the case of non-miscible aqueous and organic reactants [10,11]. In this case, the polymeric membrane favours the transfer of the organic reactant to the active phase, which allows the contactor to perform better than conventional reactors. The other contactor mode is the *flow-through contactor*. In this second mode, the mixture of reactants is forced through the membrane, i.e. through the catalytic pores. Contact time and permeation regime in the active pore *itself* can be directly adjusted from the operative conditions and adapted to required values, which is hardly feasible in conventional reactors. Such reactors have been used for gas and gas-liquid reactions, and showed improvements in activity [12,13] and selectivity [14].

Let us now have a look to the situation of the catalyst in these three different CMR configurations. A first question is:

3. CMRs: a catalytic membrane or a conventional catalyst with a membrane?

The choice will depend on the CMR type and the application concerned.

3.1. Extractor

From the literature, it appears that in most examples of the *extractor* mode, the catalyst is a conventional packed-bed (more rarely, a fluidized one), combined with a membrane acting only as a transfer-control material. Both catalyst and membrane should have compatible capabilities. In an extractor, the membrane

must extract the amount produced by the catalyst and inversely, the catalyst must generate enough product that ought to be extracted.

However, there are also some examples of extractor using a *catalytic membrane*. Nevertheless, in such arrangements, the amount of catalyst is often too small to compete with the membrane efficiency. A *porous* catalytic membrane does not seem to be the right material, as reactants will have to penetrate in the active pore, and therefore might also diffuse without reaction to the permeate side. *Dense* Pd membranes, used as catalytic membranes for equilibrium displacement of hydrogen-producing reactions, do not suffer from reactant loss. However, their intrinsic catalytic activity is generally insufficient for industrial application in dehydrogenation or reforming processes. Therefore, they are often combined with a conventional fixed-bed that provides most of the catalytic conversion.

3.2. Distributor

Here also, the literature gives mainly examples of CMR combining conventional catalysts and transfer-control membranes. However, are catalytic membranes suitable materials for such application? A *porous* catalytic membrane will more act as a contactor, as both reactants may penetrate into the active pore. The control, in the reaction zone, of the ratio distributed/non-distributed reactants will be difficult, as it will depend on different parameters, such as the reactants diffusivities, the position of the catalyst, the reaction kinetics, etc. *Dense* mixed-oxide membranes, developed to separate oxygen from air, are used for hydrocarbon partial oxidations in CMR. Oxygen from air is selectively fed through the dense membrane, in a distributor configuration. The mixed-oxide membrane itself is catalytically active and it has been proposed [15] that the oxygen species diffusing through the membrane generate at its surface very active and selective oxygen entities that give higher yields than molecular oxygen. However, these membranes are also combined with fixed-bed catalysts in some studies [16].

3.3. Contactor

Per se, the concept of contactor necessarily involves the use of catalytic membranes, because reactants are

either fed from each side of the membrane (interfacial contactor) or forced to flow through the active pore (flow-through contactor).

4. How could a membrane modify the catalyst way of life?

4.1. Extractor

When compared to a conventional reactor, the removal of a reaction product will change the composition of the reactive mixture existing around the catalyst, which may affect (positively or negatively) its performance in terms of activity, selectivity or stability.

4.1.1. Catalyst activity

In the case of equilibrium-restricted reactions, the selective extraction of a reaction product by the membrane will shift the equilibrium. The higher the extraction efficiency, the higher is the shift. In principle, if the extraction is selective, the reaction conversion may increase up to 100%. However, this is not the case if the catalyst intrinsic efficiency is too low to follow the membrane performance. For these conditions, the catalyst itself will limit the CMR performance. Even if the catalyst was active enough to reach equilibrium in a conventional reactor, it may not be effective enough in the extractor.

Such a situation has been illustrated in a detailed study of isobutane dehydrogenation in an extractor-type CMR [17–20]. The catalyst, a PtIn/zeolite-based phase, has been chosen on the basis of activity and especially stability criteria, after a comparison with typical dehydrogenation catalysts [17]. Placed in a conventional fixed-bed reactor, this catalyst allowed equilibrium conversion.

