Polymeric Membranes in Catalytic Reactors

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1. Introduction

It was about three decades ago that the first papers appeared in the literature in which membranes were combined with reaction engineering. It was Alan Michaels who drew the process engineers world's attention to the fact that semipermeable membranes had become available as a practical and economical technique to separate molecules in high-capacity, continuous processes. He predicted that "membrane technology would become a significant addition to the chemical process industry's kit of process tools".[1] Since then, a multitude of different catalytic membrane reactor (CMR) concepts have appeared, all offering the opportunity to combine chemical reactions with the separation activity of the membrane. Organizing such a wide variety in one review was challenging, and a selection had to be made.

The selection on the level of membrane composition was the most clear-cut: only CMRs with polymeric membranes will be considered here, even though their specific position with respect to the more widespread CMRs with metallic and inorganic membranes will be commented on shortly. Second, the review will only cover the use of nonbiological catalysts. The main differences with enzymatic CMRs (eCMRs) will be summarized briefly with reference to some excellent reviews covering that topic. Still, whenever concepts developed in eCMRs seem prom-

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ising for polymeric CMRs (pCMRs), those will be mentioned anyhow. Processes where the membrane separation did not involve any specific knowledge of the membrane technology (e.g., separating a micron sized catalyst particle by state-of-the-art microfiltration) were discarded, as well as electrochemical processes (fuel cells and polymer-coated electrodes). To border polymeric membranes used in catalytic reactions with polymeric bound catalysts in nonmembrane applications was most difficult. To limit the review to membranes in the strict definition of a "selective barrier between two phases"[2] seemed inappropriate. For instance, many screening experiments on newly developed polymeric catalytic membranes (CMs) are actually batch experiments in which the membrane is simply cut in pieces and stirred in a homogeneous reaction mixture. Also, e.g., poly(vinyl alcohol) (PVA)-hydrogels will be discussed in Chapter 6, whereas in fact only the strongly related chitosan beads are really separating two phases. Such systems were added whenever they were considered to reveal valuable information on the related genuine CMs. Some other related classes of polymeric catalytic supports, like soluble polymers,[3] poly(ethyleneglycol) (PEG),[4] and poly(styrene) (PS),[5] will be completely absent as they are covered elsewhere in this special issue.

The main focus of this review will be on the development of new concepts and materials for pCMRs. After some introductory definitions and basic principles (Chapters 2−5), the pCMRs will be split up in four main classes. "Catalytically active" membranes are used in the first three classes. The membranes are made of polymers with the catalyst embedded in it or deposited directly on it. They can be used in a "flow-through" reactor where the membrane actually acts as a "plug-flow" reactor with both reagents passing simultaneously, as a selective barrier, or as a contactor between two reagent phases. The classes consist of membrane encapsulated catalysts in one respect (Chapter 6) and heterogeneous (Chapter 7) or homogeneous (Chapter 8) catalysts embedded in the polymeric matrix or in the membrane pores in another. The fourth type of pCMRs consists of "membrane-assisted processes", also referred to as "inert CMRs," where "catalytically passive" membranes are used (Chapter 9). The membrane itself does not have any catalytic activity here. Being part of the reactor wall, the membrane merely retains the catalyst into the reactor volume. The catalyst can be arranged as a fixed bed or can be suspended or dissolved in the reaction phase. The membrane thus merely serves as a barrier to drain off reactants or to supply products.

2. General Status of CMRs

Introduction

In every CMR, the membrane separation and the catalysis are combined in one unit operation. As will be illustrated in Chapters 6−9, such an integrated setup results in enhanced processing and economic results when compared to a traditional configuration where the two unit operations are separated in time and space.[6] These advantages will be summarized first in general, together with some possible drawbacks. Subsequently, the specificities of the "competing" metallic and inorganic CMRs will be listed and compared with the extra surplus offered by the less traditional pCMRs. Finally, the main differences between CMRs and eCMRs will be mentioned shortly.

Advantages and Disadvantages

The general advantages of CMRs are numerous and most have been proven already in several publications.

1. An integrated process involves lower investment costs, so that the economical viability of the process increases.[7]
2. Energy consumption can be saved,[8,9] e.g., by less pumping.
3. The removal of a product from a reaction mixture can shift the chemical equilibrium of the reaction and thus generate increased product yields[9−15] or lead to similar yields but obtained already at lower temperatures.[9] The latter has the extra advantage of decreasing the extent of deleterious side reactions, such as coking. Catalyst activity can then be maintained for a longer period before regeneration becomes necessary.[16] In this respect, the dehydrogenation reaction has undoubtedly been most studied. In certain cases, like in the removal of H_2 through a Pd membrane, the product removal simultaneously generates a product with high purity.[17,18]
4. The continuous removal of product can decrease possible product inhibition, thus increasing overall reaction rates.[10]
5. The continuous removal of a product can decrease possible side reactions.
6. By selectively removing an intermediate product

in consecutive reactions, enhanced selectivities for that intermediate can be realized.[11,10]

7. The downstream processing of the products can be substantially facilitated when they are removed from the reaction mixture by means of a membrane.[10,9] A simple solvent evaporation often suffices later to obtain a highly pure product.

8. The contact between two reactants can be mediated and controlled by a semipermeable membrane.[11] In the field of oxidation catalysis for instance, this creates the possibility to separate the hydrocarbon from the oxidizing air.[11,19,20] The oxygen feeding can thus be better controlled,[12,21] or two hazardous reactants, like H_2 and O_2, can be reacted safely.[17,19,22,23] Whereas the addition of gases to the reactor is often useful to give an extra stirring to the reaction mixture, permeation through a dense, highly permeable membrane is sometimes preferred to integrate bubble-free aeration.[24,25]

9. When the membrane is placed as a contactor between two phases, solvents can be excluded and thus render the process environmentally and technically more attractive.[26,27]

10. Membrane separations often have the advantage of operating at much lower temperatures, especially when compared with, e.g., distillation. They might thus provide a solution for the limited thermal stability of either catalyst or product. Furthermore, the membrane separation is not restricted to volatile components.

11. Under specific conditions, the heat dissipated in an exothermic reaction can be used in an endothermic reaction, taking place at the other side of the membrane, like, e.g., in hydrogenation/dehydrogenation.[11,28]

Despite these advantages, combination and integration of two processes generally adds considerably to the technical complexity of the process, rendering modeling and prediction more difficult.[6] Furthermore, CMRs generally also require more research. This is mainly related to optimization and design of a suitable reactor,[29] with the adjustment of the permeation rates to the reaction rates as one of the most important.[9] Other possible drawbacks are the sealing of the reactor chambers, the manufacturing cost of the membrane and the module, and the insufficient durability of the membranes, which is related to their limited thermal, chemical, and mechanical resistance.[20]

Metallic and Inorganic (Or Ceramic) CMs

The membranes applied in CMRs with which these pros and cons were demonstrated were traditionally metallic or inorganic in origin.[30−33] Most applications studied in the literature until now were high-temperature reactions, with hydrogenations and dehydrogenations by far being studied most.[34] The reason was the existence of the remarkable Pd or Pd alloy membranes showing an almost perfect hydrogen selectivity. Despite all efforts done, no industrial upscaling has been realized yet because these membranes suffer from some important drawbacks.[17,18] The cost of the membranes is very high, and their lifetime is limited. Long-term operations may lead to surface inhomogenity and competitive adsorption may lead to poisoning (e.g., with sulfides) or fouling (e.g., with carbon deposits).[9] The intrinsically low permeability of such dense metal films is in fact the basic problem. To obtain sufficiently high permeabilities, their application is restricted to high temperatures. A reduction in membrane thickness is another possibility to go around the problem of low intrinsic permeability, but an increased risk to create pinholes or defects becomes apparent with ultrathin layers. High-temperature applications also lead to difficulties when materials with different thermal expansion coefficients are combined. Delamination of the membrane toplayer from the support and bad sealing are consequences hereof.[11] These Pd based membranes are strictly limited to H_2 permeations. On the other hand, highly selective membranes also exist for O_2 permeation. Ag membranes or mixed inorganic oxides are then the materials of preference. They basically suffer from the same disadvantages as the Pd membranes and even require temperatures above 500 °C to show sufficient permeabilities.[20]

It is clear that the technology for inorganic membrane manufacturing and high-temperature ceramic material engineering is not yet sufficiently mature.[11,12,17] True development in this area seems to be lacking, and a successful commercialisation of large scale CMR technology using these membranes has not yet taken place.[35]

Polymeric CMRs

In addition to the above-mentioned general advantages of combining reactions with membrane separations, the use of polymeric membranes in CMRs entails some important new possibilities, as will be evidenced in each specific example given in Chapters 6−9. When a heterogeneous catalyst is incorporated in a polymer matrix, a well-chosen polymeric environment can regulate the selective sorption of reagents and products with a beneficial effect on the catalyst's performance. In the case of an embedded homogeneous catalyst, the incorporation is a way to heterogenise the catalyst at the same time. The co-incorporation of additives in the membrane matrix can further increase the performance of such a heterogenised catalyst and substantially facilitate the downstream processing. For the membrane-assisted processes, a much wider choice of polymeric membranes is mostly available to select the most appropriate from, as compared with metallic or ceramic membranes.

Moreover, the technology to manufacture polymeric membranes is generally much better developed already than the one for inorganic and metallic membranes. The operation of the polymeric CMRs (pCMR)s at relatively low temperatures is also associated with less stringent demands for the other materials needed in the module construction, and especially in the sealing, and thus leaves a wider choice to select the most optimal materials.

Enzymatic CMRs

The gap between enzyme catalysis and nonbiological catalysis will probably narrow in future. Adapted

Table 1. Overview of the Membrane Processes Applied in CMRs[a]

membrane process	feed phase	permeate phase	driving force	remarks
microfiltration	L	L	ΔP	0.1−2 bar,[b] 0.05−10 μm,[c] pore flow[d]
ultrafiltration	L	L	ΔP	1−10 bar,[b] 1−100 nm,[c] pore flow[d]
nanofiltration	L	L	ΔP	10−35 bar,[b] transient[d]
reversed osmosis	L	L	ΔP	15−100 bar,[b] solution-diffusion[d]
gas separation	G	G	ΔP	
vapor permeation	G	G	ΔP	feed is vapor of a liquid
dialysis	L	L	Δc	
pervaporation	L	G	Δp	phase transition at membrane

[a] L = liquid; G = gas; p = vapor pressure; P = pressure, c = concentration. [b] Applied pressure. [c] Pore size. [d] Transport mechanism.

enzymes that, e.g., work in the presence of organic solvents are being developed, and catalysts that mimic enzymes are showing up.[36] Several aspects of the use of biocatalysts in combination with membrane separations for different classes of enzymes have been reviewed recently.[6,7,29,36,37,38] Biocatalysts are becoming commercially available to a greater extent, but generally remain expensive.[39] Enzymatic reactions are generally faster,[40] but they might need regular replacement due to denaturation.[7] Recent efforts to increase the chemical stability of enzymes and to limit their heat denaturation were directed to either genetic manipulation[6] or to immobilization of the enzymes.[29,41] During immobilization however, structural modifications and hiding of active sites might lead to decreased specific activity.[6,7] Furthermore, the methods for immobilization are often elaborate and may lead to only low immobilization yields and diffusional constraints in the supports.[29]

The fact that both the enzymatic and the nonbiological approach can have their specific advantages and disadvantages was illustrated in the direct comparison of a catalyst (oxazaborolidine) with an enzyme (alcohol dehydrogenase) for the same asymmetric reduction of acetophenone in a membrane reactor.[36] The enzyme was superior in terms of total turnover number of the catalyst and the amount of catalyst needed. However, due to the better solubility of substrate and product in the chemical system (using tetrahydrofuran (THF) instead of an aqueous solution), a much higher space−time yield could be obtained there. The different reaction environment in the chemical system brought about an uncatalyzed reaction, which led to a decreasing enantiomeric excess (ee) in the course of the reaction as the catalyst got deactivated. The easier access to the catalyst and the possibility to switch from *R* to *S* product by a simple change to the other enantiomeric form of the catalyst were other advantages of the chemical system.

3. Basic Principles of Polymeric Membranes

Introduction

A molecule or particle is transported through a membrane when a driving force is exerted. In general, this force can be a gradient in either pressure, concentration, electrical potential, or temperature.[2] The membrane in fact forms a compound-dependent resistance to the transport and hence determines the selectivity and the flux of the process.

In the membrane-assisted processes, the only factor that relates the catalyst to the membrane, apart from a possible fouling of the membrane, is its retention, which can be a matter of size, affinity, diffusion, or driving force.[42] For the catalytically active membranes, the selection of the most adequate polymeric material for the membrane will be much more crucial. Moreover, unless the functional groups on the polymer chains are themselves the catalytical groups, all these membranes have to be self-prepared. Their preparation is mainly determined by the chosen material, in addition to the desired membrane structure. The most common membrane preparation techniques will be mentioned shortly.

The driving force, the material of the membrane and its structure, going from very open to nonporous or dense, determines the type of application. Table 1 summarizes the membrane processes that have been coupled to catalysis, with some of their main characteristics.

Polymer Selection

A major issue in the selection of polymers for CMRs is undoubtedly their mechanical, thermal, and chemical stability under reaction conditions.[11] Polymeric membranes are of course less resistant to high temperature, aggressive solvents, and oxidative conditions than their inorganic or metallic counterparts. But these limits are relative: Nafion and poly(dimethylsiloxane) (PDMS), e.g., proved already to remain stable, even under rather harsh conditions. Furthermore, there are ample possibilities for applications in fine chemical synthesis or in the catalytic water treatment where many reactions take place under mild conditions and at temperatures well below 250 °C.

In view of the mechanical properties of the polymer, a high catalytic loading of the catalyst should be possible without bringing about brittleness of the films. When heterogeneous catalyst are embedded, the polymer should adhere well to the filler. In all cases, the film forming properties of the (hybrid) polymer should be excellent.

Besides this stability, the polymers should possess good transport properties for the reagents and products. In membrane-assisted catalytic processes, membrane flux and selectivity determine directly the necessary membrane area required for a certain separation. With catalytically active membranes, mass transfer of reagents to the catalysts and of the products away from the catalyst should be as fast as

Table 2. Gas Permeabilities P (in Barrer) and T_g (in °C) of Several Membrane Polymers, with CA = Cellulose Acetate, PI = Poly(imide), and PPO = Poly-(2,6-Dimethyl-1,4-phenylene oxide)

polymer	P_{O_2}	P_{N_2}	T_g
PTMSP	10000	6745	200
PDMS	600	280	−123
PPO	16.8	3.8	210
PI	2.5	0.49	
CA	0.7	0.25	
nylon-6	0.093	0.025	50
PVA	0.0019	0.00057	85

possible in order not to limit the reaction. Two distinct situations arise here.

In porous CMs, the choice of polymer is of less importance, as permeation does not take place through the polymer matrix. The only impact of the membrane polymer is on stability and surface properties, such as wettability and fouling. Depending on the pore and molecule size, molecules are transported through porous membranes via viscous flow, Knudsen flow, molecular diffusion, surface diffusion, capillary condensation, or molecular sieving.[43]

Transport through dense membranes follows the solution-diffusion model, according to which a molecule first sorbs in the polymer before it diffuses through it and finally desorbs again. Sorption of a compound in a membrane can be obtained by simple sorption experiments in which a piece of membrane is immersed in a solution of that compound or in the pure compound, if it concerns a liquid. The Hildebrandt theory[44] can be used to predict the mutual affinity between the compound and the membrane polymer, and hence the sorption in the polymer or its swelling. It reflects the ability of compounds and polymers to form hydrogen bonds or undergo London-dispersion forces and polar interactions. Alternatively, the Flory−Huggins theory,[45] which describes the entropy of mixing, can be applied. Apart from the thermodynamical aspect of sorption, diffusion describes the kinetical aspect of transport through dense membranes. The two most important parameters of the membrane polymer in that respect are the glass transition temperature (T_g) and the degree of crystallinity. They are both determined by structural factors, such as chain flexibility, chain interactions, and molecular weight of the polymer. The chain flexibility is much lower in the glassy state (at temperatures below T_g) than in the rubbery state (above T_g). The reaction temperature will thus be extremely important in determining the transport through the membrane. Crystallinity mainly occurs when polymer chains have very regular structural units that can pack in a regular pattern. The formed crystallites can act as physical cross-links that diminish the flux, inasmuch as transport can only take place through the amorphous rather than the crystalline regions.[2]

To correlate the structural parameters of a polymer with its permeability, some examples are given in Table 2. As can be seen, the (gas) permeability of polymers can differ by as much as 5 orders of magnitude. Rubbery polymers, also called elastomers, are generally very permeable, and glassy polymers are not, but there are some striking exceptions: e.g., poly(trimethylsilylpropyne) (PTMSP), due to its high free volume, and PVA, due to its high degree of crystallinity.[2]

Membrane Preparation

The kind of technique employed to prepare a membrane depends mainly on the material used and on the desired membrane structure.[2]

Coating

To decrease the thickness of the membrane, a thin layer is mostly applied on a more porous sublayer to create a composite membrane. The actual flux and selectivity are determined by the thin top layer, while the sublayer merely serves as mechanical support. Several coating procedures can be used. In interfacial polymerization, two very reactive monomers (or a pre-polymer) react at the interface of two immiscible solvents. In dipcoating, an asymmetric support layer is immersed in a dilute coating solution that contains a monomer, prepolymer or polymer. When the membrane is removed from it, a thin layer adheres, and the solvent can be evaporated. Very thin, dense toplayers can also be obtained by plasmapolymerization in which an ionized gas creates radicals on the reactants that will form the polymer.

In certain cases, however, a critical minimal thickness exists below which the support might become rate-limiting, or where intrusion of the toplayer in the porous support overcompensates the reduced membrane thickness. The porous membranes that are used as supports are generally prepared by one of the following techniques.

