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Dense organic catalytic membranes for fine chemical synthesis

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Abstract

As membrane reactors are mostly applied at high temperatures, organic polymers are generally out of focus for preparing the catalytic membranes. The much milder conditions encountered in fine chemical synthesis justify their use in this area. As a dense polymer, they can actively interfere in the reaction by modulating sorption and diffusion of reagents and products, leading to significantly enhanced catalytic activities. Both heterogeneous and homogeneous catalysts can be occluded. For the latter, these membranes additionally provide an easy way of dispersing and immobilising. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Dense membranes; PDMS; Catalysis; Fine chemicals; Catalytic membrane reactor

1. Introduction

Catalytic membrane reactors (CMRs) are generally applied in high temperature reactions (400–1173 K) [1]. It is therefore not surprising that organic polymers are hardly ever used as material for catalytic membranes, as they lack thermal and chemical stability under these harsh conditions. In the field of fine chemical synthesis, however, much milder conditions are generally applicable and organic polymers were applied successfully [2–12]. Whereas Armor [13] states that some of the main challenges for inorganic, porous membranes in CMRs are the control of the thickness, the large-scale preparation, and the crack free membrane synthesis, all these are much less problematic with polymer-based catalytic membranes. Furthermore, in contrast to porous membranes, a dense polymer phase can actively take part in the reaction by influencing sorption and diffusion of reagents and products.

The most studied polymer system for catalytic reactions is undoubtedly polydimethylsiloxane (PDMS) [2–12] (Fig. 1). This highly permeable elastomer is prepared easily and combines a fairly high thermal (up to 250°C) and mechanical stability with chemical resistance, the latter being of utmost importance under reactive conditions.

Some general consideration of these dense, organic catalytic membranes will be given first before illustrating their potential in fine chemical synthesis with two selected examples.

2. Membrane preparation

Depending on the nature of the catalyst — homogeneous or heterogeneous — different requirements are imposed on the membrane synthesis. PDMS (General Electric, RTV-615) is a two-component system (Fig. 1), consisting of a vinyl terminated prepolymer with high molecular weight and a cross-linker,

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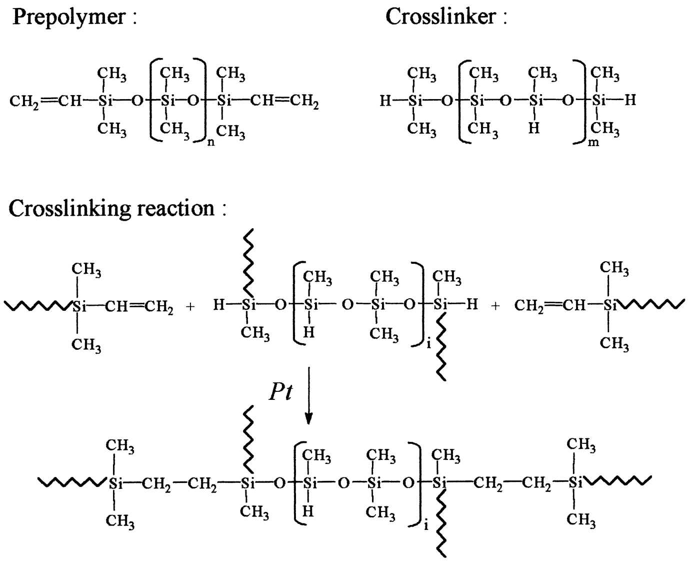

Fig. 1. Cross-linking reaction of PDMS.

containing several hydride groups on shorter polydimethylsiloxane chains. The PDMS-membrane is cured via a Pt-catalysed hydrosilylation reaction to form a densely cross-linked polymer network.

The incorporation of a solid phase catalyst in a polymer matrix is the least crucial. A good dispersion of the heterogeneous catalyst in the polymer solution should be realised before membrane casting. In order to improve the dispersion of the catalyst in the polymeric solution, the use of a solvent is mostly necessary to decrease the viscosity of the prepolymer/cross-linker mixture. Whereas the solvent improves the dispersion, problems can occur with such diluted mixtures at the moment they are cast to form a membrane. Indeed, the solid phase catalyst might settle down from the casting mixture while the solvent evaporates. This can be prevented by including a prepolymerisation step [14]: before the catalyst is added, the two PDMS-components are mixed in a solvent and partially cured by slightly increasing the temperature for a certain period (typically 1 h at 60°C for a 25 wt.% PDMS-solution). The thus formed partially cross-linked polymer network prevents the catalyst from settling down during solvent evaporation. When incorporating wide pore heterogeneous catalysts (zeolite Y, [3,8] MCM-41, [7] ...), this synthesis procedure has additional advantages. Indeed, unreacted PDMS-chains might sorb in the pores of the catalyst when these are large enough (from ± 6 Å onwards) [15], rendering the catalytic species inside the pores inaccessible for the reagents. Evidently, when such catalyst is contacted with a prepolymerised PDMS-network, pore blocking is excluded.