Two types of tubular membrane were used for the CMR study. A first membrane was obtained by MFI zeolite crystallization in the macropores of a tubular α -alumina host material (Pall-Exekia T1-70), using the pore-plugging method [21]. In gas separation experiments (i.e. without catalyst), this membrane showed $H_2/i-C_4$ separation coefficients close to 8 or 10 (co or counter-current sweep, respectively) for the experimental conditions used ($T = 730$ K, sweep to feed flow-rates ratio = 4). It was also observed that hydrogen extraction was close to 100% in counter-current sweep mode, and only 80% when a co-current sweep was used. Therefore, a better performance was expected when operating the CMR with a counter-current sweep gas. Contrariwise, very similar isobutene yields, near 35%, were observed for both sweep modes, the thermodynamic equilibrium in a conventional reactor under similar conditions being close to 10%. However, if with a co-current sweep the retentate composition always corresponded to equilibrium, this was not the case for

the counter-current sweep mode. For this last mode, the higher the sweep, the larger was the gap between the retentate composition and that corresponding to equilibrium.

In the co-current sweep mode, and whatever the sweep flow rate used here, an almost similar H_2 partial pressure existed in both retentate and permeate sides at the reactor outlet. Therefore, the driving force for hydrogen permeation was very low at the end of the catalyst bed, and the catalyst was always able to achieve the equilibrium conversion. The situation was different with the counter-current sweep: at the reactor outlet, the higher the sweep flow rate, the higher the driving force for the hydrogen permeation. When the hydrogen extraction rate existing at the end of the fixed bed happened to be higher than the reaction rate allowed by the catalyst, the CMR performance became limited by the catalyst itself [17]. This limitation has been confirmed by a modelling approach [18] that combined catalyst kinetics [19] and membrane separation laws. If the model well fitted experimental results in the co-current sweep mode, it predicted higher conversions for the counter-current sweep, because the kinetics used in the model supposed that thermodynamic equilibrium would be achieved.

A second membrane, obtained by Pd electroless deposition on the same tubular support [22] has been combined with the same catalyst. In $H_2/i-C_4$ separation, as expected, the Pd membrane showed a better performance than the zeolite one (60 versus 10). Moreover, the hydrogen permeance was also higher for the Pd membrane (6 times). In principle, for the $i-C_4$ dehydrogenation in CMR, such properties of the Pd membrane tip the scales in its favour when compared to the zeolite membrane. However, the two membrane materials gave the very same performance under the same conditions [20]. Again, this was due to the limitation of the catalyst that could not follow, in both cases, hydrogen extraction. Figure 2 shows that both membranes gave similar conversions, and that the model predicts for the Pd membrane a better performance than the zeolite one, on the basis of its better H_2 extraction data.

This example clearly shows that the catalyst may play a key role. There are likely other cases among all the studies reported in the literature, where the CMR performance is limited by the catalyst, and not by the membrane properties.

To elude this situation, it could be thought about a catalyst activity improvement through the experimental conditions. This could be done by an increase in contact time and/or reaction temperature. However, these parameters may also affect in a positive way the membrane extraction and therefore not really change the situation in favour of the catalyst. Moreover, in the above-mentioned example of isobutane dehydrogenation, the hydrogen permeation rate at the outlet of the reactor is more than one order of magnitude larger than

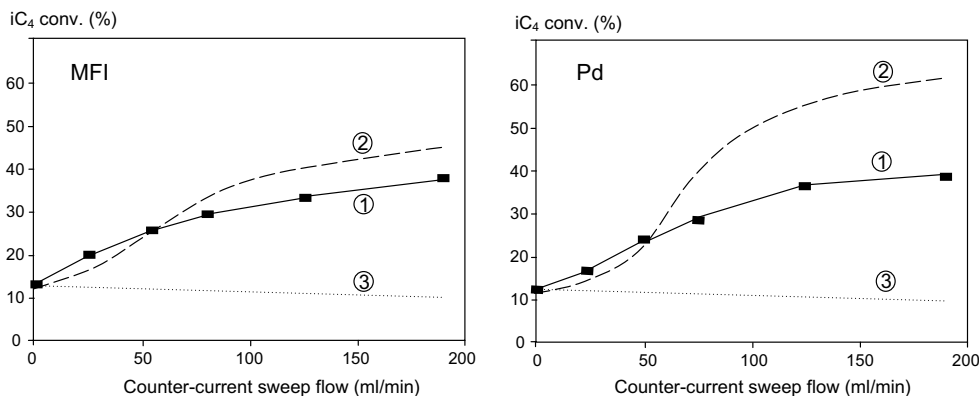


Figure 2. Isobutane dehydrogenation in an extractor-type CMR. Left, MFI-zeolite membrane; right, Pd membrane. (1) experimental data; (2) modelling; (3) thermodynamic equilibrium in a conventional reactor (the slight decrease is due to the pressure increase with the sweep flow) [20].

the catalytic conversion rate, thus making difficult for the catalyst to catch up with the membrane.

