

Review

# Catalytic polymeric membranes: Preparation and application

Sibel Sain Ozdemir<sup>a</sup>, Maria Giovanna Buonomenna<sup>b,\*</sup>, E. Drioli<sup>b</sup>

<sup>a</sup>TUBITAK Marmara Research Center, Material and Chemical Technologies Research Institute,  
P.O. Box 21, 41470 Gebze-Kocaeli, Turkey

<sup>b</sup>Institute of Membrane Technology, ITM-CNR, c/o University of Calabria,  
Via P. Bucci, Cubo 17/c, 87030 Rende (CS), Italy

Received 16 December 2005; accepted 29 March 2006

Available online 5 May 2006

## Abstract

The study of catalytic membranes is a multidisciplinary activity, which in recent years has attracted the attention of scientists in a number of disciplines, including material science, chemistry and chemical engineering. Membrane based reactive separation processes, which seek to combine two distinct functions, i.e. reaction and separation, have been around as a concept since the early stages of the membrane field, itself, but have only attracted substantial technical interest the last decade or so. According to the literature, most studies combining membranes and catalysts concern gas phase reactions at relatively high temperature. In most of these applications inorganic membrane made from ceramic or metals are applied. Polymeric membranes (porous or dense) are used when the reaction temperatures are lower, i.e. in the field of fine chemicals or when biocatalysts are present. Dense polymeric membranes in use to separate gases or liquids from mixtures by a sorption–diffusion mechanism can be coupled to catalytic reaction and then be used to separate and react in one step. The polymeric membrane should be not only highly selective, but it should also be permeable enough to give a sufficient separation.

Liquid phase catalytic reactions are involved in numerous industrial processes ranging from fine to bulk chemical synthesis; polymeric membranes may also play a significant role in this field.

In this paper, a review on the preparation and application of polymeric membranes in the field of fine chemicals with adequate performance in catalysis both in gas phase and liquid phase reactions is presented and discussed.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Polymeric membranes; Heterogeneous catalysis; Fine chemicals

## Contents

1. Introduction	168
2. General considerations on polymeric membranes	168
3. Membrane/catalyst arrangements used in PCMR	170
4. Catalytic polymeric membranes in reactors with gas permeation	170
4.1. Membrane preparation	171
4.1.1. Immobilization of metal complex catalyst in polymeric membranes	171
4.1.2. Metal nanoclusters catalyst in polymeric membranes	171
4.1.3. Entrapment of the catalyst in a reactive layer on top of supporting membranes	172
4.2. Membrane application	173
4.2.1. Hydrogenation	173
4.2.2. Reduction of nitrous oxide	174
4.2.3. MTBE decomposition	175
4.2.4. Dimerisation of isobutene	175
5. Catalytic polymeric membranes in liquid phase reactions	176
5.1. Membrane preparation and application	176

\* Corresponding author. Tel.: +39 0984492014.

E-mail address: [mg.buonomenna@itm.cnr.it](mailto:mg.buonomenna@itm.cnr.it) (M.G. Buonomenna).

5.1.1.	Acid catalysed hydration of $\alpha$ -pinene . . . . .	176
5.1.2.	Hydrogenation of methylacetoacetate . . . . .	177
5.1.3.	Catalytic oxidations . . . . .	178
6.	Pervaporation . . . . .	179
6.1.	Membrane preparation . . . . .	179
6.1.1.	Bifunctional membranes prepared with polymer blend . . . . .	179
6.1.2.	Bifunctional membranes prepared by catalyst entrapment in polymeric matrix. . . . .	180
6.2.	Applications . . . . .	181
6.2.1.	<i>N</i> -Buthyl alcohol–acetic acid esterification . . . . .	181
6.2.2.	Hydrogenation of 4-chlorophenol . . . . .	181
6.2.3.	Epoxidation of propene to propene oxide . . . . .	181
7.	Conclusions. . . . .	182
	Acknowledgement . . . . .	182
	References . . . . .	182

## 1. Introduction

The subject of membrane-based reactive separation otherwise also known as membrane reactors (MRs), has attracted much interest over the last decade or so. Although some small industrial installations already exist, the concept has yet to find larger scale industrial applications. One of the important impediments for further commercial development of MRs are the membrane themselves, which still need optimization. Reviews of applications for MRs mainly concern *inorganic catalytic membrane reactors* [1–6]. In particular, most of these studies, concerning reactions in the high-temperature range from 300 to 1000 °C, are related to the major challenges in the development of inorganic catalytic membrane reactors for large scale application: material science (synthesising defect-free membranes; reducing membrane thickness, etc.), catalytic science and chemical engineering.

At low temperature (room temperature up to about 150 °C), also *polymeric membranes* can be used in MRs and could have some advantages over the most expensive inorganic membranes made from ceramic or metals. The most important realisations with *polymeric membrane reactor* to date are in the field of biotechnology [7]: the membranes used are typically porous, and the function of the membrane is mainly for immobilizing enzymes, eliminating product inhibition, recycling enzymes and other biocatalyst, and manipulating substrates and nutrients. However, besides applications in the field of biosynthesis, also production of fine chemicals may profit from the membrane reactor concept. Recent developments in polymeric membranes are pushing the envelope for their application. A number of studies as a result have also appeared discussing the use of such membranes on high temperatures catalytic membrane reactor application [8].

Dense polymeric membranes for the separation of gases, vapours or liquids from mixtures can also be made catalytically active, so that they can be used to separate and react in one step [9,10].

In 2002, Vankelecom [11] gave a survey of polymeric membranes in Catalytic Reactors for fine chemical synthesis: some examples of incorporation of heterogeneous catalysts, heterogenisation of homogenous catalysts and membrane-

assisted catalysis were given and the problems related to the catalytic membrane preparation and stability and the CMR set-up are discussed.

In this review after a rapid overview of the working concepts of MRs, the two types of application of polymeric catalytic (but non enzymatic) membranes, i.e. in reactors with gas-phase and liquid-phase reactions are reported and discussed. In particular the mentioned literature has been reviewed and discussed from a materials-oriented viewpoint (synthesis of catalytic membranes). Recent developments with a special emphasis on catalytically active membranes for pervaporation and related synthesis methods have been also analysed.

## 2. General considerations on polymeric membranes

Polymeric membranes can be based on rubbery or glassy polymers. When an amorphous polymer is heated to a temperature above the rubbery transition temperature,  $T_g$ , the polymer passes from the glassy state to the rubbery state. Rubbery polymers usually have high permeabilities for gases, but a relatively low selectivity, while glassy polymers have high selectivity and lower permeability, which allow to obtain a high purity. Table 1 gives an overview of commercial polymers used as membranes and other polymers with high potential for application as a membrane material.

Apart from the evident need for resistant and efficient polymeric membranes for the process, an important parameter to be maximised, in all applications is the membrane permeability. The performance of dense polymeric membrane can be improved by decreasing membrane thickness, and by developing new materials. Research on the synthesis of more selective, permeable membrane materials for gas phase reactions is still on going.