Phase Inversion

During the process of phase inversion, a polymer is transformed in a controlled manner from a liquid to a solid state. The process of solidification is often initiated by a transition from one liquid phase into two liquid phases (liquid−liquid demixing). At a certain stage during the demixing, one of the liquid phases will solidify, and a solid matrix is formed. By controlling the initial stage of phase transition, the membrane morphology can be determined; i.e., porous as well as nonporous and integral as well as asymmetric membranes can be prepared. The concept of phase inversion covers a range of different techniques, with immersion precipitation as the most common. A polymer solution is then cast on a suitable support and immersed in a coagulation bath that contains a nonsolvent.

Sintering

A powder of particles is pressurized at elevated temperatures. The technique is suitable to prepare porous membranes from insoluble polymers, such as PTFE.

Stretching

An extruded film or foil from a (semi-)crystalline polymeric material is stretched perpendicular to the direction of the extrusion. Small ruptures thus occur and a porous structure is obtained.

Track-Etching

A film is subjected to high energy particle radiation applied perpendicular to the film. When subsequently immersed in an appropriate solution, the polymer is etched away along the tracks formed by the damaging particles. It results in very uniform cylindrical pores with a narrow pore size distribution.

4. Module Design

The smallest unit, into which a certain membrane area is packed, is called a module. Thanks to this modular design, the upscaling of membrane processes is generally easy. The choice of a certain module configuration is based on economic considerations, with the correct engineering parameters being employed to achieve this. By passing through the module, the feed inlet stream is separated into a permeate (passing the membrane) and a retentate (retained by the membrane). Two types of membrane configuration, flat and cylindrical, form the base of a number of module designs.

The cylindrical membranes are subdivided according to their dimensions: “tubular membranes” with a diameter of more than 10 mm, “hollow fibers” (HF) with a diameter of less than 0.5 mm, and “capillary membranes” with intermediate dimensions. When the membranes are packed closely together in a module, a diameter between 5 and 0.05 mm corresponds to a surface area per volume between 360 and 36 000 m^2/m^3. Tubular membranes are placed inside a pressure-resistant tube. The capillary and HF membranes are assembled in a module with the free ends of the fibers potted with, e.g., epoxy resins or silicone rubber. The most recent development in this field are the submerged membranes (Figure 1).[46,47] They developed fast in the past few years and are mainly used in water treatment. In most applications, aeration induces sufficient turbulence to prevent their fouling. Expensive and energy consuming circulation pumps are thus redundant, and the modules are clearly simple and cheap.

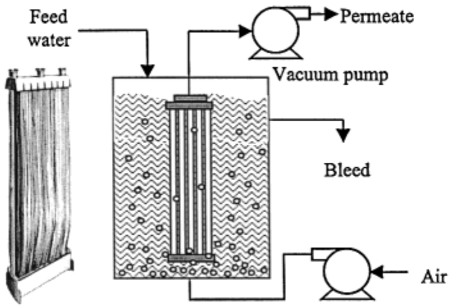


Figure 1. Submerged membrane module as applied in wastewater treatment (right) and a more detailed module (left).

Flat membranes can be either arranged in a plate-and-frame or in a spiral-wound module, with packing densities of respectively 100−400 and 300−1000 m^2/m^3 (Figure 2). In a plate-and-frame module, sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other and separated by spacers. When such a plate-and-frame module is wrapped around a central collection pipe, a spiral-wound module is obtained.

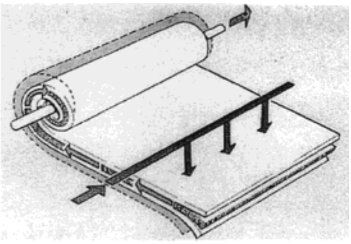


Figure 2. Schematic representation of a spiral-wound module.

In view of a CMR application, the chemical composition of the module materials, as well as that of the sealing and potting polymers, is extremely important with respect to stability under reactive conditions and interference with the catalytic behavior. Submerged modules seem promising here as their fibers can be coated with a layer of catalyst containing polymer. No reaction liquid would then contact module parts or potting material and a high catalytic membrane surface could be created in a small volume.

Whatever arrangement, the feed and permeate flow can be either cocurrent, countercurrent, or, in the case of cylindrical membranes, perpendicular. Alternatively, mixing can be applied at either both sides, or at only one side of the membrane.

5. Preparation of Polymeric Membranes Endowed with Catalytic Entities

Introduction

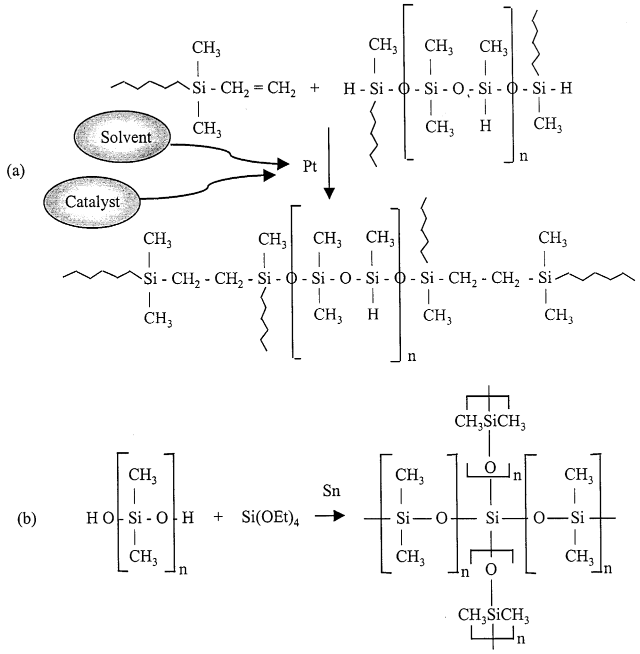
When the catalytic species are added to existing membranes, the common functionalization techniques which were developed for the preparation of heterogeneous catalysts can be applied.[48−50] When catalysts are embedded in the membrane during the membrane synthesis, complicated interactions can occur between the catalyst and the polymer solution. During the phase inversion process, e.g., the catalyst can be seen as an additive that might change the membrane morphology, sometimes drastically, even at low loadings. Of course, the selection of the polymer material, the membrane preparation method, and its final structure can influence on their turn the catalytic behavior. The most critical issue with respect to the catalyst is the fact that its activity should remain guaranteed over the whole membrane formation process. Moreover, a stable suspension (in the case of a heterogeneous catalyst) or good dissolution (in the case of a soluble catalyst) should exist during the whole membrane synthesis process.

The two most widely used CMs, PDMS and Nafion, will receive some extra attention and will be used to illustrate some general issues related to the preparation of CMs. Furthermore, they also possess some peculiarities which are essential to understand the examples given later.

PDMS

PDMS is the only membrane polymer that has been applied already in all four classes of pCMRs covered in this review, basically because of its excellent permeability combined with an easy preparation and the commercial availability of a wide variety of building blocks. Moreover, it is a cheap material with excellent thermal, mechanical and chemical resistance.[51] PDMS was found to be stable in O_2 to well above 200 °C, with a 10% mass loss not occurring typically until ca. 400 °C. It was unaffected in 2M H_2SO_4 but digested readily in 2M NaOH.[52]

Scheme 1. (a) PDMS Prepared Following a Hydrosilylation Reaction and (b) via a Condensation Reaction



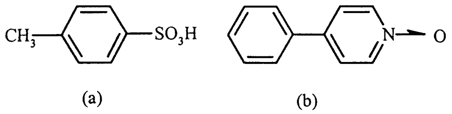
Typically, PDMS is a two-component system (Scheme 1), consisting of a cross-linker, containing several hydride groups, and a vinyl terminated prepolymer. The PDMS membrane is cross-linked via a Pt-catalyzed hydrosilylation reaction. Alternatively, silanol terminating PDMS chains can be linked to tetraethoxysilane (TEOS) in the presence of a Sn catalyst.[52] Porosities up to 65% can be created when NaCl powder is mixed with the hydrosilylation mixture.[53]

Improved dispersions of solid-phase catalysts in a PDMS solution were realized by adding a solvent to decrease the viscosity of the prepolymer/cross-linker mixture. However, during the membrane formation, the solid-phase catalyst might settle down from the casting mixture while the solvent evaporates. This can be prevented by a prepolymerization (typically 1 h at 60 °C for a 25 wt % PDMS solution)[54] before addition of the catalyst. When incorporating wide-pore heterogeneous catalysts, such synthesis procedure[55] had the additional advantage to prevent pore blocking. Indeed, unreacted PDMS chains sorb in the catalyst pores when these are large enough (from ± 6 Å onward),[55] rendering the catalytic species inside the pores inaccessible for the reagents. The filler then acts like as a physical cross-linker and can decrease membrane swelling drastically. But even in the absence of pore intrusion, this cross-linking effect can already be significant.[55−57]

Generally, dispersion problems become much more significant when occluding transition metal complexes (TMCs) in polymers. This should not be surprising, as a complicated mixture is generated of a polymer (with in certain cases, like for PDMS, reactive groups), a catalyst (sometimes oxygen or water sensitive), a suitable solvent, and, in certain cases, another catalyst for the polymer cross-linking. On top of this, dispersion should remain perfect, also during the whole membrane formation process, while, e.g., the solvent evaporates. For PDMS membranes, apolar and low boiling solvents are ideal. Indeed, the solvent should be removed easily at temperatures where the catalyst remains stable, possibly by applying reduced pressure. During synthesis, the homogeneous catalysts might interfere with the membrane formation, like, e.g., in the PDMS cross-linking reaction. It was found that certain counteranions of TMCs inhibited curing of the PDMS membrane. In those cases, other types of polymers or other types of cross-linking reactions for PDMS might offer a solution.[57]

An even more complex synthesis mixture arises when additives are co-incorporated in the membrane. First of all, these additives should be soluble in the same solvent as the TMC and the polymer. Certain compounds, like *p*-(toluene sulfonic acid) (pTSA) or 4-phenylpyridinoxide (4-PPYNO) (Scheme 2), could only be occluded in PDMS in low concentrations. High concentrations prevented the PDMS polymer from curing or even created some porosity. A way to circumvent these curing problems was to immobilize the catalyst first and then sorb the additive from an aqueous solution. Spectroscopic evidence showed that TMCs are incorporated in PDMS without disturbance of their structure and free of electronic interactions between the central metal ion and the surrounding polymer.[58]

Scheme 2. Additives in PDMS: PTSA and 4-PPYNO



Nafion

Nafion is a registered trademark for Dupont's brand of perflourinated ion exchange polymer. Nafion has excellent mechanical, thermal, and chemical stability (similar to Teflon), coupled with a high conductivity and ionic selectivity, which depend strongly on the water content. These excellent properties have led to the use of Nafion in a wide variety of applications: mostly as pellets in acid catalysis,[59] as films in electrochemical cells (fuel cells, water electrolyzers), and as fabric reinforced films in electrochemical applications.[60] Nafion contains sulfonic or carboxylic ionic functional groups compensated by

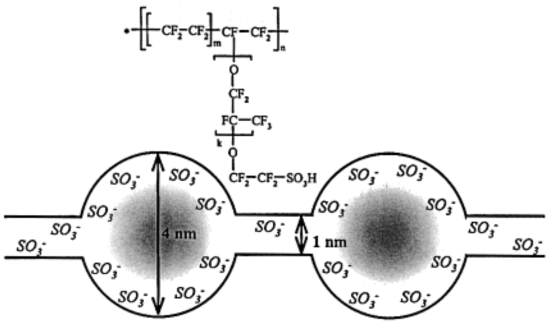


Figure 3. Nafion perfluorinated ionomer.

a metal cation in the neutralized form or by a proton in the acid form. A typical chemical structure is shown in Figure 3.[61]

Nafion's unusual properties arise from its complex morphology. Still, the exact structure is not known, and several models have been proposed. According to the Gierke Cluster Network Model,[62] e.g., Nafion has a structure like the one shown in Figure 3. As a result of electrostatic interactions, the ionic groups tend to aggregate to form tightly packed regions, referred to as clusters. The hydrophobic region is composed of the polymer fluorocarbon backbone, while the hydrophilic region contains the ionic groups and their counterions. The presence of these electrostatic interactions enhances the intermolecular forces and thereby exerts a significant effect on the properties of the polymer. Upon hydration, Nafion can increase its dry weight by as much as 50% or more, leading to increasing cluster diameter and number of exchange sites.[63]

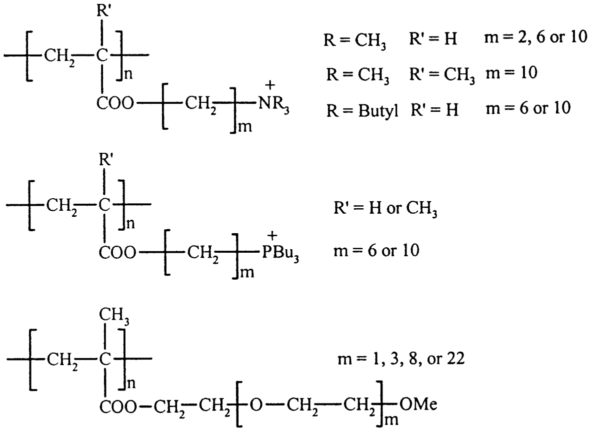
6. Encapsulation

When encapsulating a catalyst or enzyme, the confinement is meant of a liquid solution within small capsules enclosed by a polymer or a surfactant. A potentially high interfacial specific area is thus created, and the recovery of the catalyst is facilitated. The selective sorption through the membrane can further increase catalytic performances. Scaling up is easy, but attention should be paid to prepare capsules that are as small as possible in order to prevent extra resistance to mass transfer in the nonagitated encapsulated volume.[6] A recent review evaluated the materials and encapsulation technologies.[64]

The concept of capsule membrane supported phase transfer catalysts (CM-PTC) was introduced by Okahata et al.[65] In phase transfer catalysis, two immiscible phases are contacted, and a phase transfer catalyst (PTC) is used to transfer a reactant from one phase to another so that reaction can occur. This catalysis is normally conducted in dispersed-phase systems under vigorous stirring. PTCs act as emulsification agents, being an advantage during the actual reaction, but complicating the subsequent product purification substantially.[66] To deal with this problem, PTCs were grafted onto the surface of an ultrathin, porous capsule membrane. The capsule membranes could be easily separated from the reaction mixture, but their activity was often less than that of soluble PTCs.

The (nylon 2,12)-capsule membranes were prepared via interfacial polycondensation between ethylenediamine and (chlorocarbonyl)decane. Vinyl groups were introduced by grafting with ethylene glycol dimethacrylate. These were then further reacted in the presence of a radical initiator with the acryloyl monomers of the phosphonium salt, ammonium salt, or a poly(ethyleneoxide) based PTC (Scheme 3).[67] The 2.5 mm diameter capsule membranes had a wall thickness of 5 μm. The capsules were immersed in a chloroform solution of benzylbromide to obtain reagent filled capsules (Figure 4), which were subsequently dropped into aqueous solutions of NaN_3. A first step in the reaction was the exchange of the counteranions of the PTC capsule from Br^- to N_3^- in the outer aqueous phase. The second step was the phase transfer of N_3^- from this aqueous phase across the membrane to the inner organic phase. The third, and rate-limiting, step was the actual nucleophilic substitution reaction. After reaction, the capsules were easily removed from the solution and crushed in order to recover the formed product. No induction period, as frequently observed with resin-supported PTCs, was observed. The extent to which the PTC-grafted capsules accelerated the reaction depends on the graft amount, the spacer chain length, the ionic strength of the outer aqueous phase and the hydrophobicity of the onium salt monomers.

Scheme 3. Different PTCs Used in the CM-PTC



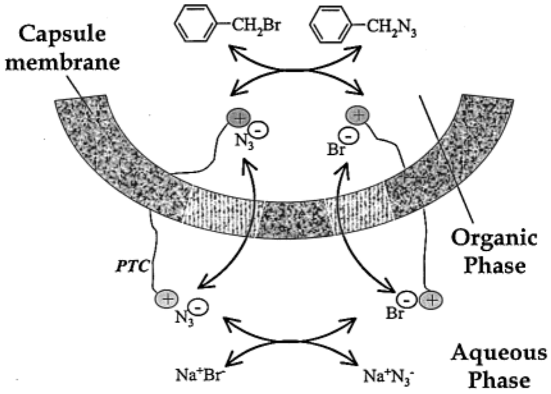
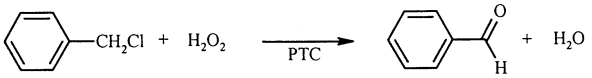


Figure 4. Schematic presentation of the CM-PTC (adapted from ref 67).

Nylon capsules were also used by Yadav and Mistry.[68] They were prepared by adding dropwise a basic solution of amine to an organic solution of terephthaloyl chloride that also contained the trimesoyl chloride cross-linker. The tetra-alkylammonium PTCs were supported on the thus obtained thin (7.6 μm), small (1.7 mm) nylon capsules and were subsequently filled with benzyl chloride. The filled capsules were then added to an aqueous solution of hydrogen peroxide. The H_2O_2 was transferred to the organic phase as a solvate of the PTC, which simultaneously prevented its decomposition (Scheme 4).