Another way would be to play with the ratio (catalyst volume)/(membrane area). However, this may be limited in the case of fixed bed catalysts, as the extraction efficiency may suffer from an increase of the distance between catalyst and membrane. Solutions could be found in fluidized bed catalysts or conversely, in hollow fibres distributed in a fixed-bed.

A further solution would be to design catalysts presenting a higher activity. This is certainly not the easiest way, as a lot has already been made for conventional dehydrogenation processes. Nevertheless, due to the new set of experimental conditions brought about by CMRs, one can think that there is still work possible in this direction.

It should also be noticed, that, in some cases, even if a reaction did not reach equilibrium, the selective extraction of a reaction product by the membrane may affect in a positive way the catalyst activity. This is especially the case if the extracted product has a negative order with respect to the reaction kinetics [23].

4.1.2. Catalyst selectivity

In an extractor-type CMR, the membrane can affect the catalyst selectivity following different ways.

There will be a positive effect on the selectivity if the extracted product may participate in non-desired secondary or side reactions. Besides being selective, the product permeation should be of course faster than secondary or side reaction rates. The extracted species could be either a co-product (e.g. hydrogen in dehydrogenation reactions) or the target product. Such a positive effect has been reported for ethylbenzene dehydrogenation, where the extraction of the hydrogen co-product limits the undesirable hydrogenolysis side reactions [24,25]. In other examples, the targeted product is selectively extracted [26,27], producing a clear increase of the yield. It also has been pointed out, that beside the positive effect on the selectivity itself, the

extraction of a product may also increase the contact time and concentration of reactants, thus favouring conversion.

4.1.3. Catalyst stability

Though subject of a rather limited consideration, this is likely one of the key points of the catalyst behaviour when placed in a CMR. As a matter of fact, the specific conditions prevailing in an extractor might promote or even mutate deactivation mechanisms.

For instance, the withdrawal of hydrogen during dehydrogenation in a CMR will likely favour coking processes, which are already crucial in conventional dehydrogenation (in the UOP Oleflex process the feed even contains H₂ to limit deactivation). This problem has been recently pointed out in a study of propane dehydrogenation in an extractor-type CMR [28]. In this study, two typical commercial dehydrogenation catalysts, a bimetallic PtSn/Al₂O₃ and a Cr₂O₃/Al₂O₃, have been combined with microporous silica membranes showing hydrogen permeances adapted to the catalyst activities. The obtained performances were compared to those of the same catalysts placed as fixed-bed in conventional reactors. If, as expected, the initial propene yields were clearly higher in the CMRs, the membrane reactors showed a faster performance decline than the conventional ones. After 3 h time on stream, depending on the catalyst used, the CMRs gave either equivalent or even lower C₃H₆ yields. These results were attributed to an enhancement of coke deposition owing to the hydrogen removal through the membrane. In their conclusions, the authors underlined that more stable catalysts have to be developed for such membrane reactor application.

There are other equilibrium-restricted reactions that might suffer from enhanced catalyst deactivation when performed in an extractor-type CMR. For instance, hydrocarbons steam reforming or ethylbenzene dehydrogenation are commonly performed using a steam-hydrocarbon feed, and the hydrogen generated by the

reaction certainly participates in the preservation of an adapted oxidation state of the catalyst. The situation would be quite different should there be a continuous extraction of hydrogen, and new deactivation processes may take place.

There are however examples where the product extraction affects in a positive way the catalyst stability. Such effect has been reported during Fischer–Tropsch synthesis when the water produced by the reaction is removed by selective permeation through a zeolite ZSM5 membrane [23]. It is indicated that, as water deactivates Fe-based catalysts and moreover tends to oxidize metallic Co- and Fe-based catalysts, the use of a membrane extracting water from the reaction zone favoured the global performance.

4.2. Distributor

When compared to what exists in a conventional reactor, the distribution of one reactant through the membrane will modify the local reactant composition in the catalyst bed. This may directly affect the catalyst state.