The synthesis of PDMS-membranes containing homogeneous catalysts is more complicated as dissolution of the catalyst forms a new prerequisite. Moreover, the number of solvents suitable for dissolution is restricted since the polymer should also dissolve and cure in it. For PDMS, this restricts the choice to apolar and low boiling solvents like chloroform, dichloromethane, hexane, toluene and methylisobutylketone. Indeed, the solvent should be removed at temperatures where the catalyst remains stable. Application of a vacuum during solvent evaporation might help to realise this.

An even more complex synthesis mixture arises when additives are co-incorporated in the membrane. It was found that certain compounds, like *p*-toluene sulphonic acid or 4-phenylpyridinoxide (4-PPYNO), co-incorporated with the Ru–BINAP-complex ([2,2′-bis(diphenylphosphino-1,1′-binaphtyl]chloro(*p*-cymene)-ruthenium chloride, Fig. 2) and the Katsuki-catalyst (Fig. 3), respectively), could only be occluded in PDMS in low concentrations. High concentrations prevented the PDMS-polymer from curing, possibly due to interaction of the additive with the Pt-catalyst needed for the PDMS cross-linking.

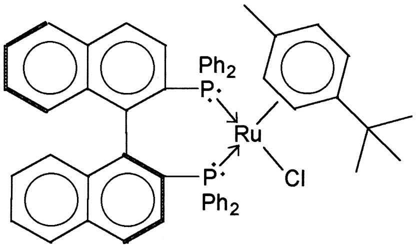

Fig. 2. Ru–BINAP.

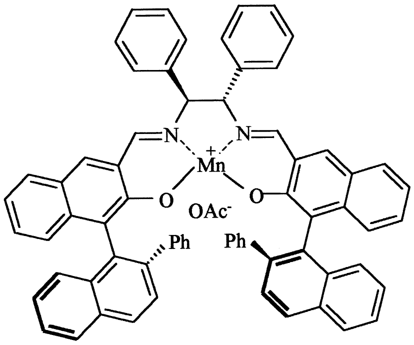

Fig. 3. Katsuki catalyst.

A way to circumvent these curing problems was found for the TDCPP(Mn)Cl complex ([5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] manganese (III) chloride, Fig. 4). Imidazole and 1-butylimidazole were used here as axial ligands for the complex. Their supplementary coordination around the transition metal is essential in order to allow epoxidation of deactivated substrates such as 3-penten-2-ol with H_2O_2. Co-incorporation of the axial ligand with the complex at the moment of membrane synthesis was impossible as curing of the PDMS-polymer was inhibited. So as to avoid this problem, the transition metal complex was first immobilised in the polymer without axial ligand. It was only after complete curing of the catalytic membrane that imidazole was added as an aqueous solution: the rather hydrophobic imidazole was selectively sorbed from the water into the membrane. Spectroscopic evidence (UV–Vis) showed that the imidazole ligand formed indeed a real coordinative link with the porphyrin metal centre, even in the constraint environment of the PDMS-polymer.

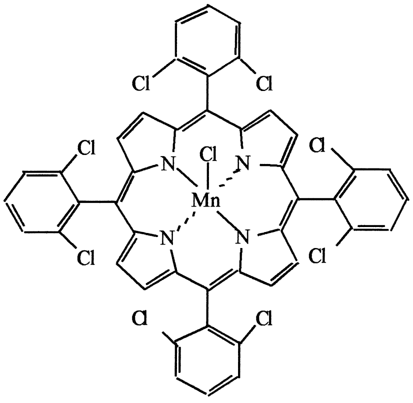

Fig. 4. TDCPP(Mn)Cl.

Spectroscopy (ESR, UV–Vis,. . .) also showed that homogeneous catalysts like TDCPP(Mn)Cl are incorporated in PDMS without disturbance of their structure and free of electronic interactions between the central metal ion and the surrounding polymer [12]. The results obtained with the chiral catalysts [4,11] indirectly confirm the preservation of the intact structure, since too strong an interaction between the polymer and the complex would destroy the chiral induction.

3. Membrane polymer properties

Apart from being chemically, thermally and mechanically stable, one of the most important properties of the membrane polymer is its affinity for the reagents. The Hildebrand affinity parameter [16] Δ can be used for its predictive value in selecting an appropriate polymer for a certain reaction. A high $\Delta^{\text{polymer-reagent}}$ value indicates a low affinity of the polymer for this reagent, thus a low sorption and a limited availability of the reagent at the catalytic site. Depending on the activity of the catalyst, this sorption might become rate determining in the reaction and another polymer choice might be more appropriate then.