Scheme 4. Oxidation of Benzyl Chloride with PTCs



With PTC: trioctylmethyl ammonium chloride
or tetrabutyl ammonium bromide
or cetyltrimethyl ammonium bromide

A problem associated with such capsules is the fact that there is no way to provide fresh organic phase to the inner portion of the capsule or to remove continuously product from that phase. They either have to be leached or broken at the end. Even though not really proven experimentally, a solution was proposed by the inverse CM-PTC, in which the aqueous phase was placed inside the capsule and the organic substrate in the outside bulk phase.[69]

An interesting type of entrapment of (bio)catalysts or powder-like materials in polymers was developed by the group of Vorlop. These materials consist of immobilized cells,[70] mycelia,[71] enzymes,[70,72,73] or catalysts, such as Pd on alumina or colloidal Pd[74-77] in polymers such as PDMS,[78] PVA,[71-74,79,80] or sulfoethyl cellulose.[70] In the specific case of PVA, they are named “Lentikats”, as commercialised by Genialab.[81] Lentikats have a lenticular shape and possess a high mechanical and chemical stability. The beads are generated by the “jet cutting method”,[82,83] in which a solid jet of fluid is cut when it comes out of a nozzle. Due to surface tension, the thus formed cylindrical segments form beads on their way to a hardening device filled with chilled liquid (Figure 5). With dimensions of 1.5−5 mm diameter and a thickness of 200−400 μm, they showed minimized diffusion limitations and could be used continuously[77] or recycled batchwise by filtration.[72] The fast diffusion is due to the high water content of the gel (up to 90%).[76] When the embedded catalysts were prone to leaching, enlargement was realized by linking them to chitosan.[63,72] The Lentikats were mainly used for nitrate and nitrite reduction[75-77,79,84] and in the synthesis of fine chemicals.[72]

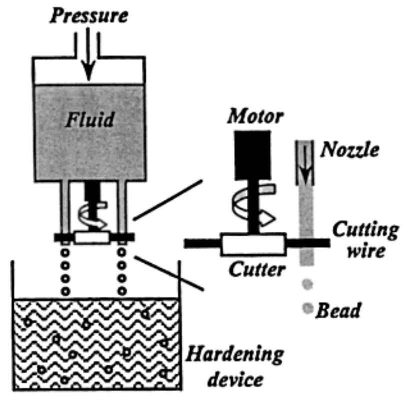
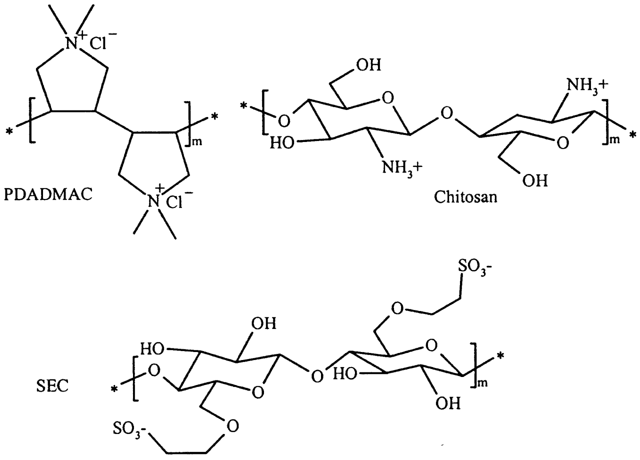


Figure 5. Schematic drawing of the jetcutter (adapted from ref 81).

The particles can be hydrogels, like in the case of PVA, cross-linked elastomers[78] or hollow beads. Sulfoethyl cellulose (SEC) hollow beads (Scheme 5), e.g., were prepared by dripping an aqueous solution of the anionic SEC into a stirred solution of a polycation, either chitosan or poly(diallyl dimethylammonium chloride) (PDADMAC). The core of the capsule remained liquid here.

Scheme 5. Structure of PDADMAC, Chitosan and SEC



Similar PDMS spheres with typical diameters between 50 and 200 μm were formed via suspension polycondensation of TEOS with oligomeric silanols in an immiscible continuous phase of either liquid paraffin, ethylene glycol or water. Chloromethylphenyl, amine, pyridine, or alkyl groups were introduced by changing the monomeric Si species. The pyridine residues were used to retain Mo species, which were successfully applied in the highly selective epoxidation of cyclohexene with *tert*-butylhydroperoxide (tBHP). The activity was superior to both that of soluble $MoO_2(acac)_2$ and of poly(benzimidazole)-supported Mo.[52]

7. Incorporation of Heterogeneous Catalysts

Introduction

A decreased consumption of Pd or other noble metals in the preparation of hydrogen-permeable membranes, was the main purpose in the pioneering work of Gryaznov on CMRs. In a first approach, a PDMS coating simply served as a “gutter layer” on which a very thin metallic film was deposited. Not being self-supporting, this film could be kept extremely thin, thus resulting in both a high flux and a 100-fold reduction of the necessary amount of expensive noble metal.[85] In a later patent, the incorporation of heterogeneous Pd catalysts in a silicone matrix was described.[86] Pd was ligated to an organosilicon compound that was covalently bound to a silica surface. The patented membranes were only exemplified for the gas phase hydrogenation of cyclopentadiene. It was only much later, after a publication in Nature,[87] that similar types of CMs received more attention and were tested in a variety of reactions with different kinds of catalysts.[51,57,88]

All catalysts mentioned in this Chapter are as such already of a heterogeneous nature. They are embedded in a membrane in order to improve their selectivity or activity, thanks to a changed sorption in the catalyst, or to enable different reactor setups.

Zeozymes

Fe–Phthalocyanine in Zeolite Y (FePcY)

Mimics of enzymes in zeolites are referred to as “zeozymes”. A zeolite Y with Fe−phthalocyanine (FePc) complexes immobilized in its cages (Figure 6) was the first zeozyme to be incorporated in PDMS.[87] When this catalyst was brought in a membrane reactor setup for the oxidation of cyclohexane (Scheme 6) with tBHP, a remarkable 6-fold increase in activity was observed as compared with the best possible experimental setup for nonembedded FePcY. The main reason for this effect was the influence of PDMS on the relative amount of reagents that were sorbed in the zeolite pores. Indeed, when the composite membrane was mounted in the membrane reactor, the solvent acetone became redundant since the two immiscible reagent phases were now contacted through the membrane. It made the system more environmentally friendly and facilitated the subsequent product purification. As a result of the hydrophobic environment created by the PDMS matrix, water molecules, present in the peroxide phase, were excluded from the hydrophilic catalyst. At the same time, both reagents were excessively sorbed in the PDMS to form an abundant reservoir of reagents. The PDMS thus formed an optimal “solvent phase” bringing about strongly enhanced activities.[88,89] The concept was claimed to be applicable to any catalyst applied in reactions that involve immiscible reagent phases, provided the choice of the appropriate polymer with respect to selective sorption and diffusion of reagents and products.[87]

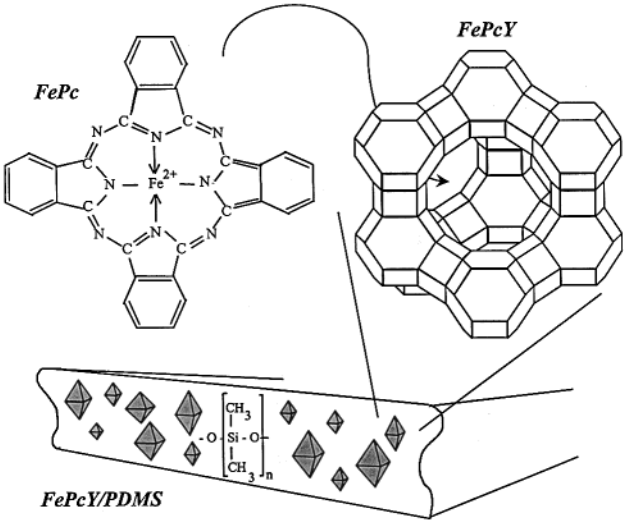
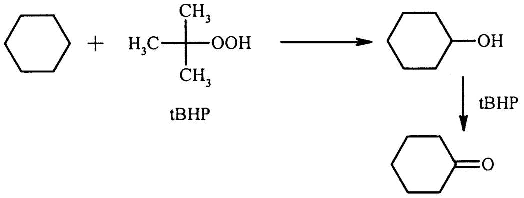


Figure 6. Schematic representation of the incorporation of FePcY in PDMS (adapted from ref 87).

Scheme 6. Oxidation of Cyclohexane with TBHP



Over longer reaction times, a reversible catalyst deactivation was observed, attributed to too strong a sorption of the oxidation products in the zeolite pores.[88−90] In the cyclohexane oxidation, cyclohexanol and cyclohexanone were found in both the aqueous and the organic phase.[89,90] On the other hand, it was proven in the oxidation of the more hydrophobic n-dodecane that such kind of liquid phase CMRs could actually be applied to integrate reaction and a full separation in one single process unit.[90]

The influence of several membrane parameters on this FePcY/PDMS system was studied.[90] Until a membrane thickness as high as 200 μm, the reaction was kinetically controlled. Despite the increased tortuosity in the membrane with increasing zeolite loading, no significant effect of loading on reaction rate could be found for a 200 μm thick membrane.

The mass transfer in these FePcY/PDMS membranes was modeled, and the diffusion through the composite catalytic membrane could be predicted from mass transfer coefficients that were obtained separately on the nonembedded catalyst and the unfilled polymer material.[91] Further modeling was done on the alkene epoxidation, where it was shown how the organophilic membrane phase lowered the excess of peroxide at the catalyst site and thus reduced peroxide decomposition and catalyst deactivation.[92] In addition to the work by Baron and the work of Kaliaguine mentioned later, only few other papers modeled reactions with dense polymeric CMs.[93−95]

[Mn(bpy)$_2$]$^{2+}$-Y

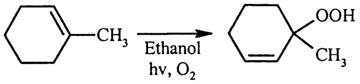
Another zeozyme, [Mn(bpy)$_2$]$^{2+}$-Y, was incorporated in PDMS for the epoxidation of olefins. A good catalytic activity was obtained for reagents that diffused easily through the polymer and sorbed well in the zeolite. This was either obtained when the substrate itself had a high affinity for the membrane polymer or when a solvent with a high affinity for the membrane was used. The membrane would then swell and thus facilitate the diffusion of the substrate. At the same time, the solvent should have an as low as possible affinity for the zeolite in order to minimize competition with the reagents for sorption at the active sites. Hydrogen peroxide was less reactive as oxidant than tBHP, due to its lower affinity for the membrane phase.[57,88,96]

ZnPcY

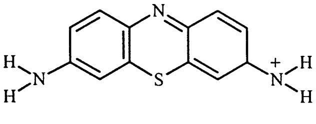
Thanks to its transparent, hydrophobic, and highly permeable nature, incorporation of heterogenised sensitizers in PDMS improved their performance in selective photooxidations. Sensitizers significantly increase the activity of catalysts by sensitizing the semiconductor outside its optical absorption range at wavelengths greater than that corresponding to the band gap. For synthetic purposes, the reactive intermediate in photooxidation is singlet molecular oxygen. This active form of molecular oxygen is mostly obtained via an energy transfer from an excited sensitizer to the ground state of molecular oxygen. During this energy transfer, the very reactive superoxide O_2^- is sometimes formed which is of interest in degradation processes, but surely not in selective oxidations.[97]

Zn-phthalocyanine zeolite Y (ZnPcY) was used in the photosensitized oxidation of 1-methyl-1-cyclohexene in ethanol (Scheme 7). When incorporated at a 1 wt % loading in a 750 μm thick PDMS membrane, the activity of the catalyst almost doubled, due to enrichment of the substrate in the membrane. However, increasing the catalyst loading decreased the activity, following enhanced reflection of light and densification of the polymer matrix. The related thionine-Y sensitized systems (Scheme 8) further proved the beneficial effect of the PDMS surrounding: traces of water were completely excluded from the hydrophilic zeolite, thus stabilizing the sensitizer and enhancing activity 4-fold. Some important solvent effects were illustrated in the oxidation of 2,3-dimethyl-2-butene. Ethanol, which was considered as a good “cleaning solvent” for the zeolite pores, led to much better results than hexane, despite the 3 times longer lifetime of singlet molecular oxygen in hexane. Excessive amounts of hexane were assumed to be present in the membrane and to compete with the substrate for sorption at the active sites.[98]

Scheme 7. Photosensitized Oxidation of 1-Methyl-1-cyclohexene in Methanol



Scheme 8. Structure of Thionine



Thionin

Ti Catalysts in Selective Oxidations

The versatility of the PDMS-occluded membrane systems was further proven with the Ti-containing catalysts TS-1[99] and Ti−MCM-41,[100] a microporous and a mesoporous titaniumsilicate, respectively. They were applied in the bi-phasic solvent-free oxidation of hexane and the epoxidation of *cis*-cyclooctene, respectively.[101] Thanks to the absence of a solvent, undesired blank reactions were suppressed, and the absence of water in the catalyst pores limited the epoxide ring opening.[102] However, there was a drawback: consecutive oxidation reactions gained importance, as no solvent was present anymore to remove the products from the catalyst pores.[101] In the epoxidation of *cis*-cyclo-octene, the olefin and the epoxide were completely absent in the aqueous phase, implying an important facilitation of the final product recovery.[57]

The group of Kaliaguine[103,104] further tested and modeled this system for hexane oxygenation. Increasing temperatures were accompanied by a remarkable increase in the alcohol/ketone ratio, an effect that was exactly the opposite of the one observed in conventional slurry reactors. This was attributed to a faster diffusion of the alcohols than the ketones in the membrane phase. In contrast to the cyclohexane/FePcY system,[90] a higher catalyst loading resulted here in an increased reaction rate. This was attributed to an increased water flux through the membrane as the catalyst acted in fact as a hydrophilic filler, hence increasing the water (and thus peroxide) sorption.[104] Reaction rates could be increased by adding modifiers to the membrane,[26] or by blending hydrophilic polymers with the PDMS. These observations were related to an improved balance between the sorbed amounts of peroxide (increased) and alkane (decreased).[103]

With the oxidation of propylene with H_2O_2, this group also patented the only gas/liquid membrane reaction with PDMS described till now. Compared with conventional bubble-slurry reactors, the secondary reactions could be suppressed since the propylene oxide that is dissolved in the H_2O_2 solution, is no longer contacting the catalyst.[26]

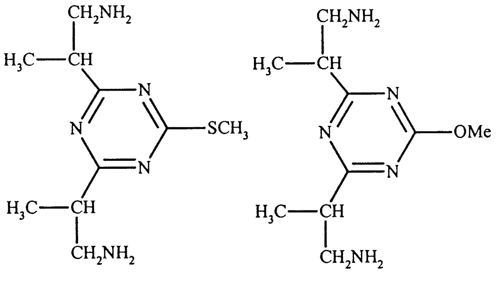
Frisch and co-workers were the only ones to use pseudo-interpenetrating networks (PIPN) as polymer systems for catalyst incorporation. In the dehydrogenation of cyclohexane over Ti and Ni zeolite X, the poly(ethylacrylate) (PEA) PIPNs showed considerably less cracks than the comparable membranes made by conventional mixing of the zeolite with a polymeric solution. On the other hand, conversions with the PIPNs were lower, as ascribed to active site blocking by the penetrated polymer chains. This follows from the preparation method in which the zeolite was mixed with a monomeric solution of ethylacrylate.[105] With a Co ion-exchanged zeolite, the PIPN membranes were used in the cis to trans isomerization of 1,3-pentadiene.[106]

Ti Catalysts in Photomineralization

A different type of Ti-containing oxidation catalyst was incorporated in polymeric membranes that were used for photomineralization (breakdown to CO_2, water and, in the case of halogenated compounds, to halide-ions[107]) of pesticides,[108−111] alkanoic acids,[99,112,113] azo dyes,[114] and phenols[107,109] in wastewaters, or of volatile organics from air.[115] This photocatalytic oxidation forms, together with the photo-Fenton chemistry mentioned later, an important new type of advanced oxidation processes in water treatment.[107] The finely divided TiO_2 is normally dispersed in a UV-radiated aqueous solution as a slurry. Given the small particle size, the subsequent separation from the decontaminated water is often problematic. For this reason, anchoring of the TiO_2 to a suitable support is wanted. A transparent membrane matrix with a good adsorption capacity for the organic compounds is required here. Furthermore, neither mass transfer limitation nor catalyst deactivation should take place.[116]

Hydrogen peroxide was most commonly used as the oxygen source,[107,108,112−114] in addition to oxygen,[117] ozone,[110−113] and air[115] in some specific cases. The latter two had to be used in the degradation of prometryn and prometon (Scheme 9) because cyanuric acid is produced as the final and photostable product with H_2O_2.[108] With ozone, a nonphotocatalytic reaction was also observed.[112,113] The technology to produce these membranes is based on the photografting of an (acrylate solution)/photocatalyst (mostly 30 wt % TiO_2) solution on a support, most commonly a nonwoven polyester. The final porosity can be regulated by controlling the rheology of the acrylate coating solution to be 2−4 μm, exceptionally 0.02−0.1 μm, thus maintaining a high active surface area.[118] In certain cases, sensitizers, generally organometallic forms of Fe, Co, and V, are co-incorporated.[109−113,115,118] The systems were patented by Chimia Prodotti e Processi, an Italian company,[119] and were developed up to pre-industrial scale. To exploit the full radiation field appropriately and thus increase the rates of photodegradation, the membrane geometry had to be chosen carefully. The small-scale reactors consisted of a cylindrical reactor in which both the radiation source and the membrane were placed coaxially (Figure 7). This photocatalytic membrane technology relies on the formation of short-lived oxidative radicals (mostly hydroxyls) generated on the immobilized semiconductor.[109] A kinetic model was successfully applied to interpret the photodegradation curves.[107,112,113]

Scheme 9. Structure of Prometryn and Prometon



Prometryn Prometon

In an alternative approach, TiO_2 catalysts were incorporated in Nafion, by mixing a TiO_2/2-propanol (IPA) sol with a Nafion/IPA solution. In the photodecomposition of acetic acid to yield methane, the membrane-occluded catalyst was clearly less active than the reference TiO_2 catalysts. The sulfonic acid groups on the Nafion were assumed to bind too strongly to the positively charged sites of TiO_2 which serve as the active sites for adsorption of the acetate ions.[120]

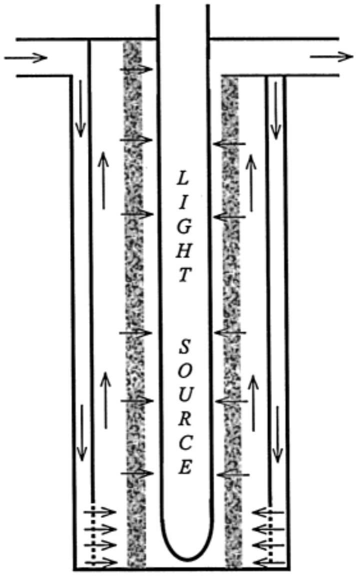


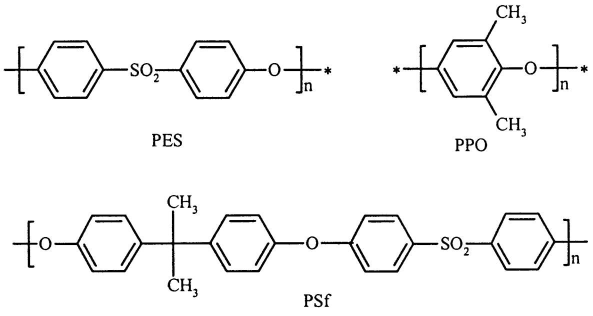
Figure 7. Schematic presentation of the small-scale reactors used in photo reactions with a coaxially placed light source (adapted from ref 117).