The major physicochemical factors influencing the gas permeability and permselectivity of polymers are (1) the mobility of polymer chains (as reflected in many cases by glass or sub-glass transition temperature of the polymer), (2) the intersegmental spacing, which is taken as a measure of the mean free volume of the polymer, and (3) the penetrant-polymer interactions (as reflected by the solubility of the penetrant gases in polymers) [12]. From a material viewpoint,

Table 1  
Some polymers for membranes

Material	Membrane formation	Application
CA: cellulose acetate	Casting/ Melt extr.	RO, UF, MF, D, GS
CTA: cellulose triacetate	Casting	RO
CN: cellulose nitrate	Casting	UF
PE: polyethylene	Melt extr	PV, GS
PVC: poly(vinyl chloride)	Casting	MF
PVDF: poly(vinylidene fluoride)	Casting	UF, MF, ED
PTFE: polytetrafluorethylene	Melt extr	MF, ED
PAN: polyacrylonitrile	Casting	D, UF
PMMA: polymethyl methacrilate	Casting	D
PVA: poly(vinyl alcohol)	Casting	D, PV
PP: polypropylene	Melt extr	MF, MD
PMP: poly(methyl pentenal)	Melt extr	GS
PET: poly(ethylene terephthalate)	Melt extr	MF
PBTP: poly(butylene terephthalate)	Melt extr	GS
PC: polycarbonate	Casting	D, MF
PDMS: polydimethylsiloxane	Casting	GS, PV
PTMSP: poly(trimethylsilyl propyne)	Casting	GS
Psu: polysulfone	Casting	UF
PESu: poly(ether sulfone)	Casting	UF
PPO: poly(phenylene oxide)		UF, GS
PA: polyamide	Melt extr.	UF
PEBA: poly(ether block amide)	Casting	PV
PEI: poly(ether imide)	Casting	GS
PAI: poly(amide imide)	Casting	GS, UF
PPN: polyphosphazene	Casting	GS, PV
PEEK: poly(ether ether ketone)	Melt/Casting	GS

at least in glassy polymers, polymer chain mobility or stiffness and intersegmental distance are the two critical factors in determining transport properties. Typically, chain rigidity results in increased permselectivity but lower permeability whereas greater intersegmental distance correspond to a higher permeability, but a lower selectivity. To achieve simultaneously higher permeability and selectivity, chain stiffness should be coupled with an increase in interchain separation [13]. In the literature, several studies can be found in which bulky side groups in glassy polymers such as polysulfones, polycarbonates [14], polyarylates [15] and poly(2,6-dimethyl-1,4-phenylene oxide) [16]. In particular, a correlation between structure and gas transport properties of silyl-modified polysulfones and poly(phenyl sulfone)s was found [17]: the size of the substituents in the ortho position relative to either the ether or sulfone linkage of polysulfone and poly(phenyl sulfone) chains were systematically increased from trimethylsilyl to dimethylphenylsilyl and to diphenylmethylsilyl. The results lead to the conclusion that substituent mobility rather than the size of the pendant side group is the critical factor in determining free volume and transport properties. Aromatic polyamides are potential thermoplastic materials for gas separation because of their outstanding combination of chemical, physical and mechanical properties. Application of aromatic polyamides, however, is more difficult because of their high melting point and their limited solubility in organic solvents.

Hu et al. [18] prepared a series of fluorine-containing aromatic polyamides by direct polycondensation of 4,4'-hexafluoroisopropylidene-dibenzoic acid with various aromatic

diamines. The aromatic polyamide membranes, prepared by the phase inversion technique, have excellent solubility in polar organic solvents. It was observed that both the specific volume of membranes and the Langmuir capacity constant of oxygen increase as a function of the size of the diamine segment in the polymer backbone [19].

Poly(dimethylsiloxane) (PDMS) has received considerable attention as a membrane material for gas separation due to its high intrinsic permeability to gases and vapours (the highest among rubbery polymers). However, almost all the important membrane separation processes of industrial interest use membranes made of glassy polymers because of their high selectivity and good mechanical properties.

In general, polymers with a high permeability and a low selectivity are in the rubbery state at room temperature. In contrast, the polymers with a high selectivity and low permeability are in the glassy state. A notable exception are the glassy poly(1-trimethylsilyl-1-propene) (PTMSP) and poly(perfluoro-2,2-dimethyl-1,3-dioxole) (PFDMD) [20], which have the highest intrinsic gas permeability for all known synthetic polymers, though with low gas selectivity.

In the search for a membrane material capable of separating higher hydrocarbon the most promising materials, polyoctylmethylsiloxane (POMS) and poly(trimethylsilylpropyne) (PTMSP), were compared to the standard material polydimethylsiloxane (PDMS) [21]. POMS is a silicone with a glass transition temperature far below the experimental temperatures. This polymer seemed to be mechanically stabilized and supported by the pore of a substructure, which one might call a sub surface membrane (SSM). With the system POMS-SSM, butane/methane selectivity from mixed gas tests was enhanced from 5 to a value of 12.

PTMSP is an exceptional glassy polymer with a glass transition temperature above 540 K. Because of its stiff backbone, in combination with the bulky  $\text{Si}(\text{CH}_3)_3$  side-group, PTMSP is known to have a fairly high fractional free volume  $> 25\%$ . The gas permeability coefficients were one order of magnitude higher than those obtained for PDMS. The chemical structure of POMS and PTMSP in comparison with PDMS is shown in Fig. 1.

Most of the polymers can be easily manufactured in different shapes (hollow, spiral wound, flat sheet, etc.); they are elastic, they resist to fatigue, they have satisfactory diffusion and

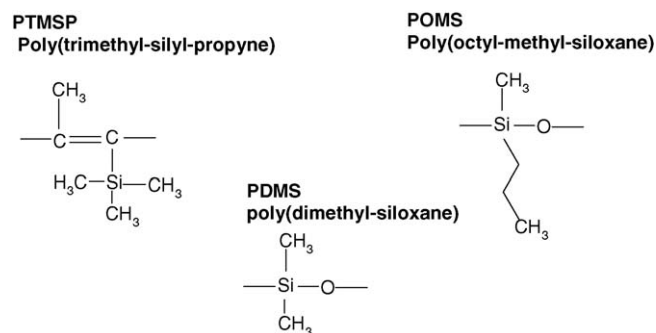


Fig. 1. Chemical structures of PTMSP, POMS and PDMS.

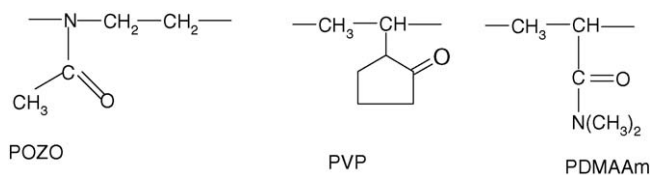


Fig. 2. Typical examples of organic polymers in the network matrix of inorganic materials.

sorption coefficients, they can be produced with incorporated catalysts as nano-sized dispersed metallic clusters [22,23], zeolites and activated carbons [24], or metallic complexes [25–31] and in some way, tailored as needed.

There are also some promising ways to create materials with significant chemical and thermal resistance [32]. Uniform dispersion of nanoscopically sized particles (nanoelements) may lead to a large interfacial area between the constituents per volume of material. In particular nano-ordered composite materials consisting of organic polymers and inorganic compounds attracted attention for their use in creating high performance polymeric materials.

The term “hybrid polymers” describes blends of organic and inorganic components with molecular-level dispersions. Hybrid materials are also potential candidates for catalysts [33–36]. The sol gel procedure allows to incorporate the organic polymer segments in the network matrix of inorganic materials [37–41]. Typical examples of organic polymers used for this purpose are poly(2-methyl-2-oxazoline) (POZO), poly(*N*-vinylpyrrolidone) (PVP) and poly(*N,N*-dimethylacrylamide) (PDMAAm) (Fig. 2).

### 3. Membrane/catalyst arrangements used in PCMR

A catalytic membrane reactor (CMR) is a unit that acts simultaneously as a separator and a reactor. Combining the reaction and separation in a single stage will simplify the process in accordance to strategy of Process Intensification. An appropriate reactor design can improve the yield or reaction selectivity, and this can also decrease downstream separation costs [42].