On the other hand, it is not only sorption that is important for the catalytic reactions, but also diffusion of the components through the polymer. This diffusion is partly influenced by the sorption: a high sorption of a component means a strong swelling of the polymer and thus an increased sorbent mobility. Another important factor in this respect is the degree of polymer cross-linking. In first instance, this degree is determined by the polymer composition, but the presence of

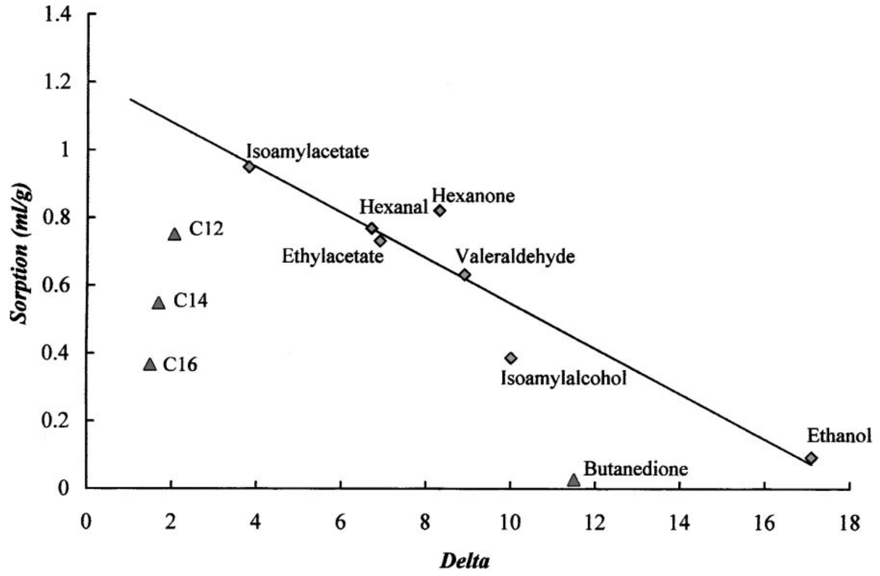

Fig. 5. Sorption (ml/g) in PDMS as a function of Hildebrand parameters for a set of organic compounds (C12, C14 and C16 refer to methyl laurate, methyl myristate and methyl palmitate, respectively).

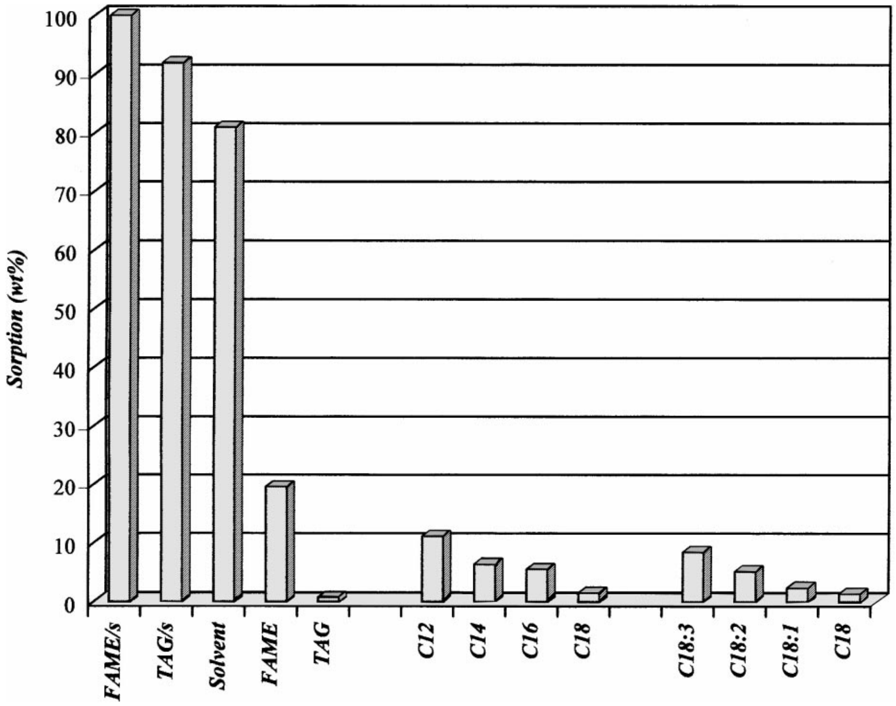

Fig. 6. Sorption (expressed as wt.% = 100 × (sorbed/g membrane) in PDMS of TAGs and a FAME mixture (mainly C16, C18, C20 unsaturated FAMEs; exact composition given in ref. [10]). In the first series (sorption temperature = 20°C), the TAG and FAME entries represent sorptions of undiluted compounds; solvent = pure iso-octane; /s = 5 wt.% solution in iso-octane). The second and third series represent sorptions from a 5 wt.% solution in decane at 25°C.