Heteropolyacids

Mainly the group of Lee combined different types of heteropolyacids (HPA)s with a set of polymers. HPAs have both acidic and redox catalytic properties. They have a characteristic adsorption behavior: most nonpolar chemicals are adsorbed only on their surface, while the more polar ones penetrate into the bulk to form pseudoliquid phases.

$H_3PMo_{12}O_{40}$ was incorporated in poly(sulfone) (PSf) (Scheme 10) using dimethylformamide (DMF) as the casting solvent. The decreasing T_g with incorporation of catalyst in the polymer showed that a mere physical blending of the HPA with the PSf took place.[121] Two competing reactions took place when 2-propanol was permeated as a gas through the catalytic membrane:[122] an acid catalyzed dehydration to propylene and an oxidative dehydrogenation via a redox mechanism to acetone. The incorporation of the catalyst in the membrane drastically changed the reaction selectivity. First, DMF sorbed strongly on the acidic sites of the HPA, thus greatly decreasing the propylene formation. Second, the incorporated catalyst was much more active in the formation of acetone due to the enlarged active surface. The large surface was created by the uniform and fine distribution of the HPA in the PSf.[121] Third, the twice as high permeability of the membrane for acetone than for propylene was suggested to further increase the selectivity for acetone. All together, the incorporation in the membrane led to a 15-fold increase of the

Scheme 10. Structure of PES, PPO, and PSf



acetone/propylene ratio as compared with a reaction in a fixed bed with unsupported HPA.[122] Similar results were obtained later for ethanol conversion.[121]

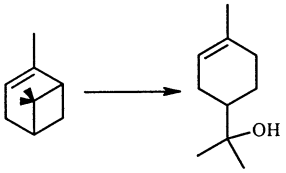
The same HPA was also incorporated in poly(ethersulfone) (PES) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The observed increase in T_g for PPO upon incorporation indicated a certain interaction between both phases. This was also reflected in the different catalytic behavior for this membrane. With water vapor as the nonsolvent, catalytic membranes with a controlled porosity could be prepared via phase inversion.[121]

The tungsten analogue, $H_3PW_{12}O_{40}$, was incorporated in PVA and was used in the esterification of acetic acid with *n*-butanol. Considerable leaching of the catalyst was observed, which could be prevented by cross-linking the membrane with glutaraldehyde.[123]

Acid Catalysts

Heterogeneous acid catalysts were incorporated in PDMS and used in the hydration of α-pinene to form α-terpineol (Scheme 11).[93,124] With ultrastable zeolite Y, zeolite β, and sulfonated carbons as catalysts, membranes with varying thickness and catalyst loading were tested. As could be anticipated, incorporation of the catalysts in the hydrophobic matrix decreased the hydration activity. The influence on the α-terpineol-selectivity, on the other hand, was much less straightforward and ascribed to the substantial difference in particle size for the different catalysts (from 0.1 to 20 μm) and the different water sorption.

Scheme 11. Hydration of α-Pinene



Pd on Carbon

Originally applied in electrochemical devices, gas-permeable ionic liquid (IL)/polymer gels were used to incorporate Pd/carbon catalysts. The IL, as a very interesting but rather expensive reaction medium,[125] and the Pd catalyst were thus incorporated simultaneously, and the resulting membrane was applied as a contactor in the hydrogenation of propene. The membrane was formed from a 4-methylpentan-2-one solution containing 1-*n*-butyl-3-methylimidazolium hexafluorophosphate as the IL, Pd on activated carbon as the catalyst, and poly(vinylidenefluoride)-hexafluoropropylene (PVDF-hexafluoropropylene) copolymer as the membrane-forming polymer.[126]

8. Heterogenisation of Homogeneous Catalysts

Introduction

With homogeneous catalysts occluded in a polymeric membrane, all above-mentioned advantages still remain, and similar important increases in selectivity or activity were sometimes obtained. But additionally, the membrane occlusion results here in a rather easy way of heterogenisation and a good dispersion of the catalyst.[57,88,101] Given the extremely high prices of many of them—especially the chiral TMCs—the possibility to recycle such catalysts forms an important challenge, whereas good dispersions can generate higher stabilities and activities. In a similar way as for the homogeneous catalysts, additives can also be incorporated.

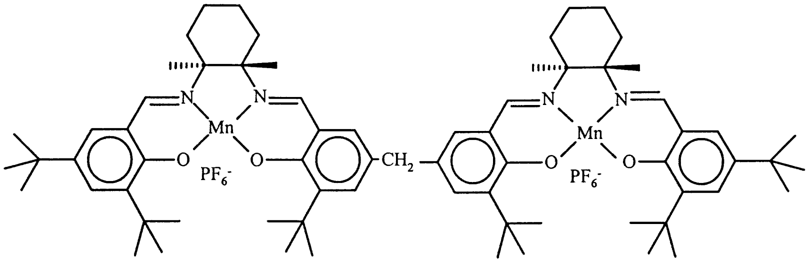
A specific and important problem occurring in liquid-phase reactions with such membrane-occluded homogeneous catalysts is leaching of the complex and/or the co-incorporated additive out of the catalytic membrane into the liquid reaction phase.

Retention of TMCs in a Polymer Matrix

While the absence of strong interaction forces between the complexes and the polymer is one of the strong points of this way of complex heterogenisation, this renders them at the same time susceptible to leaching. In most cases, the catalyst/polymer interaction is believed to be a combination of merely van der Waals interactions and some steric constraints of the surrounding polymer chains on the catalyst.[127]

The relation among membrane swelling in a solvent, catalyst solubility, and catalyst leaching from the polymer was studied in detail for several catalysts.[51,127,128] If solvents exist in which the complex does not dissolve at all, these should be the solvents of choice to perform the reactions in. Apart from establishing a real chemical (ionic, covalent or coordinative) bond between the complex and the polymer, this was about the only way to prevent leaching completely. Leaching could be greatly reduced by placing bulky groups on the catalyst, by preparing dimeric (Scheme 12) or oligomeric forms of it or by selecting more appropriate reaction conditions, e.g., by using solvents that combine moderate membrane swelling with low solubility of the complex.[51] On the other hand, adaptations on the level of the polymeric

Scheme 12. Dimeric Form of Jacobsen Catalyst

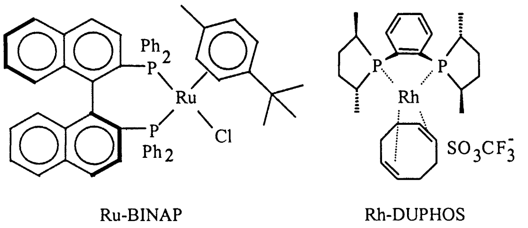


matrix could also restrict leaching: increasing the degree of cross-linking of the membrane, decreasing the MW of the polymer chains, or blending with other polymers to change the affinity.[129] It should be considered that both the shape and the solubility of the complex might change when the TMC becomes activated under reaction conditions. Jacobsen catalyst, e.g., forms a Mn−oxo complex in a folded shape when activated, leading to a clearly reduced leaching under the actual reaction conditions. Finally, especially in discontinuous reaction modes, the polarity of the reaction medium, and thus the solubility of the TMC, changes as products are formed and reagents are consumed. This is most apparent in alkane oxidations at high conversion levels, where the polarity of the reaction medium increases drastically.[51]

Chiral TMCs

Being among the most versatile and selective chiral catalysts available at that time, Ru−BINAP and the Jacobsen catalyst were the first homogeneous TMCs to be occluded in PDMS,[130] followed later by Rh−DUPHOS (Scheme 13).[131] They were used in hydrogenation and epoxidation reactions. For the Ru−BINAP/PDMS system, the same levels of conversion could be realized at more moderate conditions of temperature and pressure by co-incorporating acids in the membrane.[132] However, the long-term stability of these systems seemed to be insufficient.[128,130] One of the main reasons for this was assumed to be leaching, being a complex result of polymer, solvent, substrate, and product interactions. By preparing dimeric forms and carefully selecting solvents, leaching of Jacobsen catalyst could be effectively decreased, but never completely avoided.[127] The best solution to the leaching problem was offered for Rh−DUPHOS by using water as the nondissolving solvent.[118] In the hydrogenation of methyl 2-acetamidoacrylate, the catalytic membrane could be recycled successfully. The polarity of the PDMS matrix was changed by adding silica. Instead of decreasing the swelling of the polymer through physical cross-linking, the introduced surface silanols decreased the hydrophobicity of the membrane. As this enhanced the mass transfer in the 1 mm thick membrane, activity increased. The slightly decreased enantioselectivity of the PDMS-immobilized Rh−DUPHOS catalyst was ascribed to the competitive achiral hydrogenation activity of the hydrosilyation Pt catalyst that was still present in the catalytic membrane. The results obtained with these chiral catalysts indirectly confirm the preservation of the intact structure of a TMC in PDMS, since too strong an interaction between the polymer and the complex would have destroyed the chiral induction.

Scheme 13. Structure of Ru−BINAP and Rh−DUPHOS



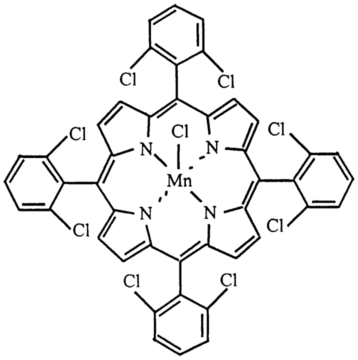
PVA was later reported as a useful alternative for PDMS. Its very different sorption characteristics could open interesting perspectives for reactions with more polar substrates that suffer from low sorption in PDMS.[133]

Nonchiral TMCs

Due to dispersion problems, the occlusion of FePc in PDMS was found to be impossible. After selecting the best solvent to dissolve this complex, a membrane could be formed, but the complexes were never monodispersed. When this membrane was used in reactions, a complete decoloration of the membrane occurred within few minutes, indicating the oxidation of one complex by another.[57,58]

The dispersion problems were case specific and not always so detrimental. With the related TDCPP(Mn)-Cl complex in PDMS (Scheme 14), oxidation reactions could be performed successfully. Leaching of the complex was completely absent in the oxidation of an aqueous mixture of cyclic alcohols with tBHP, since the complex does not dissolve in water. Together with a significantly increased activity upon occlusion, a clear correlation was found between the PDMS sorption and the reactivity of the different alcohols. Under homogeneous reaction conditions, the order of reactivity decreased as follows: cycloheptanol < cyclopentanol < cyclohexanol. With the complex dispersed in PDMS, the order of reactivity was reversed, as a clear consequence of the preferential sorption of the different alcohols in the membrane polymer.[58,134] In a competitive reaction with all three alcohols together, coupling phenomena between the three reagents, both on the level of sorption and diffusion, were evidenced. Mass transfer in the 175 μm thick membranes limited these reactions, even at very low catalyst loadings of less than 0.1 wt %.[51,58]

Scheme 14. Structure of TDCPP(Mn)Cl

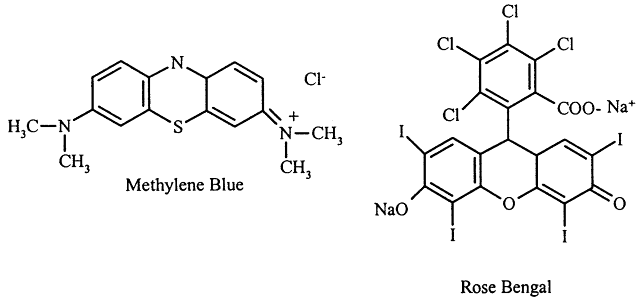


In the epoxidation of deactivated substrates, like hydroxyl alkenes, ketone formation is an important side-reaction. In homogeneous reactions, it can be partly suppressed in the presence of an electron-donating axial ligand, like imidazole. Embedded in PDMS, the ketone formation was completely absent in addition to a more than 20-fold increase in activity. This was attributed to the lowered mobility of the axial ligand in the more restrictive PDMS phase which results in a prolonged coordination to the active center and to the PDMS influence on better balanced concentrations of alkene, ligand, and peroxide around the metal center.[51,135]

Photosensitizers

Again PDMS and Nafion return as the two polymers of choice to embed photosensitizers in membranes. The dispersion problems in PDMS were similar to the ones reported for TMCs: the hardly soluble ZnPc and the charged species Rose Bengal and thionine (Scheme 15) could not be dispersed well.

Scheme 15. Structure of Methylene Blue and Rose Bengal



On the other hand, the incorporation of porphyrinic systems in PDMS was more successful. In the oxidation of 1-methyl-1-cyclohexene, leaching was completely absent for the larger chloro-containing metalloporphyrins in ethanol. To allow the use of dichloromethane (DCM), a better solvent with a higher singlet oxygen lifetime, a completely nonleaching system was created by reacting a vinyl-substituted porphyrin with the Si−H groups of the PDMS precursor. Even though demanding more preparative efforts, the activity was much higher than that in ethanol.[98] Similar systems of ZnPc and Rose Bengal covalently bound to PDMS were used in the oxidation of mercaptans.[136]

The transparent properties of Nafion, in combination with the fact that its microheterogeneous structure is often more than just a passive medium, motivated Niu et al. to use this polymer to immobilize methylene blue (MB) as a photosensitizer in the oxidation of anthracenes. MB was sorbed into the water-swollen Na^+−Nafion membrane from a dilute aqueous solution. Spectroscopic studies indicated a heterogeneous distribution of the chromophores in the water-swollen membrane. All substrates reacted much faster with the Nafion-embedded catalyst than under homogeneous conditions. This was ascribed to an active participation of the membrane: oxygen accumulated in the hydrophobic backbone of the Nafion and thus rendered the thermal decomposition reaction of the endoperoxide to the original product and O_2 more difficult.[137]

Metals and Metalclusters

A vast amount of literature is available on polymers in which metals or metalclusters are incorporated.[138]

The specific metal/polymer interactions, sometimes lead to exceptional catalytic behavior. A detailed study of this matter is however beyond the scope of this review. Basically, only papers with films actually applied in CMRs and some closely related papers will be mentioned here.

One of the most successful applications of polymeric catalytic membranes is without any doubt the Remedia Catalytic Filter System developed by W. L. Gore.[139] The Remedia filters destroy the toxic gaseous dioxins and furans from stationary industrial combustion sources by converting them into insignificant amounts of water, CO_2, and HCl (Figure 8). No chemicals have to be injected, fly ashes remain unchanged, and, unlike carbon-based systems, risk of fire is absent. In January 2002, 29 industrial plants were operated worldwide, with capacities ranging from 1000 to over 225 000 Nm^3/h. The Remedia catalytic filter consists of a Gore-tex membrane, an expanded PTFE (ePTFE) microporous film, needlepunched into a scrim with a catalytically active ePTFE felt. The catalyst is a V_2O_5 on a TiO_2 support. The microporous membrane captures the dust but allows gases to pass to the catalyst. The system works at a maximum operating temperature of 260 °C and has an expected lifetime of more than 5 years.

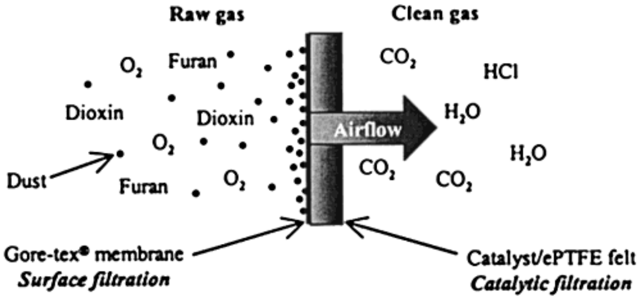


Figure 8. Schematic illustration of the combination of filtration of dust with catalytic degradation of toxic gases (adapted from ref 139).