The major areas of applications for CMR are:

- (1) Yield-enhancement of equilibrium-limited reactions: the role of the membrane is principally to selectively remove a

reaction product from an equilibrium restricted reaction from the reactor, in order to increase the yield compared to conventional reactors (Fig. 3a). It is proposed to name this type of membrane reactor an *extractor* [4].

Membrane-based reactive separations were first utilized with reactions, for which the continuous extraction of products would enhance the yield by shifting the equilibrium. Reactions of this type include dehydrogenation and esterification.

- (2) Selectivity enhancement: the role of the membrane is to dose a reactant that may reacts in successive reactions (*distributor membrane reactor*) (Fig. 3b). In this way the concentration of the reactants is kept low by controlled addition through the membrane. This limits side reactions or subsequent reactions of the product. Controlled addition can also be used to prevent catalyst deactivation and to avoid dangerous increment of temperature in exothermic reactions (Fig. 3c). Partial oxidation of hydrocarbons is the most relevant application. Controlling the addition of the oxidant through the membranes results in a better yield of the intermediate oxidation products.

The membrane’s role in a membrane reactor could also be to improve the contact between different reactive phases: the membrane acts as medium providing the intimate contact between different reactants, which are fed separately in either side of membrane or by forcing them to pass together.

Another classification of MRs is based on the relative position of the two most important MR elements of the reactor: the membrane and the catalyst. Three main configurations can be considered: the catalyst being physically separated from the membrane; the catalyst being dispersed in the membrane; the membrane being inherently catalytic. The first configuration is often called “inert membrane reactor” (IMR) in contrast with the two others configurations which are “catalytic membrane reactors” (CMRs). In the CMRs the reaction and separation are integrated realising a *reactive separation* [42].

### 4. Catalytic polymeric membranes in reactors with gas permeation

Polymeric catalytic membrane reactors (PCMR) offer added flexibility over their conventional reactor counterparts because

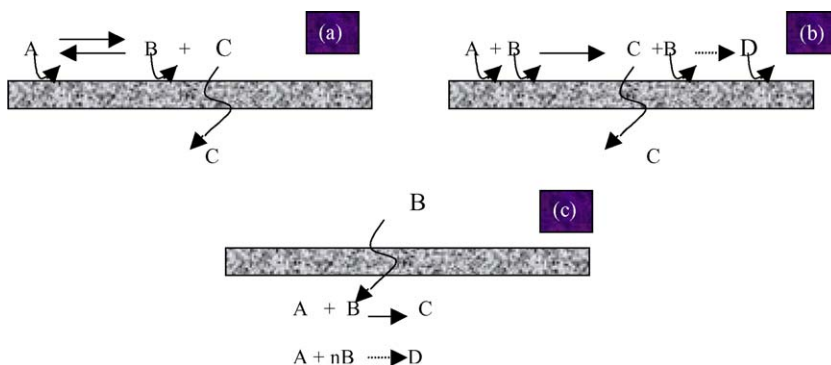


Fig. 3. Some possible applications of CMR to improve yield (a) or selectivity (b–c).

Table 2  
Several polymeric membranes in reactors with gas permeation

#Entry	Kind of reaction	Membrane type	Catalyst–membrane material
1	Hydrogenation of cyclopentadiene [44]	Catalytic	PVP–Pd/CA, PVP–Pd/PAN, EC–Pd/CA, AR–Pd/CA
2	Hydrogenation of butadiene in 1-butene [45]	Catalytic	Mono- and bimetallic polymeric fibers
3	Partial hydrogenation of alkynes [46]	Catalytic	Pd–PVP/CA
4	Hydrogenation of ethylene and propylene [23]	Catalytic	Pd/PolyMTD
5	Hydrogenation of methylene–cyclohexane [47]	Catalytic	PdPVDF <sub>20</sub> PVP <sub>10</sub> , PdPVDF <sub>20</sub>
6	Reduction of nitrous oxide [22]	Catalytic	Pd, Ag/PAIs, Pd/Ag
7	MTBE decomposition [48]	Catalytic	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /PPO/Al <sub>2</sub> O <sub>3</sub>
8	MTBE decomposition [49]	Inert	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /CA
9	Dimerisation of isobutene [52]	Catalytic	Nafion SAC-13/Teflon/PDMS

they have the capability to combine reaction and separation in a single operation unit. Sousa et al. [43] for example, carried out a study on performance of a complete mixed PCMR. The membrane is a polymeric dense membrane where the catalyst is distributed in nanoclusters inside the entire membrane. The feed gases permeate through the membrane, contacting with the catalysts nanoclusters. The diffusion and sorption role of the reactants and products on the conversion is studied as a function of the Thiele modulus and of the contact time.

Several catalytic polymeric reactors with gas permeation are summarised in Table 2. In general, research on gas phase reactions with catalytic membranes is still limited, *selective hydrogenation* being the most important application. In the next paragraphs (Sections 4.1 and 4.2) an overview of catalytic polymeric membrane preparation for the PCMR listed in Table 2 is given.

As applications, a particular accent is given to selective hydrogenations, followed by other examples of applications.

#### 4.1. Membrane preparation

##### 4.1.1. Immobilization of metal complex catalyst in polymeric membranes

Polymeric hollow fibers reactors, manufactured with a polymer anchored catalyst (Pd) on polymeric hollow fibers, can be used (see Table 2 for references) in e.g. the *selective hydrogenation of cyclopentadiene to cyclopentene*, in the *purification of the crude propene containing propadiene and propyne impurities and of crude 1-butene fraction*.

In particular, Gao et al. [44] gave complete details about the preparation of the catalytic polymeric hollow fibers. The catalytic hollow fibers, PVP–Pd/CA, PVP–Pd/PSF, PVP–Pd/PAN, EC–Pd/CA, and AR–Pd/CA (PVP: polyvinylpyrrolidone, EC: ethyl cellulose, AR: melamine formaldehyde resin, CA: cellulose acetate, PSF: polysulfone, PAN: polyacrylonitrile) were prepared by supporting the soluble polymer anchored palladium complexes of PVP–Pd, Ec–Pd, and AR–Pd on the corresponding CA, PSF and PAN hollow fibers, respectively.

All the CA, PSF and PAN fibers had a dense thin layer supported by a microporous sponge layer. Polymer-anchored Pd complexes were prepared by a reaction of polymer and an aqueous solution of PdCl<sub>2</sub> in an appropriate solvent. Subsequently, the prepared solution was pumped through the inside

of the CA, PSF or PAN fibers with a circulating pump, and an aqueous solution of hydrazine was pumped through. It was observed that the permeabilities of the H<sub>2</sub> and N<sub>2</sub> in the catalytic hollow fibers were lower than in the original CA and PSF fibers, while their H<sub>2</sub>–N<sub>2</sub> permselectivities were higher (6–10 times higher for CA). It was stated that the reason for this decrease of permeabilities might be caused by a loss of free volume available to the gas mixture in the catalytic fiber membrane.

##### 4.1.2. Metal nanoclusters catalyst in polymeric membranes

For good turn-over rates in catalysis, high loading with catalyst and a large accessible surface are needed. The smaller the particles of the catalyst the higher the surface per unit volume. Therefore, membranes with nano-sized, ultrafine clusters uniformly distributed throughout the membrane are favored.