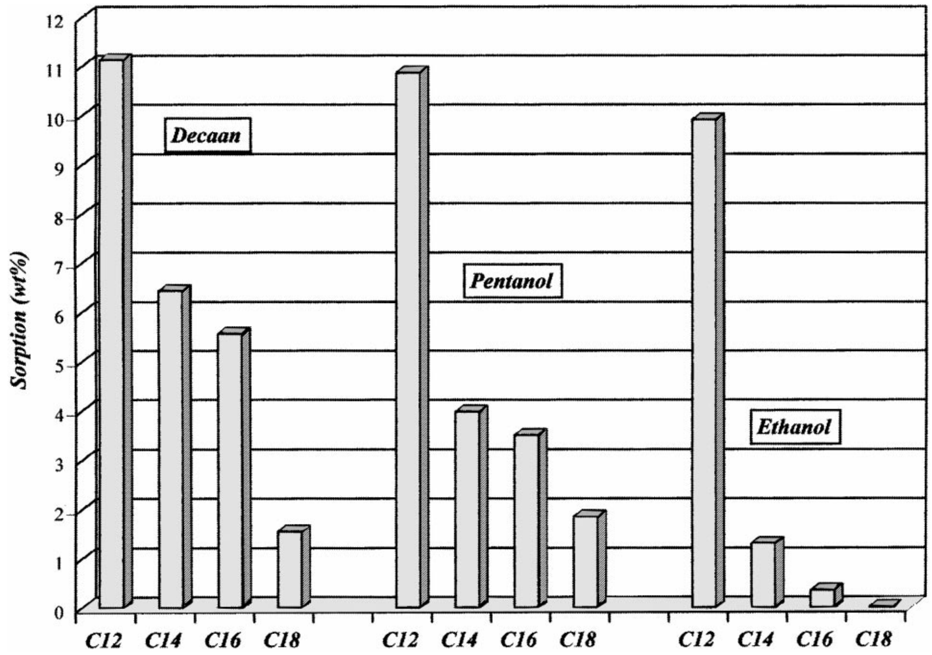

Fig. 7. FAME sorption in PDMS from solvents with different polarity.

a solid phase catalyst in the polymer might cause additional physical or even chemical cross-linking [15].

As shown in Fig. 5, the predictive value of the Hildbrandt-parameter was found not to be generally applicable, e.g. for sorption of small bifunctional molecules like butane dione [17] and fatty acid methyl esters (FAMEs) [10] in PDMS. For components with the size of FAMEs, the shape of the molecules seems to be dominating the sorption in the cross-linked polymer (Fig. 6). In both the series with increasing chain length and increasing degree of saturation, the largest molecules sorb less in PDMS in spite of their more hydrophobic character. Sorption measurements of triacylglycerides (TAGs, rapeseed oil with a composition given in ref. [10]) in PDMS proved that solvents are actually needed for these compounds in order to break up the very strong interactions between the entangled molecules before allowing sorption in the polymer. When applying such solvents in a hydrogenation reaction, it should be considered that the amount of reagent sorbed in the membrane depends on the polarity of this solvent. Indeed, a partitioning of the reagent exists between the solvent phase and the membrane phase as proven in Fig. 7 for different FAMEs in PDMS from solvents with different polarity.

4. Catalyst leaching

A specific problem occurs in liquid phase reactions with membrane occluded homogeneous catalysts: leaching of the complex — and the co-incorporated additive, if present — out of the catalytic membrane into the liquid reagent phase. Indeed, occlusion of complexes in a polymer does not involve — and this is at the same time one of the strong points of this way of complex heterogenisation as pointed out above — strong interaction forces between the complexes and the polymer. ‘Van der waals wrapping’ might be an appropriate term to describe this interaction which is a combination of steric constraints of the surrounding polymer chains on the catalyst and Van der waals interactions between the catalyst and the polymer.

Earlier, the relation between membrane swelling in a solvent, catalyst solubility and catalyst leaching from the polymer was studied in depth for the Jacobsen catalyst and its dimeric form (Fig. 8) [11]. Table 1 displays analoguous results for the Katsuki catalyst. If solvents exist in which the complex does not dissolve at all (or hardly dissolves, like heptane in the case of the Katsuki catalyst), these should be the solvents of choice to perform the reactions in. Apart from