Fe has been embedded in Nafion and alginates through ion-exchange. The Nafion membranes were successfully applied by Kiwi and co-workers in the photo-Fenton process to abate nonbiodegradable azo dyes. The degradation process is based on the light enhanced generation of mainly OH radicals from H_2O_2 in the presence of added Fe^{3+}. The membranes were used to eliminate the need in wastewaters to remove free Fe ions after pollutant degradation.[140,141]

The membrane was successfully reused 25 times in the abatement of Orange II (Figure 9). The membrane became about 40% more active after a first regeneration, as ascribed to the formation of highly stable Nafion/Fe(II) species. Discrete Fe clusters were homogeneously distributed over the membrane with a size distribution narrowly centered around 3.7 nm.[140] The system was modeled in order to optimize the reaction parameters.[141] The same dye, together with several chlorophenols, was mineralized later by using the much cheaper poly(ethylene)-based anhydride-modified blockcopolymer films with immobilized TiO_2, Fe_2O_3, or Fe^{3+}. Similar or even higher activities were found for all immobilized catalysts as compared to their respective suspensions or homo-

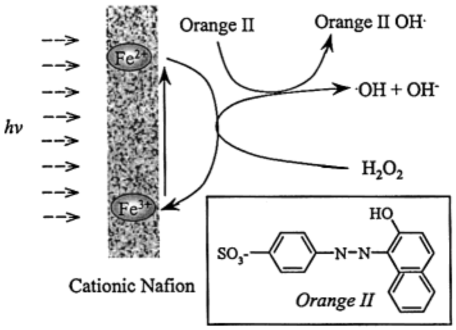


Figure 9. Simplified scheme of the photodegradation reaction of Orange II (adapted from ref 140).

geneous solutions. This was ascribed to the high transparency of the film polymer, in combination with a much better dispersion of the catalyst in the polymer and the absence of aggregate formation. The poly(ethylene) remained unattacked by the OH-radicals, and no leaching was noticed.[142] In an alternative approach to decrease the costs of the membrane, very thin Nafion films were coated on glass-fiber mats, leading to a 15-fold reduction of the amount of Nafion used.[143]

The alginate gel beads were formed by dripping an aqueous Na-alginate solution in a bath containing $FeCl_3.6H_2O$. The Fe ions replaced the Na ions and thus cross-linked the beads. As a consequence of the preparation method, the Fe ions were mainly present at the outer border of the beads. In contrast to the above-mentioned Nafion/Fe system, a pH above 5 could be applied here to mineralize Orange II. This is important since it allows the subsequent biological treatment to start immediately without pH adjustment[144] and avoids the costly initial pH adjustment of many effluents to attain acidic conditions.[143] For the degradation of 2,4-dichlorophenol, a pH up to 11 could even be used with an Fe/Nafion membrane.[145]

Parmaliani and co-workers[146−148] used the same Nafion-Fe/H_2O_2 Fenton system in the selective oxidation of light alkanes. However, the membrane preparation and experimental setup were completely different: a carbon/Teflon paste was deposited on carbon paper and subsequently activated. The membranes were then either impregnated with an alcoholic solution of HPA, or Nafion-H. The reaction products were trapped downstream, while a pressure was applied upstream in order to control the filling of the pores by the Fe/H_2O_2 solution. The Nafion/carbon membrane was the most active membrane due to its stability in the presence of H_2O_2, while the heteropolyacids formed inactive peroxophosphates.

Based on the success story of metallic Pd membranes in hydrogenations, several authors incorporated Pd in polymeric membranes in order to create a higher active surface area with a smaller amount of Pd. A variety of Pd precursors and membrane polymers was used to hydrogenate edible oils,[149,150] isoprene,[151,154] 1-octene,[152] cyclopentadiene,[151,153−155] propyne,[156,157] propylene,[158] ethylene,[158] propadiene,[156] and butadiene.[154,159,160]

A nylon-6 membrane was functionalized with the cluster compound $Pd_3(OAc)_6$ and compared with a conventional slurry reactor with a carbon-supported Pd catalyst. The formation of *trans*-isomeric triglycerides in the hardening of oils was successfully suppressed by using the regime of forced flow through the membrane pores, a technique which also improved other processes where internal diffusion limitation was important and where the use of finely dispersed catalysts was not desired.[149,150]

Liao and co-workers refluxed a Pd−chloride precursor in ethanolic medium with several kinds of modified PPO and PSf polymers to obtain dense CMs after casting.[151] Since these membranes were very fragile, they adapted the synthesis and prepared CMs based on hollow fibers. As it seemed impossible to support $PdCl_2$ as such on the hollow fibers, Pd was anchored first on either poly(vinylpyrrolidone) (PVP),[154] ethyl cellulose, or melamine-formaldehyde.[153] A solution of these metalated polymers was subsequently circulated through the inside of CA, PSf, or poly(acrylonitrile) (PAN) hollow fibers in order to retain them in the micropores. In a CMR setup with the diene at the inner side of the fiber and H_2 permeating from the outer side, conversion and monoene selectivity could simultaneously be higher than 90%, which was impossible in a similar fixed bed reactor. Indeed, the CMR succeeded in creating a concentration gradient of hydrogen between the inlet and outlet of the reactor that matched the one of the diene at the other side of the hollow fiber. The catalytic results depended strongly on the polymer type used to prepare the hollow fiber and also on the one used to anchor the metal: best results were obtained with PVP−Pd combined with CA or PAN hollow fibers. The CMs were later also applied in other selective hydrogenations.[155,156,159] With butadiene, the isomerization of 1-butene could be inhibited by preparing Co/Pd bimetallic catalysts. The synergetic effects between Co and Pd took only place when reduction was done with $NaBH_4$ instead of hydrazine. It was assumed that small Pd clusters were then deposited on superfine cobalt boride particles.[159]

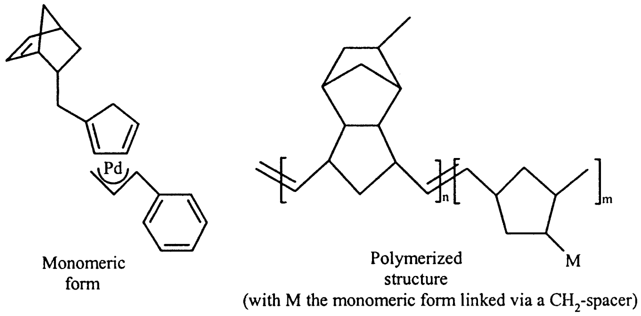
Still another method was used to bring $PdCl_2$ in phenophthalein poly(ethersulfone): the $PdCl_2$ solution was refluxed here in ethanol/benzene with a preswollen membrane. The resulting membranes were active in the hydrogenation of 1-octene.[152]

Fritsch and co-workers used Pd−diacetate as the precursor. Given their high hydrogen permeability, poly(imides) seemed most promising to prepare CMs, but visible holes appeared in the films after the Pd reduction. Poly(amides) (PAs) were tried as an alternative, since the hydrogen bond formation associated with the amidebond, increased the mechanical stability. However, H_2 permeability was lower by more than 1 order of magnitude.[161] The best of both polymers was finally combined in poly(amide−imide)s (PAIs). The membrane preparation method was claimed to be limited only by the solubility of the metal salts in solvents such as *N*-methylpyrrolidone (NMP), and the fast accessibility of the active sites by, e.g., hydrogen.[162] The research was later broadened to the incorporation of bimetallic clusters, like Pd/Cu, Pd/Co, and Pd/Pb in PAIs. The cluster sizes were determined by the solvent used and the stirring time of the metal salt/polymer solution. They varied consistently between 1 and 3 μm with a smaller amount of clusters up to 30 nm. When silicones were used instead of PAI, larger aggregates up to 80 nm were obtained, due to the higher mobility of the atoms in the silicone matrix.[163,164]

Another two-step synthesis procedure for nanosised Pd clusters was reported later.[157] For this purpose, asymmetric PAN, PEI, and PAI membranes were first dipped into a solution of tetraethyltitanate. After hydrolysis, TiO_2 remained deposited in the pores. Pd−acetate was subsequently introduced in the membrane from a methylethyl ketone solution. TiO_2 was selected because of its easy in situ preparation and its wide use as a catalyst support.

In an attempt to prepare monodisperse Pd nanoclusters, norbornene monomeric species were derivatized that could coordinate one Pd atom each (Scheme 16).[158,160] They were then used in a diblock copolymeric film in which the microdomain interfases were supposed to control cluster nucleation and growth. The polymer only succeeded partly in stabilizing the clusters since their size increased from 20−30 to 30−35 Å after repeated use in hydrogenations. The reuse was also accompanied by a changed polymer structure as visualized in a rough surface and the appearance of 15−60 μm voids inside the film.

Scheme 16. Structure of the norbornene Monomeric and Polymeric Forms



A final application of Pd-containing membranes was in the controlled synthesis of hydrogen peroxide directly from molecular hydrogen and oxygen outside the explosion range.[22] A Pd/carbon catalyst was coated here from an alcohol/water solution of Nafion on a PTFE/carbon paper membrane. The catalyst side of the membrane was contacted with an aqueous solution to which oxygen and acids were added. This oxygen reacted with the H_2, which permeated from the other side to form H_2O_2.

Acid Catalysis

Cation exchange membranes (CEMs) were used as acid catalysts in the esterification of oleic acid with methanol. The reaction mixture was circulated between two CEMs. At the other side, these CEMs were in contact with a catalyzing acid, diluted in methanol. The proton thus appeared at the surface of the membrane which was directed to the reaction mixture, while the anion associated to these protons remained at the other side. None of the six different catalyzing acids that were tested was lost this way and a downstream separation became superfluous.[165]

9. Membrane-Assisted Catalysis

Introduction

The key success factor of this concept is the choice of an appropriate membrane that allows the full retention of the catalyst and the complete passage of the products. In particular, a stable catalyst, but also a short reaction time (to realize high space-time yields), and a highly selective reaction should be involved.[37] In all cases, the aim is to achieve a high total turnover number, an easy recovery of the catalyst, or to operate in continuous or semi-batch (also called “repetitive batch”[166]) modes. In contrast with a fixed bed reactor, membrane-assisted catalysis has the advantage that fresh catalyst can be supplemented easily even in a continuous process.

Thanks to the recovery of the catalyst, working at high catalyst concentrations becomes much more economical, and competing non-catalyzed reactions can be controlled more easily. Especially in a continuous mode, where the reactor permanently operates at a conversion level that is as high as practical circumstances allow, the educt concentration is thus kept low. Since remaining free ligands can be washed out during the initial phase of the membrane-assisted process,[167] the catalyst purification prior to reaction can be shortened.

Pervaporation

Esterification

A. Introduction. By far the most studied reaction in pervaporation (PV) assisted catalysis, is the esterification (Table 3). It is a typical example of an equilibrium-limited reaction with industrial relevance and with well-known reaction mechanisms. This hybrid process already made it to several industrial applications.[168] The thermodynamic equilibrium in such reaction can be easily shifted and obtained in a shorter reaction time by either using a large excess of one of the reagents, or by removing one of the products. The former is accompanied with increased costs for subsequent product purification. The latter can be done by reactive distillation, which is only effective when the difference between the volatility of the products and the reactants is sufficiently large and when no azeotropes are formed. Pervaporation offers an interesting alternative since the separation is not limited by relative volatility. Moreover, energy consumption is generally lower because only a fraction of the feed is permeating to undergo the liquid to vapor phase change. PV can also be operated at lower temperatures, which can better match the optimal conditions for reaction, an aspect of high importance in biotransformations.[169]

Due to the commercial availability of excellent permselective PVA membranes (e.g., Sulzer), silica (Pervatech), or zeolitic (e.g., Smart) membranes, it is especially the removal of water which became state-of-the-art technology over the past 15 years. Several industrial plants operate already such PV coupled esterification.[171,172] Apart from several numerical simulations,[169,171,173] many experimental data have been published already. Modeling is important

Table 3. Summary of PV-Aided Esterifications

alcohol	acid	added catalyst	membrane	authors	ref
		Catalytically Passive Membranes			
butanol	acetic acid	-	PVA	Jennings et al.	183
ethanol	acetic acid	Amberlyst 15	Nafion, PVA	Pearce	184
ethanol	oleic acid acetic acid	pTSA	PEI, Chitosan, Nafion	Kita et al.	182
ethanol	valeric acid	pTSA	PI	Xiuyuan et al.	170
propanol, 2-propanol	propionic acid	pTSA	PVA	David et al.	174, 177
propanol	propionic acid	Amberlyst 15	PVA	Schaetzel et al.	175
ethanol	acetic acid	Sulfonated resin	PVA + zeolite A	Gao et al.	185
methanol	salicylic acid	NaOH			
ethanol	acetic acid	H_2SO_4	PI	Zhu et al.	176
ethanol	oleic acid	pTSA	PEI, POPMI[a]	Okamoto et al.	178
ethanol	acetic acid	-	PVA	Waldburger et al.	180
ethanol	tartaric acid	methane sulfonic acid		Keurentjes et al.	169
		Catalytically Active Membranes			
propanol	propionic acid	PSSA	PAN-PSSA PVA-PSSA bi-layered	David et al.	187
butanol	acetic acid	$H_3PW_{12}O_{40}$	PVA/PVA-$H_3PW_{12}O_{40}$ bi-layered	Liu et al.	123
methanol, butanol	acetic acid	Nafion	Nafion	Bagnell et al.	188

[a] POPMI = poly(4,4′-oxydiphenylene pyromellitimide).

for these processes because, e.g., membrane permeability may change with temperature and composition of the mixture.[169,174−181] A complex situation arises since such parameters influence on their turn the rate of ester production. A total analysis that includes those parameters could thus be important for the prediction of the behavior of the systems.[177] In general, a highly permeable membrane with long-term stability is the main requirement,[165] together with the correct membrane surface area/volume ratio: too low an A/V creates too slow a removal of the aimed compound, while too many reagents are removed with too high an A/V.[169]

B. Catalytically Passive Membranes. To our knowledge, Kita et al.[182] published the first PV coupled esterification in open literature, after two earlier patents by American Oil Company[183] and BP.[184] Their study was extended by David et al., who observed several stages in such coupled reactions.[177] Initially, the PV did not affect the reaction rate significantly due to the high ester production rate. The reaction then slowed when approaching the equilibrium value. This was only partly due to the progressive disappearance of both reagents. Indeed, a buildup of water was also observed, resulting from its slow removal by pervaporation. As the water content increased, its permeation through the water selective membrane increased. At a certain moment, these two effects led to a more rapid removal of the water than its production. The water content in the medium thus went through a maximum. At higher conversion levels, the reaction rate was lower, and the removal of water decreased equally. The authors described the influence of four different operating parameters,[174] which either influenced the esterification kinetics, the pervaporation kinetics, or both. Temperature had the strongest influence because it acted on both. The second most effective parameter was the initial acid/alcohol molar ratio. This may change the economy of the process significantly because an extra separation step would be required to recover the unreacted compound. Third, an increase in the membrane area/reaction volume ratio in batch reaction led to a faster conversion. In continuous processes, this parameter should be replaced by the flow rate which determines the contact time of the mixture with the membrane. And finally, the catalyst concentration influenced the process, but only weakly. It was also made clear that a cost optimization could yield other values to be the most optimal.

Another important complicating factor was signaled, specifically with PVA as water selective membrane: the secondary alcohol groups in the PVA could also be esterified by the acid. This would lead to the loss of the separative properties of the membrane.[174,177] During a 24 h long PV-coupled esterification at 50 °C with 8 wt % pTSA, no such ester formation was observed. This was explained by the competition between the hydroxyl groups of the alcohol in solution and the hydroxyl groups of PVA which are immobilized in the polymer. For the latter, there is a diffusion limitation of the reactants and the catalyst into the membrane. Moreover, PVA sorbs water preferentially, which favors the reverse reaction. However, ester formation in the PVA membrane was actually observed when the membrane was reused several times.[177] Such membrane modification was prevented by using a strong acidic ion-exchange resin, but at the expense of catalytic efficiency.

Gao et al. used PVA membranes to show how incorporation of hydrophilic small pore zeolite A in PVA strongly enhanced the reaction, as a consequence of the increased water transport through the zeolite crystal.[185]

Crespo and co-workers pointed out how PV could be interesting for esterifications with ionic liquids as the solvent. As these ILs lack a measurable partial pressure, no driving force exists for these molecules to permeate in PV. Consequently, no IL was detected in the permeate, either during removal of water from an esterification reaction or in the recovery of ethylhexanoate, chosen as a typical target product.[186]

C. Catalytically Active Membranes. Other solutions to solve the problem of unwanted esterification of PVA functional groups are the so-called catalytically active membranes, i.e., "bifunctional" membranes endowed with both catalytic and separative properties. David et al. prepared membranes from blends of a strongly acidic polymer (the protonated form of sodium poly(styrene sulfonate) (PSSA)) with highly hydrophilic polymers (like PAN and PVA) that are insoluble in the feed mixtures. However, it was the extractability of the PSSA in the feed phase that formed a problem. It could be solved by a heat treatment to cross-link the PVA phase. The separative properties of the resulting membranes seemed insufficient, and a multilayer membrane was finally prepared by casting the blend polymeric mixture on top of a commercial PVA membrane.[187] Liu et al. used a similar bi-layered PVA/PVA-$H_3PW_{12}O_{40}$ membrane to increase the conversion of *n*-butanol in the esterification with acetic acid.[123]

H-Nafion tubes were used as one-layered bifunctional membranes that functioned both as reaction catalyst and as PV membrane. The intrinsic separative properties of the catalytically active membrane changed as soon as reaction took place, due to the presence of the formed products in the membrane.[188]

Dehydration

The same HPA-containing PVA as above was used in the dehydration of ethanol coupled to a PSf membrane to remove the produced vapors. The selectivity for ethylene in the permeated stream was 7 times higher than that for a fixed bed reactor. This was ascribed to the greater ethylene permeability: the less permeable compounds ethanol and diethyl ether were better retained and could thus readsorb into the bulk of the HPA to be converted to ethylene.[189]

Condensation

Goa and co-workers applied their zeolite A-filled PVA membranes also in the NaOH catalyzed condensation of methanol with acetone to form 2,2-dimethoxypropane. Just like in the esterification, the zeolite filled PVA membranes performed better than the unfilled PVA.[185]

Oxidation

An interesting effect of PV on the selectivity of oxidation reactions was realized by Solovieva et al.[173] The authors pervaporated a solution of KOH, *n*-butanol, and *n*-hexanol using air as the sweep gas at the permeate side. This air stream supplied simultaneously the driving force for the PV and the oxygen for the reaction. Nafion-like hollow fibers were used to bind the Cu− and Co−tetraphenylporphyrinate oxidation complexes. Whereas a mixture of all types of C_1-C_6 acids and aldehydes was formed at low temperature (60−70 °C) under homogeneous conditions, no C−C bond breaking at all was observed for the immobilized catalysts. Moreover, 90−95% of the products in the PV-assisted oxidation were aldehydes, as a result of the relatively high permeability of aldehydes through this membrane type.