Ciebien et al. [23] synthesized palladium nanoclusters within microphase-separated diblock copolymer films of [MTD]<sub>113</sub>[Pd(Cp<sup>N</sup>)PA]<sub>50</sub> (MTD = methyltetracyclododecene, Cp<sup>N</sup> = endo-2-(cyclopentadienylmethyl) norborn-5-ene, PA = η<sup>3</sup>-1-phenylallyl). Three factors contribute to the well-controlled formation of nanoclusters within micro-phase separated diblock copolymers:

1. the metal ions are initially homogeneously distributed within the organometallic domains,
2. the presence of the microdomain interfaces helps to control cluster nucleation and growth,
3. the well-defined, thermodynamically controlled polymer morphology leads to a uniform distribution of clusters throughout the polymer matrix.

The organometallic repeat units were reduced by exposing the films to hydrogen at 100 °C, leading to the formation of nearly monodisperse Pd nanoclusters. The nanocomposites were active catalysts for hydrogenation of ethylene and propylene.

Bottino et al. [47] prepared polymeric membranes with catalytic activity, and compared their performance with that of a ceramic membrane using the *hydrogenation of methylene–cyclohexane* as a probe reaction. The reaction can proceed either by direct hydrogenation of methylene cyclohexane



(MNANO) to methyl-cyclohexane (MLANO) or by isomerisation to methylcyclohexene (MLENE), that in turn can be hydrogenated to MLANO.

Two types of polyvinylidene fluoride (PVDF) membranes were prepared by phase inversion technique. The first type was obtained from a 20% (w/w) solution of PVDF in DMF. The second type of membrane was prepared by adding polyvinylpyrrolidone (PVP) to the above mentioned PVDF solution in DMF. The subsequent casting operations and impregnation conditions were the same: after the detachment of the membrane from the glass plate, and rinsing with water to remove DMF, the membranes were impregnated with an acid solution of PdCl<sub>2</sub>. Then the membranes were washed in order to remove excess catalytic precursor, and palladium was reduced to the metallic form by NaBH<sub>4</sub>. The addition of PVP to PVDF solution increases the amount of palladium in the final membrane.

As stated above, from the analysis of the previous studies [45,46] glassy polymers over rubbery polymers are favored, especially polyamides [48] and polyimides [49]. Fritch and Peinemann [22,50] studied the development of homogeneous dense catalytically active membranes to find a polymer with “high” permeability and “sufficient” selectivity and to find a method of distributing ultrafine particles uniformly inside a membrane. They synthesized poly(amide-imides) (PAIs) which combine properties of amide and imide polymers, by direct polycondensation of dicarboxylic acids (DCAs) with diamine. The polymers used were soluble in THF and in mixtures of THF with acetone or alcohols and, therefore, they were suited to draw thin-film composites on low cost microporous polymeric supports stable to these solvents. It was stated that the membranes prepared from synthesized PAIs can be used in the range from room temperature to 200 °C. They prepared 6F-PAIs homogeneous membranes, thin film composite membranes (on PVDF supports) and catalytic membranes. Thin film composite membranes were nearly free of defects and sealing of the defects by a PDMS coating yielded selectivities close to the values found for homogenous non-coated membranes. Nano-sized clusters of Pd were generated in homogeneous and thin film composite membranes by co-solving of PdAc in the casting solution and reducing the membrane by treatment with NaBH<sub>4</sub>/MeOH. It was achieved to generate nano-sized (~2 nm) noble metal catalysts in high amounts, >20 wt.% noble metal inside the membranes. Gas permeabilities up to 15 barrer for O<sub>2</sub> ( $p_{O_2}/p_{N_2} = 5.4$ ) and 100 barrer for H<sub>2</sub> ( $p_{H_2}/p_{N_2} = 35$ ) and selectivities up to 7.6 for  $p_{O_2}/p_{N_2}$  ( $p_{O_2} = 1.8$  barrer) and 100 for  $p_{H_2}/p_{N_2}$  ( $p_{H_2} = 23$  barrer) were measured.

These catalytic membranes can be used to perform catalytic reactions such as reduction of nitrous oxide by hydrogen in N<sub>2</sub>O/H<sub>2</sub>/He or argon or methane mixtures to nitrogen and water.

Fritch and Peinemann [50] also manufactured two highly gas permeable PAIs consisting of structures with moieties of 3,3'-dimethylnaphthidine and hexafluoroisopropylidene-2-bis(phthalic acid anhydride) (6FDA) and 6F. They used pure precious metal alloys (Pd, Ag, Pd/Ag) which were dispersed on

nano-scale uniformly throughout the membrane as a catalyst. Uniform non-porous films of 40–50 μm thickness were prepared from 10% THF solution. Residual solvent was exchanged by immersing overnight in methanol. The membranes were dried to constant weight in vacuum oven at 110 °C at below 1 mbar. Shrinking of the membranes by 5–10% in diameter during the reduction step was observed but they were not crumbled.

Inorganic fillers used with polymers, normally, are not permeable to gas and therefore they act as diffusion barrier and sorption effects are negligible for the micro-sized fillers. But change in sorption behaviour of nanoscale clusters due to their high surface area can be expected. Deactivated membranes were used for the measurement of permselectivity and diffusivity. The redox-process is fully reversible, even after prolonged time in air or hydrogen. For CO<sub>2</sub> the permeability, diffusivity and solubility decrease in the presence of clusters, due to hindrance by the clusters. Permeability of He decreases similarly. In contrast to this, the diffusivity of hydrogen decreases by two to three orders of magnitude accompanied by an increase in solubility by two orders. It was found that membranes with Pd/Ag were less effective in H<sub>2</sub> sorption than those with pure Pd; membranes with Ag only showed a decrease in permeability.

Two catalytically active polymeric membranes containing 15% Pd/Ag (77/23) were used for *hydrogenation of nitrous oxide*.

#### 4.1.3. Entrapment of the catalyst in a reactive layer on top of supporting membranes

Choi et al. [48] developed a method for preparing H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-polymer composite membranes and showed their successful use in catalytic membrane reactors as catalytic membranes for the vapour phase *decomposition of MTBE*. Three types of catalytic membranes comprised of 12-tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, PW) and polyphenylene oxide (PPO) were designed: PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type 1, PW = 0.023 g), PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type 2, PW = 0.01 g), and PW/PPO/Al<sub>2</sub>O<sub>3</sub> (type 3, PW = 0.066 g). Methanol and chloroform were used as a solvent for membrane preparation. A porous α-Al<sub>2</sub>O<sub>3</sub> tube was used as both an inner tube of the membrane reactor and as support for the catalytic membrane. A homogeneous solution of PW-PPO-methanol-chloroform was prepared at room temperature and coated on the tube side of the Al<sub>2</sub>O<sub>3</sub> to form PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type 1) or onto the PPO/Al<sub>2</sub>O<sub>3</sub> (type 2) (the tube side of the Al<sub>2</sub>O<sub>3</sub> coated with a solution of PPO/chloroform) to form PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub>. PW/PPO/Al<sub>2</sub>O<sub>3</sub> (type 3) was prepared by coating a homogeneous solution of the catalyst (PW-methanol-chloroform) onto the PPO/Al<sub>2</sub>O<sub>3</sub>. The catalyst was highly dispersed as fine particles throughout the type 1 and type 2 catalytic membranes. However, solid agglomerations of PW catalyst were formed in the type 3 catalytic membrane. These membranes were both catalytically active and permselective for the reaction species.