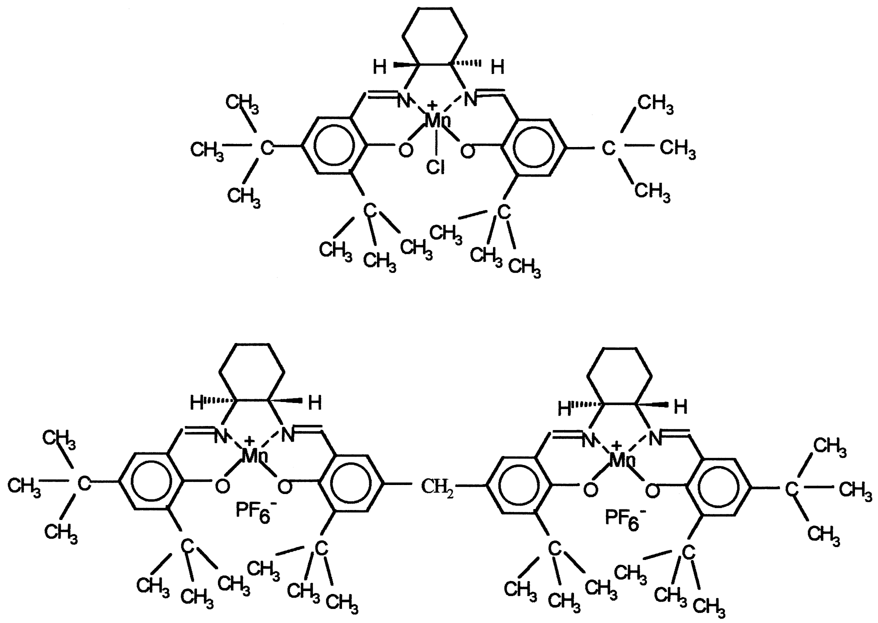

Fig. 8. Jacobsen catalyst (top) and the dimeric form (bottom).

establishing a real chemical (ionic, covalent, coordinative) bond between the complex and the polymer, this is about the only way to prevent leaching completely. In another way, leaching can be reduced by placing bulky groups on the catalyst or by preparing dimeric or oligomeric forms [11]. Finally, more appropriate conditions to prevent leaching can also be found by using solvents (like acetonitrile and methanol in Table 1) in which a low membrane swelling is combined with a low solubility of the complex.

The results for catalyst leaching presented in Table 1 were all obtained under non-reactive conditions. It should be considered that both the shape and the solubility of the complex might change when it becomes activated under reaction conditions. Jacobsen catalyst e.g. forms a Mn–oxo complex in a folded shape when activated [18]. This excludes leaching under reaction conditions, even if the applied solvent would normally induce leaching.

Furthermore, especially in a discontinuous reaction mode like in batch reactions, the polarity of the reaction medium changes as products are formed and reagents are consumed. This is most apparent in high conversion oxidation reaction where polarity of the reaction medium increases drastically, leading inevitably to different catalyst solubility and leaching.

5. CMR set-up

By far the easiest set-up to evaluate membrane occluded complexes is the batch reaction: the composite membrane is simply cut into pieces and immersed in the reaction mixture (Fig. 9a). It allows a fast screening of the catalytic membranes and a first evaluation of the influence of the surrounding polymer phase on the catalyst activity. Membranes — for as far as this term is appropriate in this set-up — do not even have to be defect free or mechanically stable. Fig. 10 gives a schematic overview of all possible factors that play a role if reaction is performed in a CMR. A com-

Table 1
Solubility and leaching of Katsuki catalyst related to the swelling of PDMS in different solvents

Solvent	Leaching (%)	Solubility (g/l)	Swelling (ml/g)
Heptane	2.7	0.1	2.18
CH_3OH	5.7	18.5	0.00
Acetonitrile	5.8	1.2	0.00
MIBK	46.8	6.5	1.35
Acetone	52.7	18.9	0.20
Ethylacetate	55.5	8.0	1.09
Toluene	63.4	23.2	1.82
CH_2Cl_2	65.8	45.0	1.25
$CHCl_3$	65.9	49.1	1.71

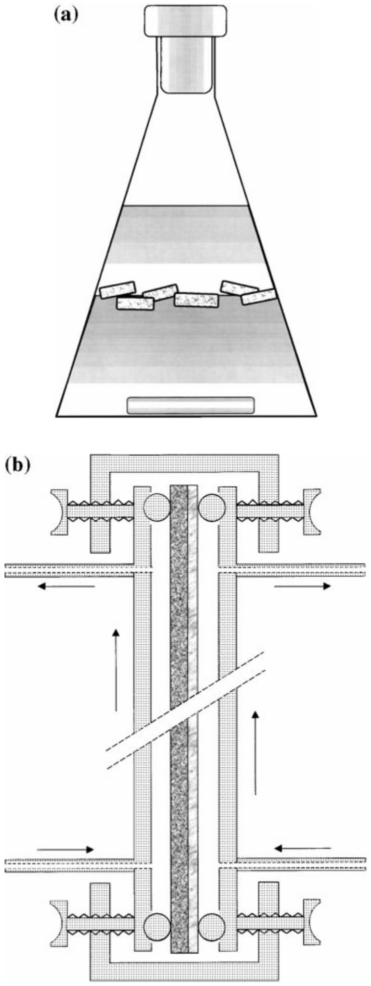

Fig. 9. Three possible set-ups for CMRs with dense membranes: (a) batch reactor; (b) flat sheet membrane reactor; (c) tubular membrane reactor.

plex combination of diffusion and sorption steps finally leads to the conversion at the catalytic site. It is clear that the presence of supplementary mass transfer steps in the batch reactions with membrane occluded catalyst will lead to lower catalytic conversions, but these experiments remain useful as a first screening. The dotted area represents additional film diffusion limitations that may appear under certain conditions. When moving towards a real CMR, new phase equilibria occur and some diffusion steps disappear so that better results might be expected.