A remarkable synergy between catalysis and separation was observed when PV was coupled to photocatalysis for the degradation of 4-chlorophenol in aqueous streams: both the photocatalysis rate of the substrate (4-fold increase), as well as the PV permeability, especially at low concentrations, were improved, thanks to the coupling. The photocatalysis took advantage of the continuous removal via PV of hydroquinone and benzoquinone. These intermediates normally accumulate and hinder the degradation of 4-chlorophenol by using the available photogenerated electrons. The PV on the other hand operated more efficiently, since the hydrophobic zeolite filled PDMS membrane (GFT) was much more efficient in removing benzoquinone than 4-chlorophenol. Furthermore, the permanent benzoquinone removal shifted the equilibrium in the reversible reaction that converts hydroquinone to benzoquinone. This had the interesting consequence that the concentrations of both intermediates could be globally decreased by removing just one of them.[190]

Diels−Alder Alkylation

In only one application, PV has been combined with a homogeneous alkylation reaction: ferric pyrophosphate hydrate-BF_3 was retained in the continuous liquid-phase production of diisopropyl from ethylene and isobutane.[191] Whereas the patent title mentions "dialytic separation", the actual membrane separation process is pervaporation since a reduced pressure at the permeate side keeps the permeation going. The patent can thus be considered as the first example of reactive PV. Thanks to the heat of evaporation needed for the compounds to permeate, the temperature of the Diels−Alder alkylation was maintained to the desired low temperature. The patent mentioned an irradiated poly(ethylene) membrane as a typical example for the type of membranes used. BF_3 is constantly added to the reactor in an amount of 1.5 parts by weight of BF_3 for each part of olefin. Its excess remains uncomplexed and is accumulated in the reactor due to selective rejection by the membrane. This limits the practical application of the process.

Hydrogenation

Enrichment and simultaneous reduction of organic compounds from an aqueous solution was realized in a one-step pervaporation process by dispersing Pd nanoclusters in a poly(ether-*b*-amide) matrix.[193] In the reduction of 4-chlorophenol to phenol (and partly furtheron to cyclohexanone and cyclohexanol), enrichment factors over 100 were obtained. Hydrogen was dissolved in the feed at pressures of 1−5 bar, and the Pd cluster size varied, depending on the preparation conditions, from 3 to 5 nm. Some unreacted 4-chlorophenol passed the 50−70 μm thick membrane, and some of the formed products diffused back to the feed.

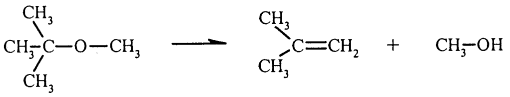
Vapor Permeation

Only one vapor permeation(VP)-coupled esterification has been mentioned, more in specific for the reaction between ethanol and oleic acid at reflux temperature.[193] The reason to prefer VP here above PV, was the stability to the membranes. The used PIs were plasticized by, e.g., ethyl oleate and oleic acid above 75 °C. Compared with PV-aided esterifications, the influence of the alcohol/acid molar ratio was quite different as a consequence of the changing reaction temperature with varying molar ratio. The reaction temperature changed in the course of the reaction, following the changing composition of the reaction mixture.[179]

Gas Separation

HPAs were successfully combined with gas separation to enhance the conversion in the acid-catalyzed, equilibrium-limited methyl-*tert*-butyl ether (MTBE) decomposition (Scheme 17). The developed CMRs showed better performances than the corresponding fixed bed reactor. Indeed, the equilibrium conversion of the reaction was exceeded by removal of the methanol through the selective membrane.[194,196] PPO/$H_3PW_{12}O_{40}$ catalytic membranes coated on PPO separative layers (1 in Figure 10) gave better results than a membrane with only an HPA-PPO coating (2 in Figure 10) or an HPA layer on top of a PPO coating (3 in Figure 10).[197,198] PPO was a superior membrane polymer in comparison with PSf, CA, poly(carbonate), and poly(arylate).[194,197] Simulated results were in good agreement with the experimental data.[199]

Scheme 17. Decomposition of MTBE



Langhendries et al.[27] developed a mathematical model to describe a packed bed membrane reactor in the earlier mentioned hydrocarbon oxidation with FePcY. An increased peroxide efficiency was envisaged by gradually adding the peroxide to the reactor through the membrane. This was realized by using membranes with a low overall mass transfer coefficient, but at the expense of lowered substrate conversion.

Ultrafiltration

When rather small catalysts, like TMCs, have to be retained in pressure driven membrane processes, three approaches are possible. Either the catalyst can be enlarged so that it can be retained by UF membranes, it can be covalently bound to soluble polymers[3] or insoluble supports,[4,5] or membranes with a lower molecular weight cutoff (MWCO) can be selected, possibly at the expense of poor membrane flow. Enlargement of catalysts is often an elaborate task involving tough organic chemistry. Whenever covalent anchoring of the catalysts is envisaged, similar laborious procedures might be involved. Furthermore, the structures of the resulting heterogeneous catalysts are often nonuniform and partly unknown. Mass transfer due to hindered diffusion can lead to low catalytic activity.[166] A decrease in the MWCO of the membranes can be achieved by selecting tighter membranes or by changing the reaction conditions that influence this MWCO, as will be illustrated for RO/NF examples.[200]

An attractive CMR concept, called “cascade CMR”, was developed using UF membranes in biocatalysis. Two examples will be given here to illustrate it. In the first one, two reactions of which the optimal reaction conditions were significantly different, were carried out in series. Two different lyases were thus used for the production of L-alanine from fumaric acid in two consecutive reactions. An UF membrane had to be used to retain both enzymes in their appropriate reactors. Each reactor could then be operated at the most optimal conditions of pH and temperature.[201] In another example, GDP-mannose was prepared by linking two reactors through a UF membrane.[202] In the first reactor, a 60% conversion was reached at Mg^{2+}(cofactor)/GTP ratios that lead to the highest enzymatic activity. To realize the remaining conversion, a slightly higher Mg^{2+}/GTP ratio was used in the second reactor. This induced self-stabilization of the system to compensate for the strong product inhibition. Even though this extra stability was achieved at the expense of some enzymatic activity, the overall enzymatic consumption in the two-step eCMR cascade was only 15% of that in the batch reactor and 45% of that in a single eCMR. The cascade reactor thus approximated the behavior of a plug flow reactor, which is more efficient for reactions showing product inhibition.[202]

Substrates with low solubility in the reaction medium are equivalent with low substrate concentrations and thus limited total turnover numbers and space−time yields. Emulsion membrane reactors

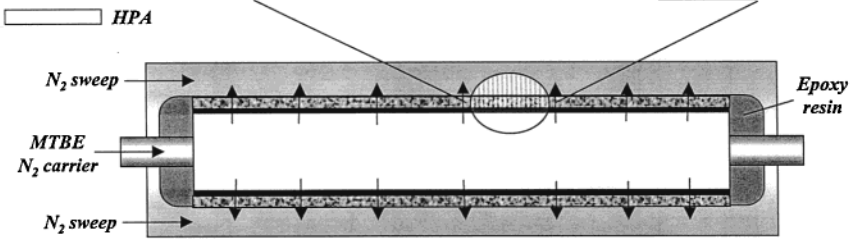


Figure 10. Schematic illustration of the reactor and membrane types used in the decomposition of MTBE (adapted from ref 197).

could overcome this limitation. In a first reactor, micelles of the organic substrates were formed. These were separated from the liquid by a hydrophilic UF membrane through which only the saturated aqueous phase permeated. This entered the second membrane reactor where the catalyst was retained by another membrane, and the product finally permeated.[203] The emulsion membrane reactor can also be applied in cases where catalysts or biocatalysts are used with a low stability in the presence of organic interphases, like those present in emulsions.

Nanofiltration

Introduction

Whereas the pore-flow mechanism describes transport through porous UF membranes, NF and RO membranes show a transient structure between porous and nonporous,[204] probably with sorption-diffusion as part of the transport mechanism also. NF is a relatively new membrane process with a nominal MWCO in the range of 200−1000 Da. Its application in water treatment has been growing rapidly, but the nonaqueous application is still an emerging field. Fortunately, excellent solvent-resistant NF (SRNF) membranes became available lately[205] which can be used in the nondestructive, energy efficient separation and concentration of reusable catalysts from products. For all the model catalysts (Jacobsen catalyst, Pd−BINAP, Wilkinson catalyst) and model solvents (DCM, THF, ethyl acetate (EA)) checked, at least one of the tested membranes (Starmem (Grace), MPF-50 (Koch), Desal-5 (Osmonics)) was adjudged compatible and combined reasonable solvent fluxes with high catalyst rejection.[206]

Aqueous NF

The catalytic oxidative detoxification of sulfides in wastewater treatment was studied using the Na salt of a tetra(sulfophthalocyanine)-Co(II) catalyst. At a transmembrane pressure of 30 bar, a PA membrane retained up to 99.9% of the catalyst from the reaction mixture. However, also a significant part of the formed products was retained, and the catalyst could not be reused with the same activity in subsequent runs.[207]

Aqueous NF played a crucial role in a continuous process developed by the group of Livingston in which wet air oxidation, membrane separation, and biological treatment were combined for the treatment of PEG-containing wastewaters. A single treatment process with wet oxidation alone was evaluated too cost-intensive. On the other hand, the rate of biodegradability of PEGs decreases substantially with their increasing MW. This problem was solved by a first brief wet oxidation pretreatment to degrade the polymers to a lower MW. The smallest fraction then passed through an NF membrane with a MWCO of 300. This polymeric membrane (AFC-40, PCI) gave better results than ceramic ones (Kerasep, Techsep) with higher MWCO. It proved to be resistant, even at 130 °C, to the oxidative conditions created by excess oxidant still present in the oxidized process streams. The integrated process thus showed a much higher treatment efficiency than any of the single optimized processes.[208]

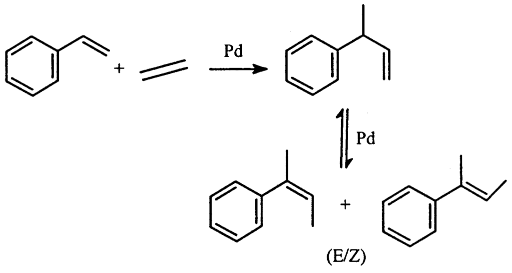
SRNF

SRNF coupled catalysis constitutes a way to bridge the gap between homogeneous and heterogeneous catalysis and combine the advantages of both. The idea to separate homogeneous organometallic catalyst using SRNF is relatively new. In their patent covering the composite cross-linked silicone MPF membranes, Linder et al.[209] claimed the general use of their product to separate homogeneous catalysts from organic solvent but provided no data or specific examples. Whu et al.[210] modeled batch and semibatch reactor processes in their coupling with SRNF to retain a catalyst. Their calculations showed that using such membranes could significantly enhance reaction conversion, speed up reaction time, and improve selectivity for the target molecule. Practical examples of the separation of a Rh−organophosphite catalyst from both acetone and butyraldehyde-based hydroformylation reaction mixtures using MPF50 were reported by Miller et al.[211] Rejections of Rh and of the free ligand were >99% in the aldehyde and >93% in acetone.

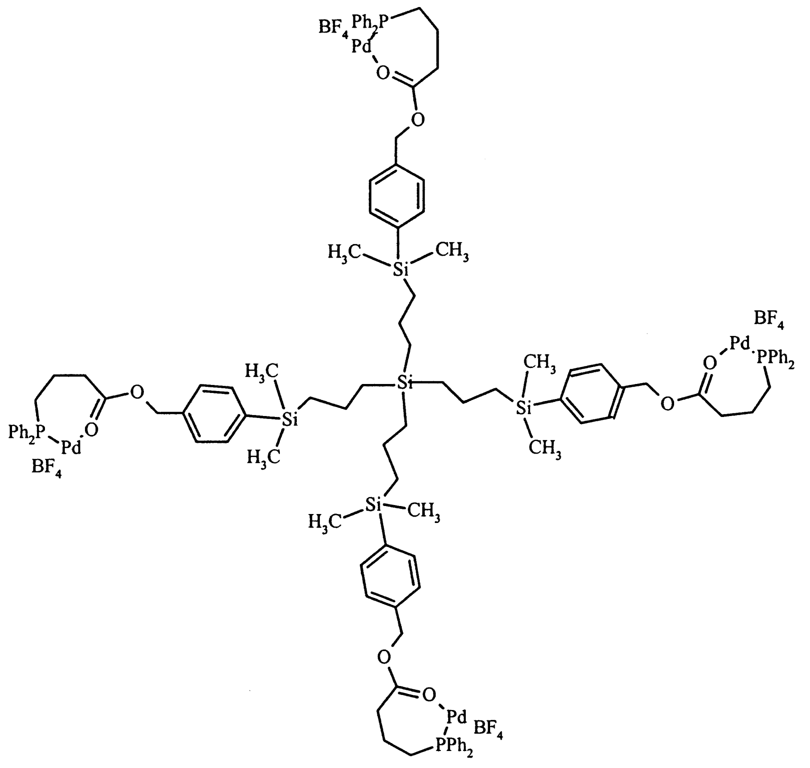
MPF-50 and MPF-60 (Koch) membranes are generally marketed as solvent-resistant nanofiltration membranes. However, being applied in solvents, like toluene or THF, these membranes swell to such an extent that they in fact act like UF membranes with drastically increased MWCO. TMCs can then only be retained when being enlarged. The enlargement via anchoring is covered elsewhere,[3−5] but the enlargement of the catalyst through synthesis of dendrimeric forms will be discussed here briefly as a link to the SRNF of genuine off-the-shelf catalysts. A more detailed review about catalytic dendrimers can be found elsewhere.[212,213] The first dendrimer for catalytic purposes was synthesized by the group of Van Koten in 1994.[214] Compared with anchoring to polymers, dendrimers show a much smaller intrinsic viscosity than comparable linear polymers. This is due to their globular shape, which is also believed to be responsible for the easy accessibility of the catalytically active sites on the periphery.[215]

In the vinylation of styrene with Pd−phosphanylcarboxylic acid derivatives, isomerization of the chiral product 3-phenylbut-1-ene to the achiral olefines (*E*/*Z*) was a serious problem, especially at high conversions (Scheme 18). To allow operation at low conversions in a continuous reactor, a dendrimeric form of the catalyst (Scheme 19) was prepared.[216] In the

Scheme 18. Vinylation of Styrene



Scheme 19. Structure of the Dendrimeric Form of the Pd−Phosphanylcarboxylic Acid Catalyst



styrene solution, the dendrimer with a MW of 1314 was retained only for 85% by the MPF-60 membrane. Combined with the formation of small amounts of Pd black on the membrane surface, this was reflected in a strongly decreasing activity. A manner to improve the unpractically low retention of this dendrimer was to prepare a next generation dendrimer (Scheme 20).[217] However, even though the activity was slightly increased, product formation still slowed with time. These results proved that the retention of the catalyst was only a secondary effect, but that catalyst deactivation occurred. Due to the flexibility of the dendritic arms, it was supposed that the phosphino groups could be brought together easily to facilitate the formation of Pd black.

For the allylic substitution (Scheme 21) with dendritic Pd catalysts, Kragl and co-workers compared two dendrimers (Scheme 22) of different generations, with MW of 10 and 16 kDa, respectively.[215] For the smallest dendrimer, a Nadir PA-5 (Nadir Filtration, previously Celgard) UF membrane and a MPF-50 membrane showed retentions of 0.992 and 0.999, respectively, in DCM. Despite this seemingly negligible difference, Figure 11 shows the important consequences of such a tiny difference after many replacements of the reaction volume. However, this leaching could only partly explain the decreased conversion after 100 residence times. Again, the formation of inactive Pd species seemed to be the more significant reason.