Fritsch et al. [51] used polymeric composite catalytic membranes for dimerisation of isobutene to isooctane (Section 4.2.4). Catalysts such as silica supported Nafion and silica

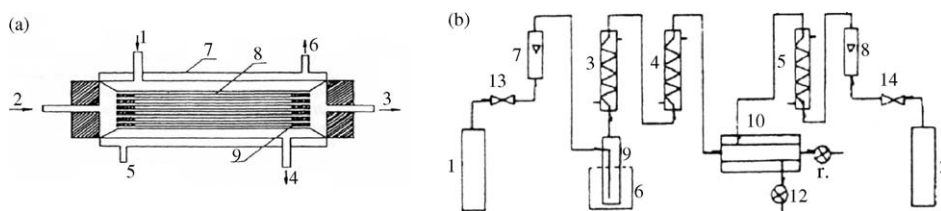


Fig. 4. (a) Structure of the catalytic hollow fiber reactor: (1)  $H_2 + N_2$  feed inlet; (2) feed inlet; (3) product outlet; (4) tail gas outlet; (5) and (6) circulating water, inlet and outlet; (7) glass jacket; (8) catalytic hollow fibers; (9) expoxide resin seal. (b) Schematic flow diagram of the hydrogenation of conjugated dienes in a catalytic polymeric hollow-fiber reactor: (1) carrier gas ( $N_2$ ); (2)  $H_2 + N_2$ ; (3) concenser at constant temperature with a thermostat; (4–6) preheaters; (7 and 8) rotameters; (9) flask containing conjugated diene; (10) membrane reactor; (11 and 12) sampling ports; (13 and 14) needle valves [44].

supported phosphotungstic acid were mixed in solution with a polymeric binder. Teflon, Hyflon, PTMSP and PDMS polymers were used as binders to form a porous, reactive layer on top of a porous polymeric supporting membrane made from polyacrylonitrile (PAN) or polyamideimide (PAI) by a casting process. They were used uncoated or coated with a thin, non-porous PDMS film. PDMS film acted as flow regulator and enabled selective product removal. Structure, porosity, catalyst partition and catalyst accessibility are all important for the final reactivity of the membrane. Proton abstraction from the catalyst surface starts and supports further reaction. A binder which is present in a catalytically active layer effects acidic properties of the catalyst by changing its proton exchange efficiency and also blocking the active sites that are placed inside the catalyst pore system.

The catalytic membranes were applied in a forced-flow catalytic membrane reactor (Section 4.2.4).

## 4.2. Membrane application

### 4.2.1. Hydrogenation

The structure of the catalytic hollow fiber reactor and the schematic diagram of the experimental unit used in the *selective hydrogenation of cyclopentadiene to cyclopentene*, in the *purification of the crude propene* and *of crude 1-butene fraction* (see above Table 2) are given in Fig. 4.

These catalytic polymeric hollow-fibers were used to establish the catalytic membrane reactors, and the selective hydrogenation of conjugated dienes was carried out in reactors under mild conditions of 40 °C and 0.1 MPa.

The *selective hydrogenation of cyclopentadiene* is efficiently performed in catalytic hollow-fiber reactors based on the PVP–Pd/CA and PVP–Pd/PAN hollow fibers, as above reported.

Both the *flowrate* and the  $H_2/N_2$  mole ratio of the  $H_2$  and  $N_2$  mixture outside the fibers can affect the selective hydrogenation of cyclopentadiene in the catalytic CA-hollow fiber reactor. By adjusting the flow rate of  $H_2/N_2$  mol ratio the conversion of cyclopentadiene was increased up to 91% or more. In Table 3 (adapted from Gao et al. [44]) the results of the selective hydrogenation of cyclopentadiene in the catalytic hollow fibers reactor are shown. The hollow fiber support, the polymer anchored palladium complex strongly influence the hydrogenation properties of the catalytic hollow fibers.

Liu et al. [45,46] studied the *purification of 1-butene* using butadiene as model impurity. The complexity of the process is that in addition to the overhydrogenation of 1-butene to butane, 2-butene may be formed in this process from the isomerization of 1-butene or 1,4-addition of butadiene in the hydrogenation. By using a bimetallic hollow fiber catalytic reactor, the isomerization of 1-butene was inhibited and the synergic effect of bimetallic catalyst was significant. The catalysts used monometallic or bimetal polymer supported, respectively PVP–Pd, EC–Pd or AR–Pd and PVP–Pd–0.5Co(Aca)<sub>2</sub>.

In Table 4 (adapted from Liu et al. [45]) the results of the comparison of the mono and bimetallic membrane reactors are presented.

A synergic effect of palladium and cobalt reduced by  $NaBH_4$  in the PVP–Pd–0.5Co(OAc)<sub>2</sub>/CA catalytic CA hollow fibers in R-4 was observed. The isomerization of 1-butene to 2-butene is inhibited significantly. The data in Table 4 also show the influence of the reducing agent on the catalyst performance: when the bimetallic CA hollow fibers are reduced by  $NH_2NH_2$ , there is no obvious bimetallic synergic effect. This is due probably to difference between  $NH_2NH_2$  and  $NaBH_4$ . In the case of  $NaBH_4$  reduced PVP–Pd–Co dispersion, palladium clusters of relatively small size deposit on the superfine particles of cobalt boride [45].

Table 3  
Selective hydrogenation of cyclopentadiene in different catalytic hollow fibers reactors (40 °C, 0.1 MPa) (adapted from Gao et al. [44])

Reactor	Supported Pd complex	Original fiber	Pd content (mg)	TOF (mol $H_2$ /mol Pd min)	Conversion (%)	Selectivity (%)
CMR-1	PVP–Pd	CA	1.13	5.9	91.0	91.0
CMR-2	PVP–Pd	PSF	4.63	1.0	68.7	96.4
CMR-3	PVP–Pd	PAN	5.27	1.3	99.0	93.4
CMR-4	EC–Pd	CA	1.46	3.3	60.0	78.0
CMR-5	AR–Pd	CA	1.19	0.9	13.2	78.3

PVP: poly(*N*-vinyl-2-pyrrolidone); EC: ethyl cellulose; AR: melamine-formaldehyde resin; CA: cellulose acetate; PSF: polysulfone.

Table 4  
Selective hydrogenation of butadiene in crude 1-butene with different mono- and bimetallic catalytic hollow fiber reactors (adapted from Liu et al. [45])

Reactor	Catalytic fibers	Reducing agent	Pd content (mg)	Products (wt.%)				
				C <sub>4</sub> H <sub>10</sub>	1-C <sub>4</sub> H <sub>8</sub>	Trans-2-C <sub>4</sub> H <sub>8</sub>	Cis-2-C <sub>4</sub> H <sub>8</sub>	1-Butene loss (%)
R-1	PVD–Pd/CA	NH <sub>2</sub> NH <sub>2</sub>	1.13	0.5	96.8	1.3	1.2	2.2
R-2	PVP–Pd/CA	NaBH <sub>4</sub>	1.15	0.5	97.1	1.1	1.1	1.9
R-3	PVP–Pd–0.5Co(OAc) <sub>2</sub> /CA	NH <sub>2</sub> NH <sub>2</sub>	1.19	0.5	97.4	1.0	0.9	1.6
R-4	PVP–Pd–0.5Co(OAc) <sub>2</sub> /CA	NaBH <sub>4</sub>	1.10	0.3	99.0	0.3	0.2	0

Hydrogenation experiments of ethylene and propylene by catalytic membrane made from Pd/PolyMTD [23] were run as batch reactions in a Fischer–Porter bottle equipped with a magnetic stirrer and a gas sampling port. The nano composite films (4–6 mg, 14 wt.% Pd) were used at 120 °C. The hydrogen/alkene ratio was 2:1 and initial reactor pressures were typically 34 psig.

Assuming that transport through the polymer matrix is the rate-limiting step, it was hypothesised that species with higher permeability in the polymer matrix would react more rapidly. A permeation study was conducted on a polyMTD sample to quantify differences in permeability among the reactants gases and to evaluate the possibility of using polymer-supported nanoclusters to selectively hydrogenate one species in a mixture. In Table 5 (adapted from Cibien et al. [23]), the diffusion, solubility and permeability coefficients for ethylene, propylene, and 1,3 butadiene in polyMTD at room temperature are summarized.