Distributors have mainly been used for selective oxidations and oxidative dehydrogenations. Figure 3 schematises the oxygen distribution for the selective oxidation of *n*-butane to maleic anhydride. As one goes along the vertical axis from the butane feed inlet to the retentate outlet, there is a permanent change of the oxygen to butane ratio. As a matter of fact, the butane concentration decreases due to its conversion, when the oxygen concentration will increase due to its continuous introduction. As a result, the catalyst placed at the butane inlet is placed in a reducing atmosphere, while, on the other hand, the catalyst at the end of the bed is in a more oxidative medium. It has been shown [29] that a conventional VPO catalyst placed under a reaction mixture similar to that existing at the butane inlet of the CMR was rapidly reduced (disappearance of the V^{5+} species). In parallel, its selectivity to MA decreased to zero at the benefit of a butene formation *via* the ODH

reaction. Contrariwise, the catalyst at the outlet was placed in oxygen/butane ratios higher than that existing in a conventional reactor. In average, the gradient of the VPO oxidation state existing in the CMR led to a MA yield a bit lower than that observed in a conventional reactor [2]. However, it was possible to take benefit of this gradient and of the local over-oxidation of the catalyst, by reversing the butane flow. After the reversal, the hydrocarbon first penetrated in the oxygen-rich VPO zone, leading to a transient high MA productivity, while the previously reduced VPO area is progressively re-oxidized, thus allowing subsequent butane flow reversal [2].

The same VPO catalyst works under very different conditions and state in a distributor CMR and in a conventional reactor. However, thanks to its very flexible V^{4+}/V^{5+} redox system, the reduced VPO catalyst can be easily reactivated under oxidative reactant mixtures. If this property makes him a potential candidate for CMR distributor application, the VPO solid suffers from its bad performance at the butane inlet, where exists a low O_2 /butane ratio. A way to limit this is to add some oxygen to the butane feed, thus improving the situation at the butane inlet [2,30].

A more convenient solution is to design a new catalyst, adapted to this type of CMR. This catalyst should be able to produce maleic anhydride even under a low O_2 /butane ratio. This was obtained by doping the VPO system by Co or Mo additives [31]. Such modified catalysts were able to keep active V^{5+} surface species even under a O_2 /butane molar ratio of 0.6. Contrary to the normal non-doped VPO systems, they showed a stable maleic anhydride production under these reducing conditions [31]. These doped VPO solids are an example of catalysts especially developed for CMRs.

Beside selective oxidations, distributors can be used for selective hydrogenations, hydrogen being progressively introduced through the membrane [5]. In this case also, the catalyst will work under a gradient of reactant composition, with a low H_2 concentration at the catalyst bed inlet, which may cause local deactivation.

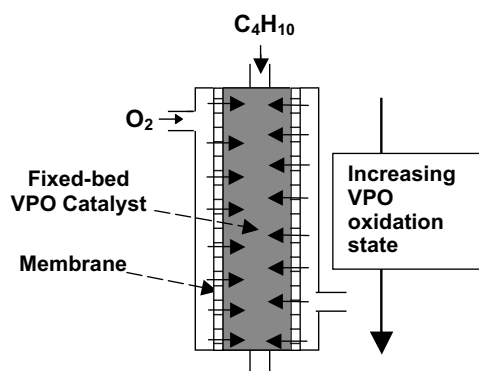


Figure 3. Schematic representation of a CMR distributor for butane selective oxidation.

4.3. Contactor

In *contactors*, catalyst and membrane are combined in a catalytic membrane and act in symbiosis. Therefore, this section will focus on the catalytic membrane rather than on the catalyst itself.

In opposition to the previous extractor and distributor modes, in a contactor, there is neither removal nor progressive introduction of any of the species involved in the catalytic process. Here, the objective is more to make use of the membrane structure, which acts as catalyst support, to optimize access of disfavoured reactants [7,10] or to control and rule residence time and contact of species in the active zone [12,14].

For the catalyst itself, the environment will not be modified in a dramatic way, as was the case in extractors or distributors. A catalyst placed in a contactor will simply take benefit from the better transfer and membrane active role in promoting the contact of the reaction partners. Very likely, as far as its chemical composition is concerned, a conventional active phase will be suitable for CMR contactors.

However, the other part of the catalytic membrane, i.e., the membrane itself, will play an important role. The membrane structure and properties should be specifically adapted to the contactor operational conditions.

As far as *interfacial contactors* are concerned, a key point is the localization of the reactants encounter, which must occur in the very volume where the catalyst was deposited. CMR interfacial contactors frequently use membranes showing a multilayered structure made of a macroporous support and a mesoporous top-layer. In the case of gas-liquid reactions, two different configurations may be used, the liquid reactant being fed either from the macroporous side (mode A) or from the mesoporous one (mode B), the gas being fed from the other side [8]. The best mode will likely depend on the reaction considered, as mass transfer resistances within the gas or the liquid phases may be direct functions of the species involved, of the nature of the membrane material surface, and of the experimental conditions. According to the literature, either mode A [7,8,32] or B [33,34] has been preferred.