For the continuous asymmetric borane reduction of prochiral ketones with a chiral oxazaborolidine catalyst, a dendritic sulfoximine was synthesized and could be retained for more than 99%. Acetophenone was reduced over a period of more than 40 residence times but with an enantiomeric excess (ee) that was lower than that under batch conditions.[218,219]

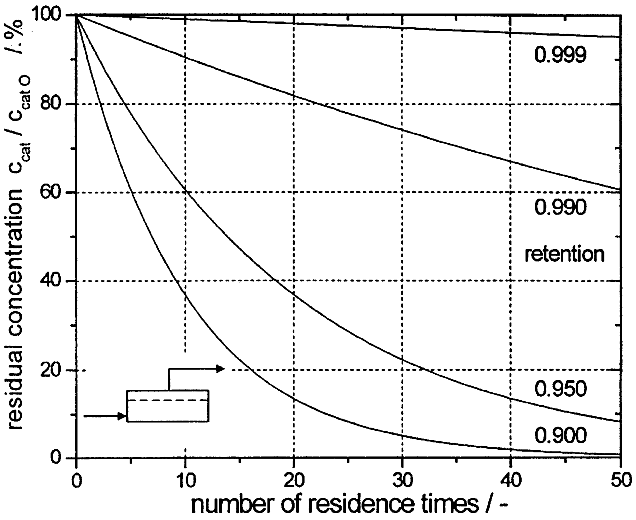
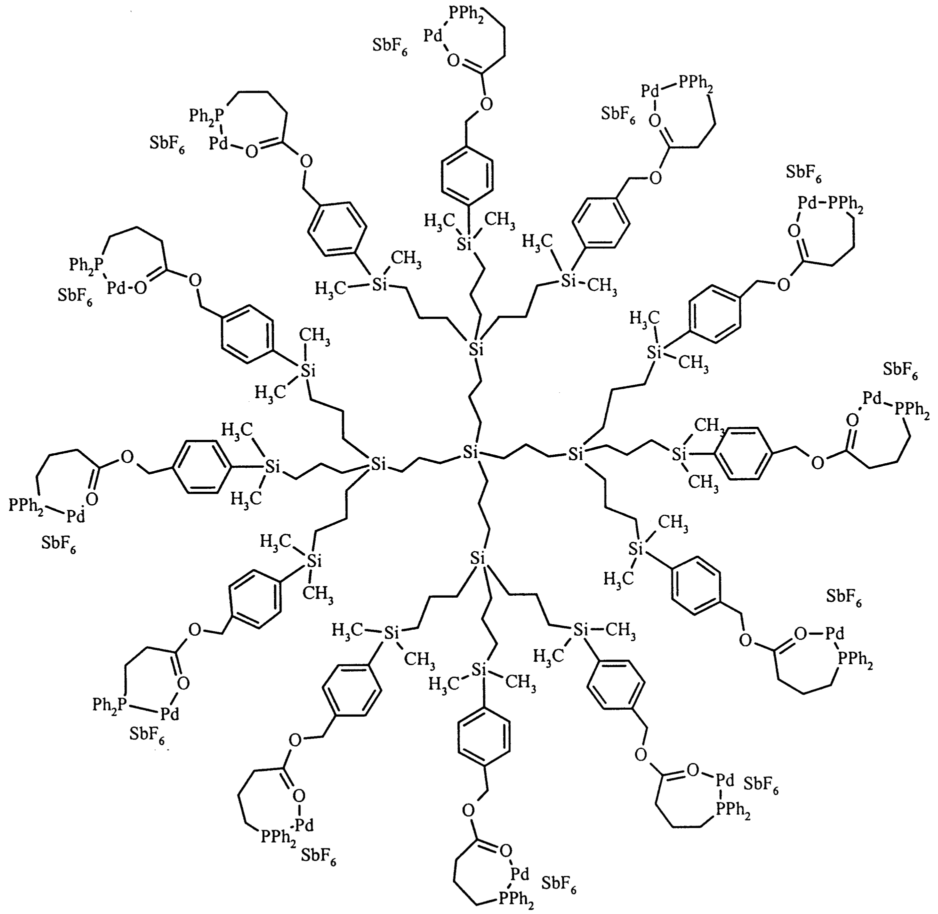


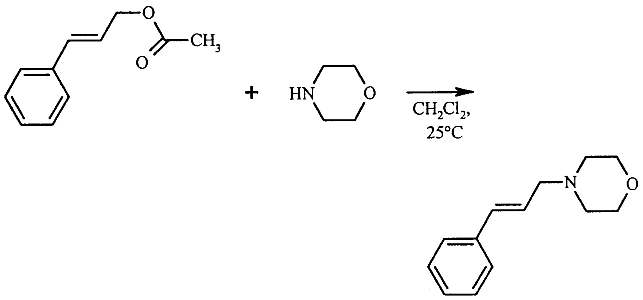
Figure 11. Residual catalyst concentration as a function of the number of residence times (taken from ref 215).

As an alternative to these monodisperse and well-defined molecules that dendrimers are, similar hyperbranched polymers (Scheme 23) were proposed. Their synthesis is cheaper and less labor intensive and can be accomplished in one single step. It is a more convenient way to prepare large quantities of large catalysts, but they inherently have a high polydispersity and their functionalization is distributed throughout the whole macromolecule.[220] A Pd form was successfully applied in the aldolcondensation of benzaldehyde and methylisocyanoacetate. The hyperbranched polymer showed an activity that was similar to the one of the single site Pd catalyst but was not yet applied in continuous reactions with CMRs.[220]

Scheme 20. Structure of the Higher Generation Dendrimer of Scheme 19



Scheme 21. Allylic Substitution Reaction

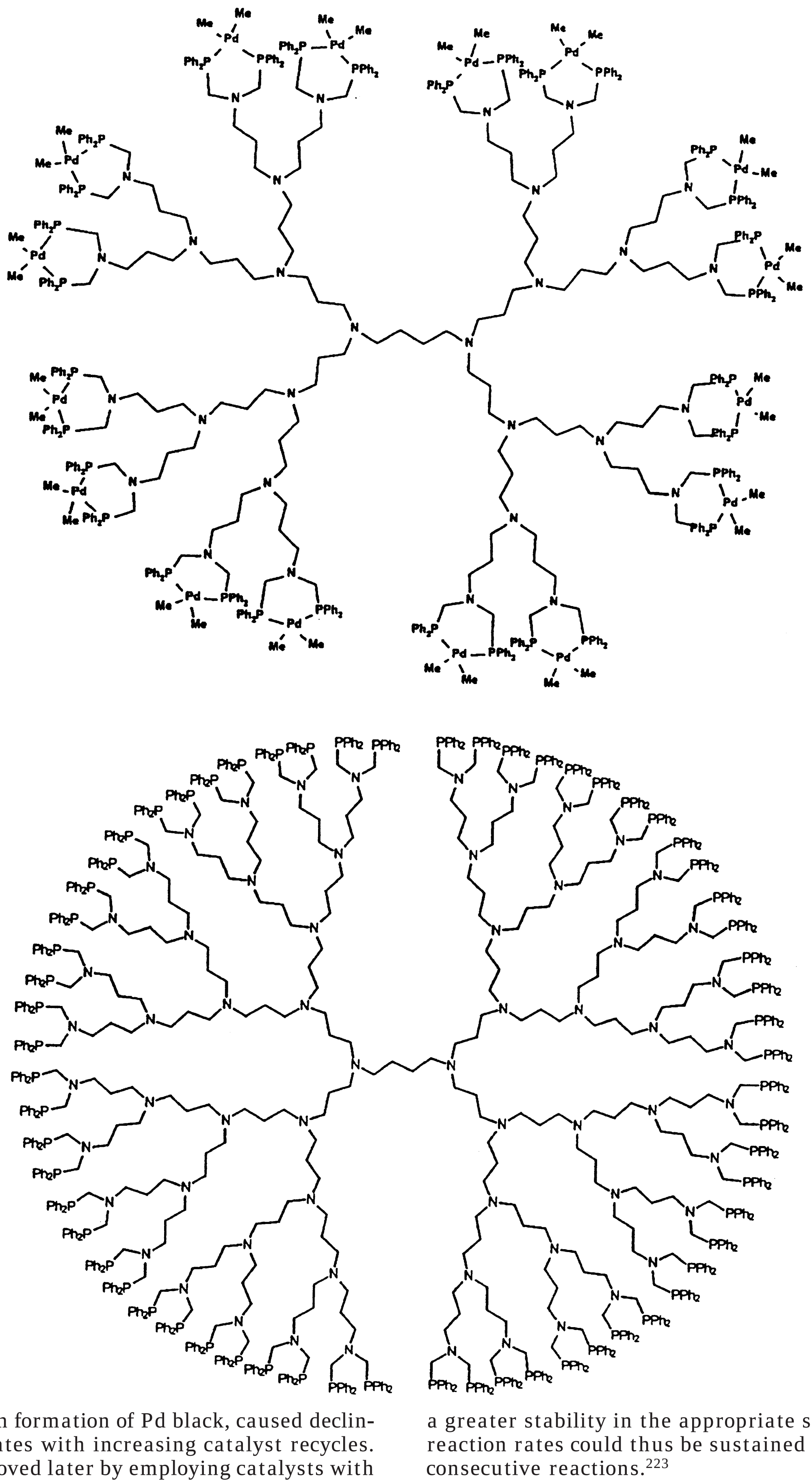


Another approach to enlarge TMCs, was to add micelle forming amphiphiles (Scheme 24) in the chiral hydrogenation of enamides.[221] The easy preparation by simply adding the triblock copolymer P105 to the aqueous solution of the precatalyst was one of the main advantages. Thanks to the hydrophobic part of the amphiphile, the ligand was effectively retained in the micellar structure, and a retention of more than 99% was realized, in contrast with only 95% for the Rh−BPPM as such. The retention of the metal was slightly lower than that of the ligand: due to the limited complex stability, some free hydrophilic ionic Rh permeated through the membrane.

All these efforts to enlarge catalysts become superfluous when the membranes are applied under the right conditions.[200] Indeed, operated as true NF-membranes, these same MPF membranes were capable to retain off-the-shelf TMCs. Ru−BINAP and Rh−DUPHOS were thus used in the hydrogenation in methanolic medium of dimethylitaconate (DMI) and methylacetoacetate (MAA), respectively. Catalysts were retained for more than 98% and 97%, respectively, and products permeated unhindered through the membrane in a continuous setup. The hydrogen pressure that was needed for the reaction simultaneously formed the driving force for the filtration without any additional cost or equipment. Up to 10 reactor refreshments could be realized with hardly any loss of activity of the catalyst and with ee's equalling those in homogeneous catalysis. This concept was claimed to be widely applicable in fine chemical synthesis, for as long as product and catalyst differ enough in retention by the membrane and within the limits of temperature/solvent/pressure combinations of the current SRNF membranes.

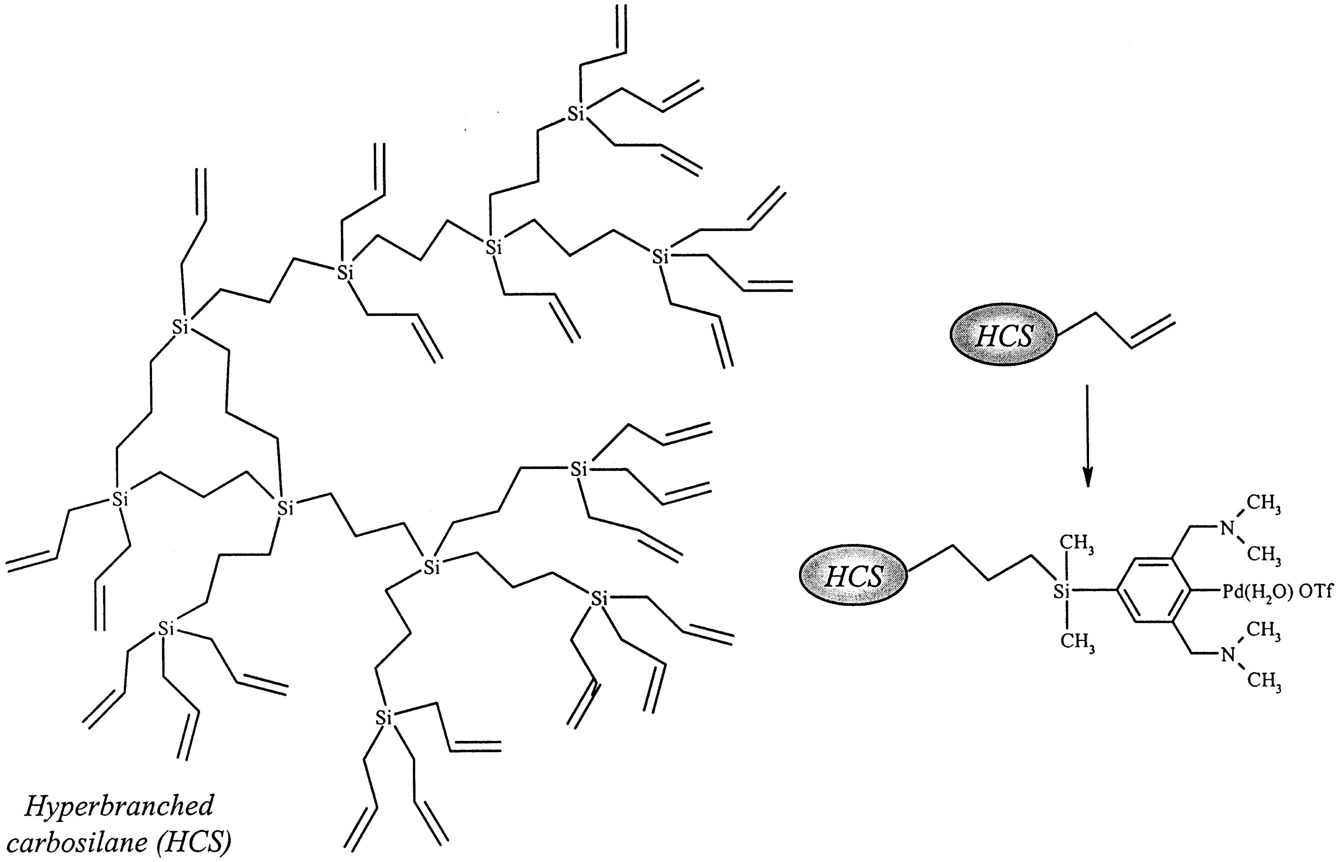
As an alternative to this continuous operation, the SRNF and the catalytic process were run in a semibatch mode in order to lower reactor occupancy.[222] Furthermore, the conditions used in the Heck coupling reaction of styrene to iodobenzene (Scheme 25) were too harsh to be membrane (PI) compatible. The ammonium salt that was formed as a byproduct during the reaction precipitated out and was removed from the reactor after filtration and before refilling it. A tradeoff was found for a given solvent (THF, EA, and MTBE) between better membrane performance (higher fluxes and selectivities) and higher catalyst activities. Catalyst deactivation,

Scheme 22. Structure of the Two Dendrimers of Different Generations Used in the Allylic Substitution of Scheme 21

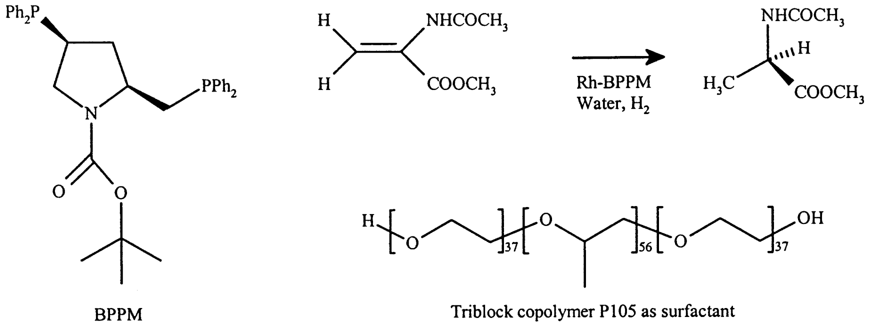


mainly through formation of Pd black, caused declining reaction rates with increasing catalyst recycles. This was improved later by employing catalysts with a greater stability in the appropriate solvents. High reaction rates could thus be sustained over multiple consecutive reactions.[223]

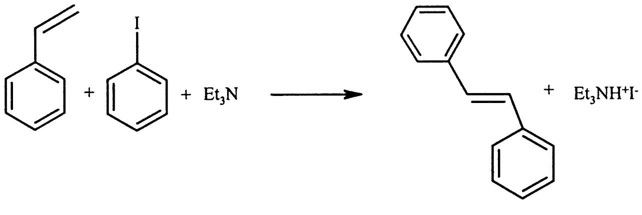
Scheme 23. Structure of the Hyperbranched Carbosilane and Its Conversion into a Pd Catalyst



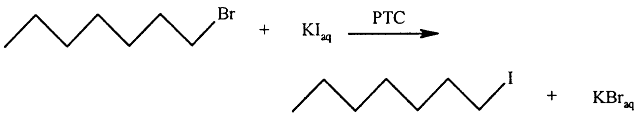
Scheme 24. Enamide Hydrogenation Reaction and the Structure of BPPM and the P105 Surfactant



Scheme 25. Heck Coupling Reaction of Styrene to Iodobenzene



Scheme 26. Nucleophilic, Aliphatic Substitution Reaction between Bromoheptane and KI



SRNF-coupled catalysis also offered a solution to the major technical problems inhibiting the use of phase-transfer catalysis in industrial applications, namely, the need to separate the product and the phase-transfer catalyst after reaction.[224] At the end of the nucleophilic, aliphatic substitution reaction in toluene (Scheme 26), the hydrophobic tetraoctylammonium bromide (TOABr) and the iodoheptane product partitioned entirely into the organic phase. Due to the salting out effect of the KI (33 wt % in water), even the more hydrophilic butyl analogue tetrabutylammonium bromide partitioned into the organic phase. These 40 mL organic phases were then filtered down to a 5 mL retentate over a PI SRNF-membrane (142A, Grace, later called Starmem 122) with a MWCO of 220 Da. This membrane was selected as the best available SRNF-membrane with respect to both flux and rejection. The retentate was successfully reused without any loss of activity. Some membrane fouling, reflected in a decreasing membrane flux, was visually observed as a film of viscous material attached to the membrane. Even though the solubility limit of the TOABr was not exceeded during the strong concentrating effect of the selective permeation, it was assumed that some catalyst came out of the solution at the membrane surface as a consequence of the presence of the other constituents in the retentate. This flux decline was proven to be reversible since a simple solvent washing of the membrane restored flux to its original value. It was later suggested that also concentration polarization and increasing osmotic pressure (roughly estimated to rise to 12 bar) could contribute to this flux decline, in addition to compaction of the membrane.[205] It should be considered that extrapolation from low volume, dead-end nanofiltration to larger systems, e.g., cross-flow nanofiltration, may be difficult.[206]

Whether a continuous or a semibatch approach is preferred will generally depend on the process specific requirements. In the batch approach, the reactor and the filtration conditions have to be identical, whereas the semi-batch approach allows reaction conditions that are incompatible with the SRNF-membrane resistance.[225] Continuous processes are generally easier to be automated and can operate economically at smaller reactor volumes. Batch-wise processes, on the other hand, have a higher flexibility and lower investment cost but might suffer from batch-to-batch variations. Their lower reactor efficiency is related to the startup and shutdown times which are lost for production and involve extra manipulations and thus higher labor costs.[226]

SRNF membranes could also be useful tools to solve the current hurdles in the application of reversed micelles with UF, where the separation of the formed products from the surfactant-containing organic solvent is still problematic.[6,227]

Reversed Osmosis

In 1973, a rather peculiar first application of RO related to catalysis was reported.[228] Using an asymmetric PI membrane, organometallic compounds with enhanced catalytic activity were synthesized. In extenso (Scheme 27), by removing the dissociated ligand from Ru−phosphine complexes, a ligand-deficient complex was obtained. Being too unstable to be isolated as such, the authors succeeded to isolate the dinitrogen compound $RuH_2(N_2)(PPh_3)_3$ by using N_2 as the pressuring gas. RO was thus used to replace a dissociated ligand (PPh_3) by a more labile one (N_2) in the synthesis of several new organometallic complexes. Under certain conditions, the dinitrogen ligand could be removed again by sweeping with Ar or H_2. It was only 4 years later that the same membranes were actually used in a catalytic process involving hydrogenations and hydrodimerization with Ru complexes, hydroformylations with Co or Rh complexes, and carboalkoxylations with Pd complexes. With pressures up to 95 atm, catalysts could be retained with varying degrees of success when separating them from the formed products.[229]

Scheme 27. Dissociation of a Ru−Phosphine Complex

$$RuH_2(PPh_3)_4 \rightleftharpoons RuH_2(PPh_3)_3 + PPh_3$$

Dialysis

A new membrane-assisted catalysis concept, in which a concentration gradient instead of a pressure gradient formed the transmembrane driving force, was reported recently to remove TMCs from reaction mixtures.[230] Substrate molecules permeated through the membrane to reach the catalyst phase where reaction took place. The formed products then built up their own concentration gradient and migrated back to the feed solution. Compared to the earlier reported NF/catalysis hybrid process, no mechanical pressure was needed here, which clearly facilitates the mechanical and safety requirements.