The cluster size within the polymer matrix was important factor in determining the catalyst activity, expressed as the moles of alkene hydrogenated per mole of Pd per second. Ethylene hydrogenation experiments showed that catalyst with cluster size of 14 Å in diameter was nearly twice as active as catalyst with nanoparticles of 30 Å in diameter. The difference in activity was explained by differences in cluster size.

Also in the hydrogenation of methylene-cyclohexane by Pd/PVDF based membrane [47] the dimension of the palladium particles in the polymeric matrix is crucial. The comparison of the catalytic activity of two polymeric membranes shows that the T.O.N (Turn Over Number) of PdPVDF<sub>20</sub>PVP<sub>10</sub> membrane is lower than that of the Pd–PVDF<sub>20</sub> owing to higher dimension of the palladium particles in the former membrane.

The overall selectivity (Table 6) was identical for both membranes, the only difference being the time necessary to complete the reaction, which was lower for the membrane with PVP because of the higher catalyst loading.

Table 5  
Diffusion coefficient, solubility coefficient and permeability for ethylene, propylene and 1,3-butadiene in polyMTD at room temperature [23]

Penetrant gas	$D$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )	$S$ ( $\times 10^{-3}$ g cm <sup>-3</sup> psi <sup>-1</sup> )	$P = DS$ ( $\times 10^{-13}$ g cm <sup>-1</sup> s <sup>-1</sup> psi <sup>-1</sup> )
Ethylene	9.1	0.28	0.25
Propylene	4.3	1.1	0.48
1,3-Butadiene	6.3	2.1	1.3

Table 6  
Catalytic activity comparison between the two types of polymeric membrane ( $T = 25$  °C, in all-through configuration) [47]

Membrane	TON <sub>MNANO</sub> ( $\times 10^{-3}$ mol/s g <sub>Pd</sub> )	Selectivity <sub>MNENE</sub> (%)
Pd–PVDF <sub>20</sub>	7.6	91
Pd–PVDF <sub>20</sub> PVP <sub>10</sub>	1.0	91

It is also possible to use dense polymeric membranes with metallic catalysts for the catalytic reactions involving hydrogen evaluation and consumption. Gryaznov et al. [51] used composite membrane catalyst (PDMS films covered with Pd layers of 20 or 80 nm) which is active in *selective hydrogenation of cyclopentadiene in cyclopentene* at temperatures of 25–160 °C. The polymer is catalytically inert.

The penetration of H<sub>2</sub> through the membrane catalyst gives higher selectivity than conventional reactions (without membrane) especially at high conversions. Gryaznov et al. [51] investigated the cyclic polyolefinic C<sub>7</sub>–C<sub>12</sub> hydrogenation and showed that reaction rate is higher in the case of H<sub>2</sub> diffusion through the membrane catalyst (W<sub>1</sub>) than for the introduction of a mixture polyolefin vapour with H<sub>2</sub> (W<sub>2</sub>) (Table 7).

From Table 7 it is seen that this effect is more pronounced for more strongly adsorbed polyolefin molecules. The increase in number of double bonds causes a raise of the amount of H<sub>2</sub> transferred through the membrane catalyst during the hydrogenation.

#### 4.2.2. Reduction of nitrous oxide

As above reported, for the *reduction of nitrous oxide* [22] two catalytically active polymeric membranes containing 15% Pd/Ag (77/23) were used. The membranes differ in permeance

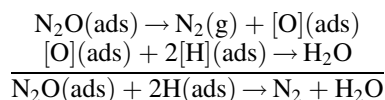
Table 7  
Influence of polyolefin structure on the rate of its hydrogenation by the diffused or mixed H<sub>2</sub> [51]

Hydrocarbon	W <sub>1</sub> /W <sub>2</sub>
Cycloheptatriene	3.0
Cyclooctene	1.7
Cyclooctadiene-1,3	1.8
Cyclooctadiene-1,5	2.0
Cyclooctatetraene	1.3
Cyclooctadecatriene	7.5



for the tested gases except He, and they differ by a factor of two in diffusivity for H<sub>2</sub> and N<sub>2</sub>O. The reaction is given as

Rate limiting step:



The composition of the feed gas mixtures varied in N<sub>2</sub>O/H<sub>2</sub> from 1/5 to 1/1 v/v; diluting gas were He, Ar, or CH<sub>4</sub>. With H<sub>2</sub> of at least molar ratio to N<sub>2</sub>O in the feed gas, no N<sub>2</sub>O was detected in the permeate. When turning of H<sub>2</sub>, N<sub>2</sub>O was identified in the permeate. Additionally, the reaction products H<sub>2</sub>O and N<sub>2</sub> were also detected in the permeate. Thus, both the membranes were found to be successful for decomposition of N<sub>2</sub>O by hydrogen. The permeance to H<sub>2</sub> and N<sub>2</sub>O was around  $2 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2\text{s cmHg}$ .

#### 4.2.3. MTBE decomposition

MTBE synthesis and decomposition have been used to yield high purity isobutene from C<sub>4</sub> raffinate. When methanol reacts with C<sub>4</sub> fractions, only isobutene is reacted to yield MTBE and subsequently the MTBE is cracked to obtain equimolar isobutene and methanol. Although MTBE synthesis is an important process due to the increasing demand for MTBE, MTBE decomposition is also an attractive reaction due to the potential demand for pure isobutene. It is well known that the MTBE synthesis and the decomposition are a reversible and acid-catalyzed reaction.

In the study of Lee et al. [49] the MTBE decomposition over H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was carried out in an inert polymeric membrane reactor. The performance of the membrane reactor was examined at 100 °C and 0.4 atm. The MTBE conversion in the membrane reactor was about 7% higher than that in the membrane-free fixed bed reactor under the same reaction conditions. The enhanced performance of the membrane reactor in this reversible reaction was mainly due to the selective permeation of methanol which resulted in a methanol-deficient condition suppressing MTBE synthesis reaction. In general, as before reported, the enhanced performance of a membrane reactor is due to a shift in equilibrium or a reduction of product inhibition. Because the reaction conditions in this experiment were not equilibrium conditions at that temperature and pressure, the enhanced performance of the CA membrane reactor is mainly due to the selective permeation of methanol and the rejection of MTBE through the CA membrane causing the reduction of product inhibition rather than the shift in equilibrium.

In the study of Choy et al. [48] the MTBE decomposition was performed in a catalytic membrane reactor by comparing the performance of three different polymeric catalytic membranes (see above the section *Membrane preparation*). A shell and tube type membrane reactor was designed in order to evaluate the performance of HPA–polymer composite catalytic membranes (Fig. 5). The reaction was examined at temperatures ranging from 80 to 100 °C and at the tube side total pressures ranging from 1.0 to 2.3 atm. The permeated stream was continuously removed by sweeping with N<sub>2</sub> gas

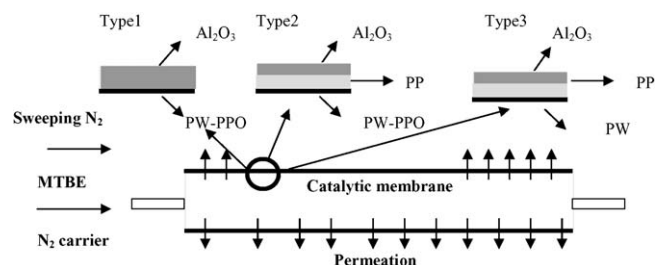


Fig. 5. Detailed structure of the shell and tube-type membrane reactor equipped with heteropolyacid–polymer composite catalytic membrane [48].