The module design for CMRs is based on the two types of membrane configuration: flat membranes and tubular membranes [19]. Flat membranes can easily be mounted in plate and frame modules where spacers separate the different membrane sheets. Spiral wound modules essentially consist of a plate and frame configuration that is wrapped around a central collection pipe. These two systems can contain an active membrane area of 100–400 and 300–1000 m^2/m^3, respectively. For the tubular membranes, classificiation is made based on the dimensions of the tube. In decreasing order of diameter, these are tubular membranes (>10 mm), capillary membranes (0.5–10 mm) and hollow fibres ($<0.5\ \mu m$). The tubular membranes contain surface areas around 300 m^2/m^3, whereas the other systems have areas up to 1200 and 30 000 m^2/m^3, respectively. The choice between them does not only depend on packing density, but also on availability of chemically resistent support layers or the need for membrane replacement or regeneration.

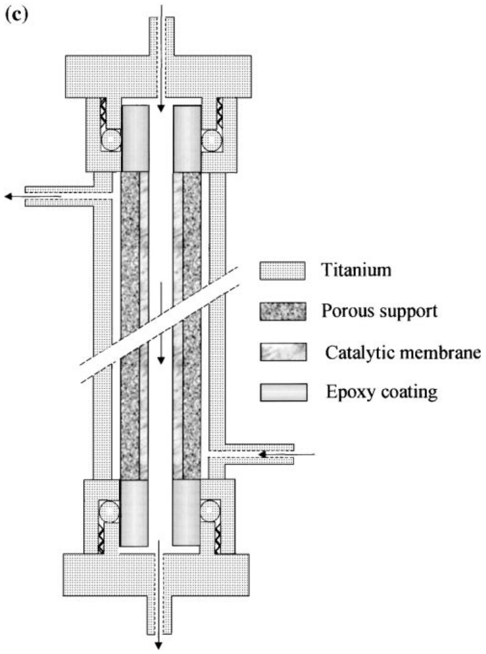

Fig. 9 (*Continued*).

In contrast to the batch reactions, defect-free membranes are essential in a plate and frame module or a tubular reactor. In the tubular shape, the use of a porous support cannot be avoided. The flat sheet membranes might be prepared supportless as long as diffusion of components through the inevitably thicker membrane

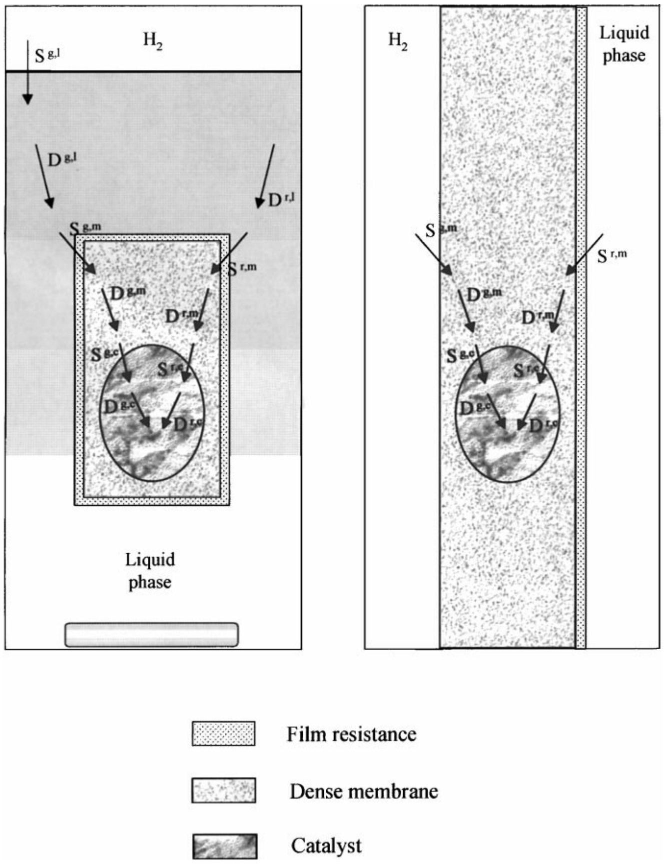

Fig. 10. Mass transfer for a gas/liquid membrane reaction in batch (left) and in a CMR (right). $S^{a,b}$, sorption of component a in phase b; $D^{a,b}$, diffusion of component a through phase b; *g*, gaseous phase reagent; *r*, liquid phase reagent; *l*, liquid phase; *m*, membrane phase; *c*, catalyst phase.

does not become rate determining in the reaction. Practical considerations favour the use of porous supports, even for flat sheet membranes. Indeed, unsupported catalytic membranes might swell so strongly that their mechanical strength and the fixing of the membranes in the reactor might become problematic.