The concept was first proven in the hydrogenation of DMI with Ru−BINAP and hydrogen gas. The catalyst was confined in a PDMS "envelop" which was submerged in the reactor. No leaching of the catalyst was observed and the reactor volume could be replaced four times without loss of activity. In the catalytic transfer hydrogenation of acetophenon with IPA (Figure 12), the PDMS membrane retained the catalyst insufficiently from the IPA solution. Instead of following the more traditional aproach to enlarge the catalyst, the membrane composition (by adding silica fillers) and the composition of the solvent mixture (using methanol as cosolvent) were changed to improve the catalyst retention. The catalyst could be reused four times but with some loss of activity.

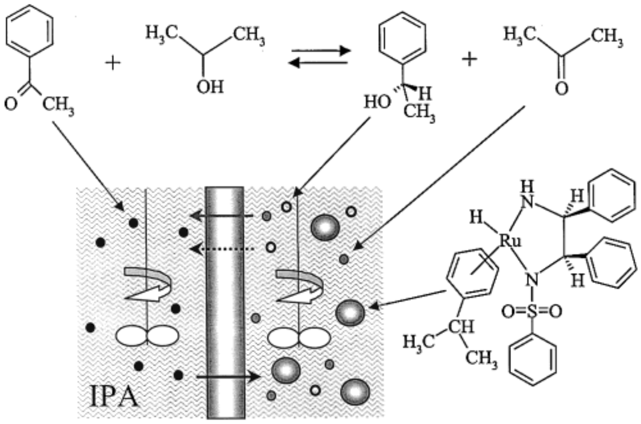
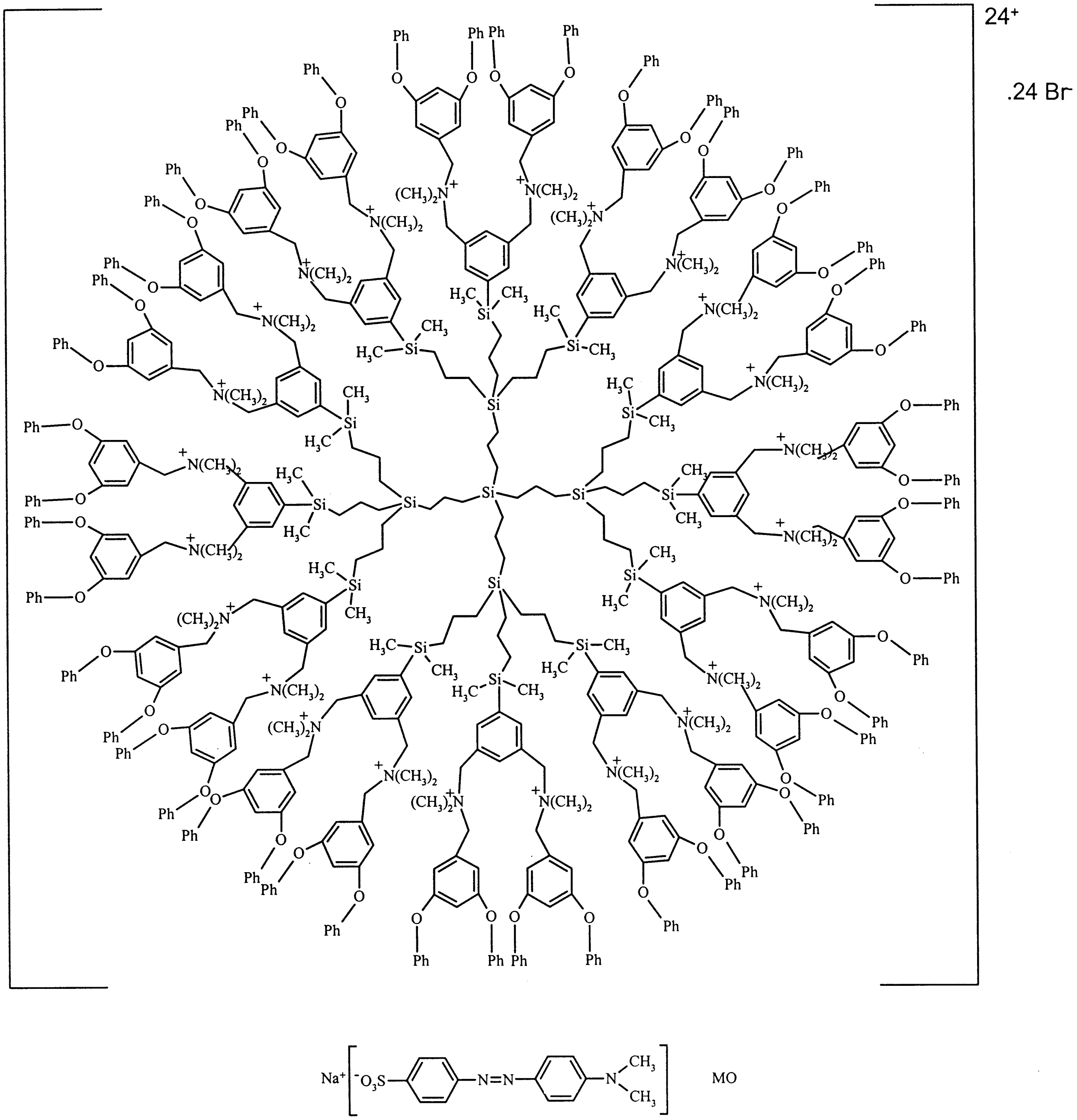


Figure 12. Schematic presentation of the reactor setup used to couple dialysis to the catalytic transfer hydrogenation of acetophenon with IPA (adapted from ref 230).

Just like in SRNF, the use of solvents that induce strong swelling of the membranes makes laborous catalyst enlargement compulsory. A special kind of dendrimers are the so-called "mixed core−shell dendrimers". They consist of an apolar core with a peripherical ionic layer which is surrounded by a less polar layer of dendritic wedges (Scheme 28). These macromolecules were active as a phase transfer catalyst in the S_N2 reaction between benzyl bromide and KCN. The molecule (after reaction with methyl orange (MO, Scheme 28) to reach a MW of 5655) was retained in DCM by an unspecified Sigma dialysis membrane with a MWCO of 1000.[231]

Scheme 28. Mixed Core−Shell Dendrimer (Top) and Methyl Orange (MO, Bottom)



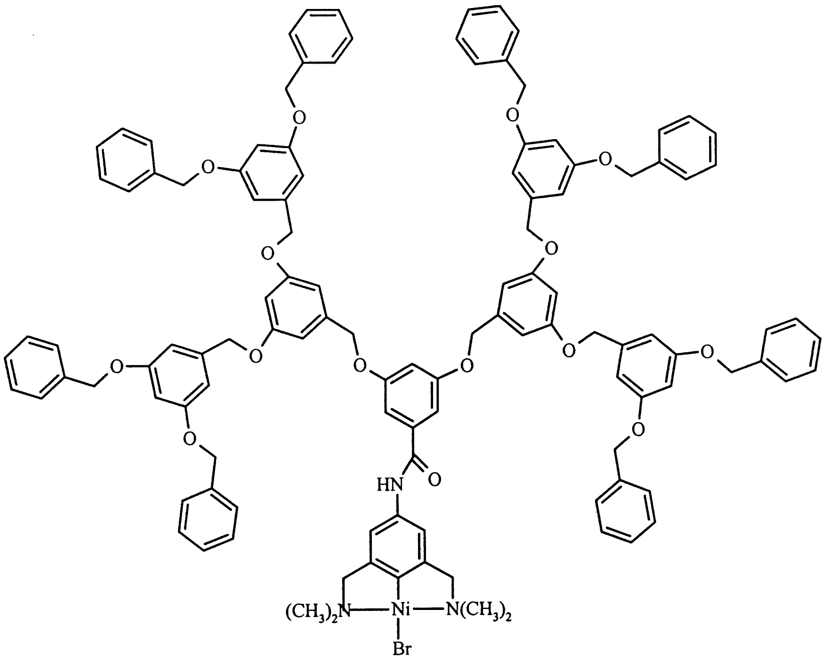
An MPF-60 NF membrane was used to retain polyether dendritic wedges of several generations.[232] A third generation dendritic wedge (Scheme 29) was clearly needed to obtain a sufficient retention in DCM. In the Ni form, the third generation dendritic wedge was used in the Kharash addition of CCl_4 to methylmetacrylate. In contrast to the earlier prepared dendrimers, this catalyst was as active as the homogeneous analogue. The reason was the mononickelation of the dendrimer, which prevented the Ni sites to approach each other too closely.

Colloidal Pd and alumina supported bimetallic Pd catalysts were used in dialysis for nitrite and nitrate removal respectively (Figure 13).[77] PVP, PVA, and their blended and copolymerized forms were used as the stabilizing polymers in the preparation of Pd colloids with sizes from 3.1 to 4.4 nm. The stabilized colloids were filled into the intracapillary volume of the HFs. The activity of the bimetallic Pd catalysts in the nitrate removal was higher with H_2 as reductant than with formic acid, due to mass transport limitation for the acid. The higher selectivity to nitrogen with formic acid was attributed to the “in situ buffering effect” of the acid which produced CO_2 to neutralize the formed OH ions. In the use of colloidal catalysts, the presence of PVP in the polymeric layer led to excellent N_2 selectivity. It proved that the specific adsorption of a polymer on a metal colloid can drastically change the catalytic properties.

10. Conclusions

From this summary on catalysis with polymeric membrane, it can be seen that there are certainly lots of opportunities and lots of promises, but there are also lots of hurdles.

Scheme 29. Ni-Functionalized Polyether Dendrimer



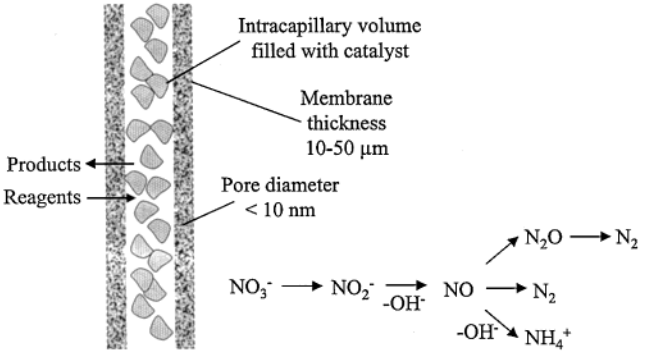


Figure 13. Scheme of the HF dialyzer, filled with catalyst and of the catalytic nitrate and nitrite reduction (adapted from ref 77).

The multidisciplinarity of the pCMRs is manifest and makes it a challenging but difficult domain. Three major fields of research are necessary to be mastered for the successful development and operation of pCMRs: catalysis, membrane technology, and reactor engineering. Developing new concepts or improving the existing ones is therefore more than just selecting the best of each field: it is the challenge to pick in each field those that will lead to the best possible combination.

On the catalytic level, it is crucial to select the right catalyst for the right reaction under the most appropriate conditions that are still compatible with the membrane. Evidently, only highly selective, stable catalysts are worth being considered, or catalysts whose selectivity would benefit from coupling the reaction to a membrane separation. However, it is often only when applied in CMRs on time scales longer than normally used by chemists to screen the potential of newly developed catalysts, that low stability might become apparent. This leaves an important challenge for chemists to allow implementation of the reported concepts to a wide range of reactions by designing more stable catalysts. CMRs also seem interesting tools for chemists to unravel mechanistic issues, such as catalyst deactivation, isolation of intermediate forms or metal leaching from complexes. High catalyst activity might be a less important selection criterion, since easy separation and reuse of the catalyst render high catalyst concentrations, indispensable then to keep residence times acceptable, economically and technically more feasible. High catalyst concentrations also open perspectives to suppress side-reactions. Even though reuse becomes less desirable the more active the catalyst becomes, separating the catalyst remains attractive to facilitate downstream processing and remove traces of metals from the product.

On the membrane level, a thorough insight in the membrane properties and a full understanding of the separation process are required to make the right selection. Even though a range of useful membranes are commercially available nowadays to offer excellent solutions for many problems, they often remain “black boxes” due to the lack of information available on their composition. This seriously limits the potential to fully understand what really happens and thus try to implement improvements. It clearly favors “in house” preparation of the membranes. For most membrane-occluded catalysts, there is no other option than in house preparation, and a careful selection of the polymer type with respect to sorption and diffusion of reagents and products is crucial here.

Given the fact that pCMRs can still be considered as an emerging technology, the engineering aspects were of a somewhat minor importance till now. Most publications only offered a proof of concept, often still suffering from important mass transfer limitations and were run under nonoptimal conditions. It is therefore the task of the engineer to advance the most promising fundamental CM devices into commercial operations through parametrization and modeling.

Unfortunately, the reported concepts were not always a proof of such successful combinations. The sometimes arbitrarily selections of catalysts, polymers or reactions, leaves the literature rather fragmented. Within catalysis, pCMRs form a small but promising niche; yet more creative thinking is certainly needed to come to new useful and innovative concepts. The fact for instance that, in contrast with mCMRs, polymers can add a surplus to the system by actively taking part in sorption and diffusion of reagents and solvents could still be better exploited. A more careful selection of the membrane and the operating conditions in inert pCMRs could also have avoided several reported “membrane failures”.

With the fast developments in polymer science, more and more polymers with great membrane potential become available, and development of new hybrid organic/inorganic materials can push this even further. Even though proven enough already to resist many harsh conditions, the polymeric CMs will thus become even more reliable and render the widespread, and often prejudiced, skepticism of engineers toward polymers in reactors less justified.

Thus, despite all potential advantages, there is still a long way to go before commercial applications could really fully proceed. However, the few rare exceptions that made it already to industrial or pre-industrial scale prove they are really worthwhile being investigated!

Abbreviations

4-PPYNO	4-phenylpyridinoxide
BPPM	(2*S*,4*S*)-N-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine
CA	cellulose acetate
CEM	cation exchange membranes
CM-PTC	capsule membrane supported phase transfer catalysis
CMR	catalytic membrane reactor
CM	catalytic membrane
DCM	dichloromethane
DMF	dimethylformamide
DMI	dimethylitaconate
EA	ethyl acetate
EC	ethyl cellulose
eCMR	enzymatic catalytic membrane reactor
ee	enantiomeric excess
ePTFE	expanded poly(tetrafluoroethylene)
FePc	Fe−phthalocyanine
FePcY	Fe−phthalocyanine in zeolite Y
HF	hollow fibers
HPA	heteropolyacids
IPA	2-propanol
MAA	methylacetoacetate
MF	microfiltration
Mn(bpy)$_2$]$^{2+}$-Y	Mn-bis(bipyridyl) in zeolite Y
MO	methyl orange
MTBE	methyl-*tert*-butyl ether
MWCO	molecular weight cutoff
NF	nanofiltration
NMP	*N*-methylpyrrolidone
PA	poly(amide)
PAI	poly(amide-imide)
PAN	poly(acrylonitrile)
pCMR	polymeric catalytic membrane reactor
PDADMAC	poly(diallyl dimethylammonium chloride)
PDMS	poly(dimethylsiloxane)
PEA	poly(ethylacrylate)
PEG	poly(ethylene glycol)
PES	poly(ethersulfone)
PI	poly(imide)
PIPN	pseudo-interpenetrating networks
POPMI	poly(4,4′-oxydiphenylene pyromellitimide)
PPO	poly-(2,6-dimethyl-1,4-phenylene oxide)
PS	poly(styrene)
PSf	poly(sulfone)
PSSA	poly(styrene sulfonate)
PTC	phase transfer catalyst
PTFE	poly(tetrafluoroethylene)
PTMSP	poly(trimethylsilylpropyne)
pTSA	*para*-(toluene sulfonic acid)
PV	pervaporation
PVA	poly(vinyl alcohol)
PVDF	poly(vinylidenefluoride)
PVP	poly(vinylpyrrolidone)
RO	reversed osmosis
SEC	sulfoethyl cellulose
SRNF	solvent-resistant nanofiltration
tBHP	*tert*-butylhydroperoxide
TDCPP(Mn)-Cl	[5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrinato]MnCl
TEOS	tetraethoxysilane
Tg	glass transition temperature
THF	tetrahydrofuran
TMC	transition metal complex
TOABr	tetraoctylammonium bromide
UF	ultrafiltration
VP	vapor permeation
ZnPcY	Zn-phthalocyanine in zeolite Y

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