(4.0 cm<sup>3</sup>/min). MTBE conversion and isobutene selectivity in the feed (tube side) were calculated as follows:

$$\text{MTBE conversion (\%)} = \left( \frac{1 - (B + C)}{A} \right) \times 100$$

$$\text{Isobutene selectivity in feed (\%)} = \left( \frac{D}{D + E} \right) \times 100$$

where *A* is the amount of MTBE in feed; *B*, *D*, and *E* the amounts of MTBE, isobutene and methanol in effluent of tube side; *C* is the amount of MTBE in permeate (shell side).

All the membranes showed catalytic activities in the decomposition of MTBE. The selective removal of methanol through the catalytic membrane led to an equilibrium shift in a direction favourable to MTBE decomposition. Among three types of catalytic membrane reactors, the PW–PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type 2) showed the best performance (60–62% isobutene selectivity instead of 50% theoretical selectivity).

The enhanced performance of the type 2 catalytic membrane reactor can be attributed to the intrinsic perm-selective capabilities of the PW–PPO catalytic membrane and the sub-layered PPO membrane. In order to verify the selective removal of methanol through the catalytic membrane, a closed loop recycling reaction was carried out in the type 2 catalytic membrane reactor. As a result, MTBE conversion and isobutene selectivities in the tube side were increased with increasing recirculation time. This result strongly indicates that an equilibrium shift can be attained in the membrane reactor. Comparison between the PW–PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membrane with bulk PW showed that reaction species in the catalytic membrane reactor have higher mass transfer resistance than those in a fixed bed reactor.

#### 4.2.4. Dimerisation of isobutene

Composite membranes made from different polymers (Table 2, entry 9) with Nafion SAC-13 and other solid acids in various composition were used in a forced-flow catalytic membrane reactor for dimerisation of isobutene to isooctene [52]. Based on known problems of sometimes low selectivity, conversion, and of catalyst poisoning in real C<sub>4</sub> raffinate streams caused by, e.g. by-products such as diolefins or acetylene, this set-up was chosen. In this way, the contact to the acid catalyst sites is no longer controlled by diffusion and no poisoning by generation of oligomers and polymers is expected and not found within operation for a 1 week. The composite

Table 8  
Conversion and selectivity at different temperatures of the catalytic membranes for isobutene dimerisation (modified from [52])

Membrane	Temperature 30 °C		Temperature 40 °C		Temperature 50 °C	
	Selec. <sub>I-C8</sub> (%)	Conversion (%)	Selec. <sub>I-C8</sub> (%)	Conversion (%)	Selec. <sub>I-C8</sub> (%)	Conversion (%)
Torlon/SAC-AF Sac-milled (32 μm)	81.6	2.8	56.8	8.0	48.1	41.3
PAN/PDMS/SAC-AF Sac-milled (32 μm) PDMS-0.26 μm	93.2	5.1	69.3	16.0	57.8	45.0

catalytic membranes used for isobutene dimerisation provide removal of the desired intermediate product isooctane, thus inhibiting secondary reactions to give trimer and oligomer compounds.

For all membranes tested with increasing temperature the conversion increased but selectivity decreased.

Silicon film makes double effect: selectivity is higher because isooctane passes through it faster than isobutene, and conversion is higher because the residence time of isobutene is longer (Table 8).

## 5. Catalytic polymeric membranes in liquid phase reactions

The research on polymeric catalytic materials has been focused mainly in liquid phase reactions under mild conditions. In Table 9 catalyst-membrane material for some liquid phase reactions, examined in the next subparagraphs are summarised.

### 5.1. Membrane preparation and application

#### 5.1.1. Acid catalysed hydration of $\alpha$ -pinene

Vital et al. in recent papers [24–26] studied the hydration of  $\alpha$ -pinene yielding  $\alpha$ -terpineol reaction catalysed by polymeric catalytic membranes loaded with molybdophosphoric acid (HPMo). The membranes were made of PDMS and PVA polymers. The effect of different crosslinking substances like succinic acid and acetic anhydride was studied in PVA based membranes in order to modulate the hydrophilic/hydrophobic properties of the catalytic membranes. In particular, treatment with acetic anhydride modified the transport and sorption properties of polymeric catalytic membranes consisting of HPMo entrapped in PVA crosslinked with succinic acid. The catalytic activity of the PVA membranes is

strongly affected by membrane acetylation. In addition, the selectivity to the desired product  $\alpha$ -terpineol achieves its maximum value for the most acetylated membrane. The increase of catalytic activity with membrane acetylation is mainly due to the improvement of membrane water transport.

In another paper [26], Vital and co-workers compared the selectivities and activities of the  $\alpha$ -pinene hydration reaction using zeolites (USY and Beta) or a surface modified activated carbon with the performance of a PDMS membrane filled with these catalysts. The PDMS membranes filled were prepared according to Vankelecom et al. [27]. The characteristics of the membranes prepared are shown in Table 10.

For the membranes filled with zeolites (denoted M1–M5) a 10/1 weight ratio of prepolymer and crosslinker was used; in the membranes M6 and M7, where sulphonated carbons were incorporated, the ratio was 10/2 and 10/4, respectively.

The amount of crosslinker was increased because a reaction between the carbon functional groups and the active polymer took place. The increase of the catalyst loading leads to an increase on the membrane activity. At low zeolite loadings the pores created by zeolite particles cannot form a continuous channel network and the reagent molecules must cross polymer

Table 10  
Characteristics of the PDMS membranes filled with zeolites or a surface modified activated carbon [26]

Membrane	Catalyst	Catalyst loading	Thickness (mm)
M1	USY 750	21.9	0.110
M2	USY 750	35.9	0.078
M3	USY 750	52.8	0.139
M4	Beta	35.9	0.181
M5	Beta	52.8	0.265
M6	Sulphonated carbon	33.8	0.207
M7	Sulphonated carbon	46.5	0.220

Table 9  
Several polymeric catalytic membrane reactors for liquid phase reactions

#Entry	Kind of reaction	Membrane type	Catalyst–membrane material
1	Hydration of $\alpha$ -pinene [24,25]	Catalytic	PVA–HPMo
2	Hydration of $\alpha$ -pinene [26]	Catalytic	USY–PDMS
3	Hydrogenation of methylacetoacetate [27]	Catalytic	Rh–MeDuPhos–PDMS
4	Cyclohexane oxidation [53]	Catalytic	FePcY–PDMS
5	Cyclohexane and <i>n</i> -dodecane oxidation [54]	Catalytic	FePcY–PDMS
6	Cyclohexane oxidation [55]	Catalytic	Fe(TPP)Cl–PDMS, Fe(TDCPP)Cl–PDMS, Fe(PCI <sub>8</sub> )Cl–PDMS
7	Epoxidation of cyclohexene and styrene [56]	Catalytic	<i>Cis</i> [Mn(bpy) <sub>2</sub> ] <sup>2+</sup> –NaY–PDMS
8	Benzyl alcohol to benzaldehyde oxidation [57]	Catalytic	(Py, Pb <sub>2</sub> Ru <sub>2</sub> O <sub>6</sub> O')–Nafion 417
9	Secondary amines and sulfides oxidations [58]	Catalytic	Ti(IV)/C3–Symmetric Trialkanolamines–PVDF/PEEKWC/PAN
10	Alcohols photooxidation [59]	Catalytic	W <sub>10</sub> O <sub>32</sub> <sup>4–</sup> –PDMS/PVDF

Table 11  
Experimental sorption in PDMS and related Hildebrandt values [28]

	$\delta_d$	$\delta_p$	$\delta_h$	$\Delta^{\text{PDMS}}$	$\Delta^{\text{water}}$	Sorption
Water	19.50	17.80	17.60	22.18	0.00	0.02
Ethanol	15.80	8.80	19.40	17.08	9.90	0.07
Propanol	16.00	6.80	17.40	14.36	11.55	0.13
Butanol	16.00	5.70	15.80	12.43	12.72	0.19
<i>Tert</i> -butyl alcohol	14.85	2.65	14.56	10.25	16.14	0.35

void interfaces. As the percentage of zeolite in the matrix increases, the channel network may mature and connect the separate voids providing an alternative path for terpene and water molecules. The increase in the membrane channelling leads to an increase of the reagent permeation and therefore higher diffusion rates to the catalyst particles.