Asymmetric porous membranes are preferably used as support material. Both organic (polyvinylidenefluoride, teflon, polyester,...) or inorganic supports (silica, alumina, stainless steel,...) can be considered. Intrusion of the active layer in the pores of the support should be prevented as much as possible [20], since mass transport decreases dramatically as soon as even small amounts of polymer intrude the support [21]. At the same time, the release of the active layer from the porous support should be prevented by providing a good adhesion of the toplayer to the support, even if the membrane is strongly swollen. The application of adhesion promotors on the support before coating the active layer might be necessary in certain cases. When gas phase reactions are studied, the use of a mechanically strong support is inevitable to keep the catalytic membrane stable under the conditions of high pressure. Whether one reagent should contact the porous side of the composite membrane — with a quasi unstirred liquid phase in the pores — or the other side with direct contact with the catalytically active layer, is a matter of mass transfer and detecting the rate-limiting step for each catalytic reaction.

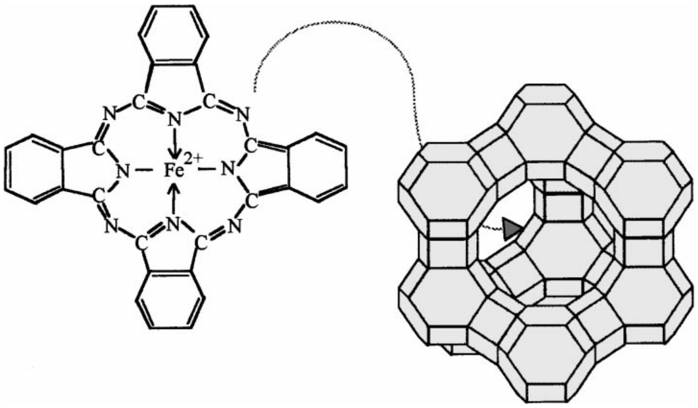

Fig. 11. FePc encaged in zeolite Y.

6. Occlusion of a heterogeneous catalyst: oxidations with FePcY

FePcY (FePc immobilised in the cages of a zeolite Y, Fig. 11) was our first catalyst incorporated in a dense polymer, illustrating very well the potentials of using membrane occluded catalysts [4]. Embedded in a membrane, the catalyst could be applied in a CMR with the membrane as an interphase between the two immiscible reagent phases: cyclohexane on one side and an aqueous solutions of tertiary butylhydroperoxide on the other. It rendered a solvent redundant and excluded the water molecules, present in the oxidant phase, from competitive sorption at the catalytic sites.

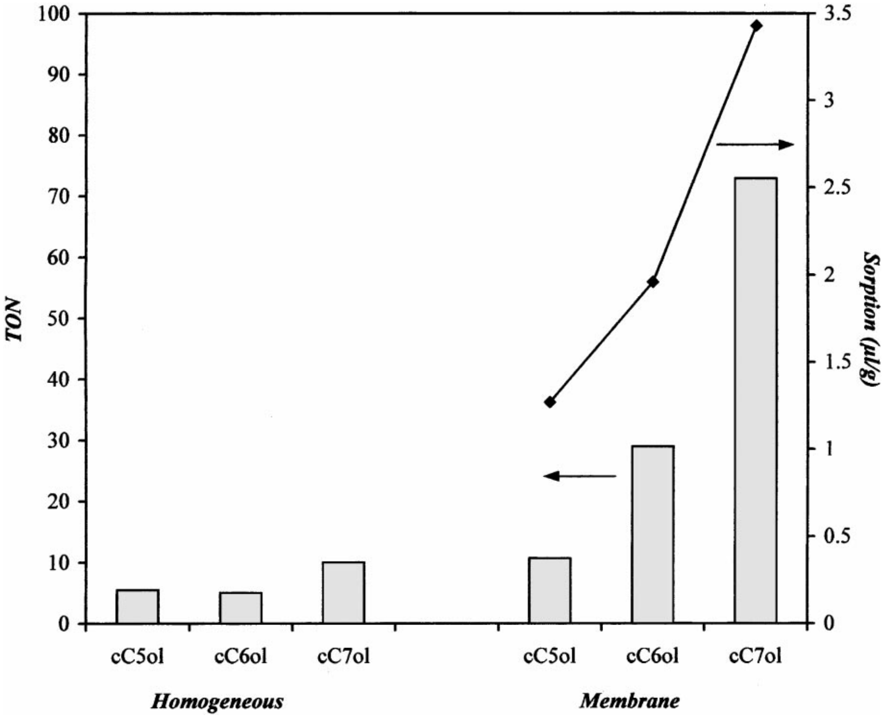

Fig. 12. The oxidation of a mixture of cyclic alcohols with *t*-BHP, mediated by TDCPP(Mn)Cl or PDMS-TDCPP(Mn)Cl and the sorption ($\mu l\,g^{-1}$) of cyclopentanol, cyclohexanol and cycloheptanol in PDMS.

As an additional advantage, the sorption–diffusion properties of the hydrophobic, dense polymer beneficially influenced the uptake of both reagents in the polar zeolite Y. It resulted in a five-fold increased catalyst activity.