In mode A, due to capillary forces, the gas-liquid interface will be located in the mesoporous top-layer, close to the external surface, unless is applied a gas overpressure higher than the pore-flushing pressure, as given by the Kelvin equation for the top-layer. In this last case, gas will flow through the membrane and the reactor will no more operate as an interfacial contactor.

In mode B, in theory, the gas-liquid interface can be moved continuously within the macroporous layers till the mesoporous top-layer, by increasing progressively the gas overpressure [35] up to the Kelvin's pore-flushing pressure of the top-layer.

The maximum gas overpressure that can be used in the contactor may be important on the viewpoint of the catalyst performance. In principle, for both modes A and B, according to Kelvin's equation, the maximum gas overpressure will be fixed by the nature (surface tension) of the liquid and by the pore size and contact angle between the liquid and the pore surface of the top-layer. As an example, with a gamma alumina top-layer of 10 nm pore size, in presence of water at room temperature, a gas overpressure as high as ca. 300 atm can be maintained in the contactor. As a consequence, beside choice between modes A and B, the characteristics of the membrane top-layer, such as its average pore size or its surface hydrophilicity properties, have to be carefully tuned up according to the contactor applica-

tion. However, in reality, due to the existence of a pore-size distribution, the maximum pressure will be fixed by the largest pores of the distribution. Moreover, in presence of defects, the operational overpressure could be much lower than expected. When using mode B, defects may even prevent controlling the gas-liquid interface position, as this interface will be moved preferentially through the defect.

The membrane geometry, and especially its pore size distribution is also a critical parameter in the *flow-through contactors*.

In gas-phase reactions, a recent study [12] demonstrated that the pore size, and accordingly the flowing mode through the membrane, was of primary importance for the CMR performance.

For both gas or gas-liquid phase reactions, in the presence of large pore size heterogeneity, the transmembrane flow will go preferentially through the largest passing-through pores, leading to a large distribution of residence time in the catalytic membrane pores. This is of course contrary to what is expected with a flow-through contactor. Moreover, in presence of large defects, the reactants will preferentially go through defects, most of the catalytic membrane being much less effective.

Beside the membrane structure, the localization and the loading of the catalyst within the membrane porous network have to be controlled [36]. Generally, it should be located in the top-layer, where the contact between the reactants and the supported catalyst is favoured and easier to control. As the top-layer presents smaller pore sizes and a larger specific area than the other layers, the deposition of the catalyst shall be favoured there. In principle, this occurs whether the catalyst application involves interaction with the membrane material, as it is the case when using anionic impregnation, or does not, as when using the evaporation-crystallization method [36]. Let us underline that catalyst localization and loading are also of importance in the case of dense polymeric membranes used as interfacial contactors [11].

5. Conclusion

According to the various CMR types and applications, the membrane and catalyst have quite different functions. Therefore, both of them will require adapted characteristics and properties.

In *extractors*, the membrane should present a high separative performance (permeance and selectivity). This is the only type of CMR where the membrane actually acts as a withdrawal barrier, as in conventional separative processes. The catalyst should present a level of efficiency in keeping with that of the membrane. This may require the development of highly active solids when the membrane is used under high extractive

conditions. Also, the catalyst should be able to withstand the specific reactive mixture generated by the product removal, which may originate deactivation phenomena.

In *distributors*, the membrane is basically a diffusion barrier used to equally spread out a reactant in the catalyst volume. In principle, the transmembrane transfers being mainly controlled by pressure gradients across the membrane, a large range of various materials and porous structures can be used [37]. The choice is of course restricted when the membrane also separates the distributed reactant from a mixture (e.g., O₂ from air). As far as the catalyst itself is concerned, the presence of a reactant composition gradient all over the membrane reactor may change the nature of the active phase. The design of an adapted catalyst may be necessary.

In *contactors*, the catalyst and the membrane are combined. The membrane support should present a rather homogeneous structure to avoid heterogeneities in the reactant-to-catalyst contact and also to facilitate CMR operation control. As for the catalyst, it should be located, in the membrane, in a position favouring the contact. Therefore, it will principally take benefit of the better access of, and contact with, the reactants. Beside this macroscopic viewpoint, its composition does not seem to require specific modifications from conventional active phases.

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