7. Occlusion of a homogeneous catalyst: oxidations with TDCPP(Mn)Cl-complexes

The advantages mentioned for occluding heterogeneous catalysts also hold for homogeneous catalysts. At the same time, such incorporation constitutes a way to heterogenise the catalyst, enabling easy catalyst recycling and continuous operation even without any chemical modification of the catalyst.

Whereas FePc-complexes could not be incorporated in PDMS due to the absence of suitable solvents to dissolve it, incorporation was successful for the related TDCPP(Mn)Cl-complexes [9]. In the detoxification of recalcitrant pollutants in waste waters, PDMS incorporation showed many benefits (Fig. 12). The activity in water for the homogeneous oxidation of cyclic alcohols with tertiary butyl hydroperoxide follows the order: cC6 $\leq$ cC5 $<$ cC7 [22]. The preferences are even more pronounced under competitive conditions. The order changes when the catalyst is occluded in PDMS. Influenced by the sorption selectivity of the PDMS-polymer, the more apolar compounds are sorbed by preference, and — being concentrated around the catalytic species — the turnover number (TON) increases drastically. When all three alcohols are oxidised competitively, the difference between the three alcohols, both on the level of catalysis and sorption diminishes due to the ‘dragging effect’: the least sorbing compound is dragged into the polymer by the preferentially sorbed. The latter makes the polymer swell. This way the interactions between the polymer chains and the other sorbing compounds are decreased.

For the epoxidation of 3-penten-2-ol [12], low selectivities under homogeneous reaction conditions (Fig. 13) are caused by competition between the substrate and the axial ligand for coordination around the metal. Consequently, ketone formation — the side reaction occurring when the complex is not coordinated with an axial ligand — is prominent. On the other

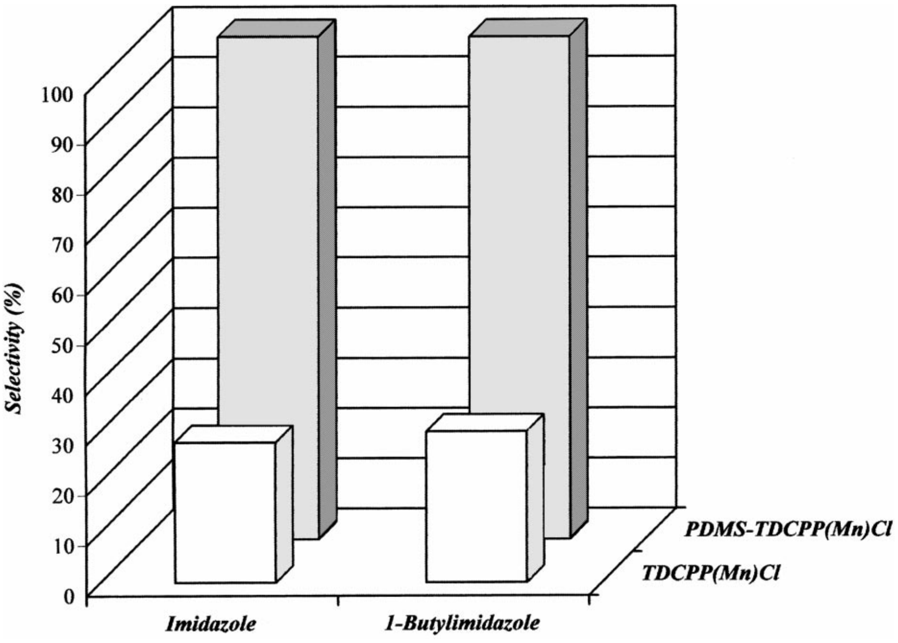

Fig. 13. Selectivity for the epoxidation of 3-penten-2-ol with H_2O_2 mediated by TDCPP(Mn)Cl and PDMS-TDCPP(Mn)Cl in the presence of imidazole and 1-butylimidazole as axial ligand.

hand, the PDMS occluded complex shows a 100% selectivity towards the epoxidation of the double bond of the component. This might be due to a reduced mobility of the axial ligand in the PDMS-environment so that it remains permanently in the close neighbourhood of the complex and avoids competition with the substrate. Whereas hydrogen peroxide is easily decomposed under homogeneous conditions due to excessive contact with the metal ion, the decomposition is drastically reduced with the membrane occluded catalyst. Indeed, peroxide sorption in the membrane is limited: just enough to allow reaction (0.165 mmol/g under reaction conditions, in contrast to no measurable sorption in the absence of substrate), but not too abundant to cause important decomposition.

8. Conclusions

The occlusion of homogeneous and heterogeneous catalysts in PDMS, or dense polymers more in general, can improve their activity, especially when operated in a CMR. In the field of fine chemicals synthesis, the lower chemical, thermal and mechanical stability of polymeric membranes as compared with ceramic membranes is no real obstacle. When occluding homogeneous catalysts, catalyst leaching during reaction should be avoided by carefully selecting the reaction conditions. Additives can be co-incorporated with the catalyst, as a further step to improve the catalyst activity and to make the heterogenisation complete.

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