The PDMS membrane seems to have complex effects on the selectivity to  $\alpha$ -terpineol. It increases for the USY zeolite, decreases for the beta and shows only a slight increase for the activated carbon.

In particular, in kinetics studies for the reaction with USY zeolites dispersed in a PDMS membrane, an induction period is verified, suggesting an autocatalytic effect. This observation suggests that the reaction product, namely  $\alpha$ -terpineol, affects the reaction system leading to an increase of the overall reaction rate.

In a study of Vankelecom [28] the incorporation of zeolites in PDMS from the viewpoint of membrane preparation led to the concept of a zeolite-dependent cross-linking action on the PDMS.

For pure PDMS, a clear relation was observed and reported in Table 11 [28] between the amount of alcohol sorbed and the Hildebrandt parameter  $\Delta^{\text{PDMS}}$ :

$$\Delta^{\text{PDMS}} = ((\delta_p^s - \delta_p^{\text{PDMS}})^2 + (\delta_d^s - \delta_d^{\text{PDMS}})^2 + (\delta_h^s - \delta_d^{\text{PDMS}})^{-1/2}$$

in which *s* stands for solute. The high *tert*-butyl alcohol sorption indicates a very strong interaction of this compound with the PDMS matrix.

Comparing filled and unfilled membranes, incorporation of all zeolites leads to a reduced swelling of the membrane, to be ascribed to the cross-linking action of the zeolite. However, a significant difference can be observed when different kinds of zeolite (silicalite, ZSM-5, zeolite Y) are compared: the former zeolite results in a higher membrane sorption capacity for the more hydrophobic alcohols and a reduced sorption for water; the fact that the silicalite-filled membrane sorbs more water than the unfilled PDMS indicates a more hydrophobic character for the polymer than for the zeolite (Fig. 6).

### 5.1.2. Hydrogenation of methylacetoacetate

In 1991, Burk developed a set of new chiral biphosphine ligands referred to as DuPHOS (1,2-bis(phospholano)benzene) and BPE (1,2-bis(phospholano ethane)) [29]. The Rh and Ru complexes of these ligands were found to be extremely effective in the hydrogenation of various unsaturated substrates.

Rh–MeDuPhos was chosen by Vankelecom [27] as a typical representative of this class of hydrogenation catalysts for the inclusion in a PDMS matrix. As model reaction was selected the hydrogenation of methylacetoacetate in ethylene glycol (EG), and in methanol. The activity of the immobilized system was lower than for the homogeneous reaction but remained constant in a second run. It proved the absence of deactivation or complex leaching. By performing the reaction in methanol the membrane activity could be increased four-fold.

This is remarkable because methanol is a good solvent for the catalyst and it was found that the use of such solvents generally causes leaching of the catalyst from PDMS-membranes. Apart from decreasing the thickness, it is expected that improved sorption and diffusion of the reagents can help further to reach comparable activities.

A new kind of well defined PDMS-network enables a better fine-tuning of the membrane polymer properties. It consists of a crosslinker [tetrakis-(dimethylsiloxy)silane], a Pt catalyst [*cis*-dichlorobis(diethylsulfide) platinum(II)], a vinyl dimethyl terminated silicone polymer with low polydispersivity and silica with a high surface area. Whereas a silica-free PDMS-network did not swell when immersed in water, more than 0.20 ml/g of water was sorbed when the PDMS contained 20 wt.% silica. Swelling of polar compounds could be further enhanced by increasing the molecular weight of the vinyl terminated PDMS-chain and by blending amphiphilic blockopolymers [PEO(polyethylene oxide)–PDMS–PEO-triblocks] with the PDMS.

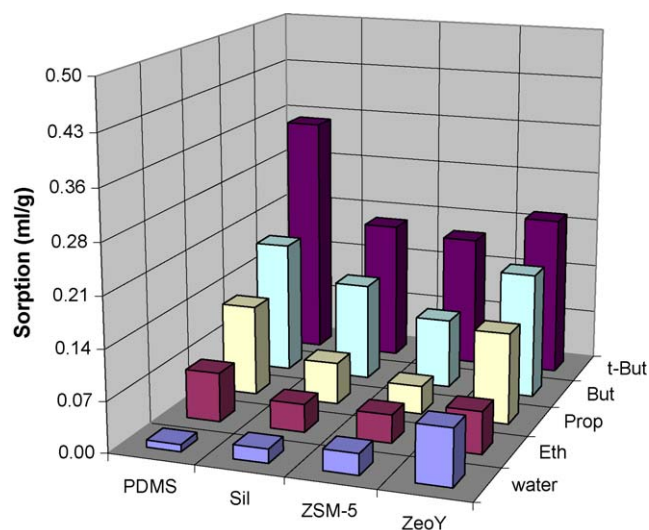


Fig. 6. Influence of the zeolite on the sorption of the different compounds [28].

### 5.1.3. Catalytic oxidations

This class of reactions is the most important route to functionalize hydrocarbons. Liquid hydrocarbons feedstocks (alkanes, alkenes and aromatic) are converted into industrial bulk chemicals using molecular oxygen and homogeneous cobalt and manganese catalyst. However catalytic oxidation reactions are often accompanied by the formation of free organic radicals, lowering selectivity. Consequently, there is a great need for catalysts that control the fate of formed radicals or avoid their formation. Nature solved this problem by developing oxygenation enzymes. Since these enzymes are able to catalyse selectively a wide diversity of oxidation reactions, it is most attractive for chemist to attempt the mimic of their active site.

Parton et al. [53] studied the room temperature *cyclohexane oxidation* using a zeolite-encapsulated complex: the zeolite catalyst was embedded in a hydrophobic polydimethylsiloxane polymer membrane (FePcY–PDMS) (Fig. 7). The hydrophobic polymer acts as a barrier between the *t*-butyl hydroperoxide and organic cyclohexane phase. An increased catalyst activity was obtained caused by the different properties of sorption and diffusion of the reactants and products into PDMS polymer.

Langenhendries et al. [54] studied the room temperature *oxidation of cyclohexane and n-dodecane* in a batch liquid phase membrane reactor, in which the organic substrate and aqueous oxidant phase are separated by a catalytic polymeric membrane (PDMS). In this reactor configuration, the organic substrate and aqueous oxidant phases are contacted through a catalytic membrane and, the necessity for the solvent completely eliminated. The influence of membrane thickness and the catalyst volume fraction (zeolite encapsulated iron-phtalocyanine) on the observed reaction rate was investigated. High reaction rates were obtained as a result of the optimized substrate/oxidant ratio achieved near the active sites of the catalyst. It was found that, in order to obtain high productivity over reactor volume ratio, thin polymer membranes ( $\sim 200 \mu\text{m}$ ) with a high catalyst volume fraction must be applied. Alcohol and ketone oxidation products were recovered from the aqueous and organic phases, depending on the solubility of the products in both phases. In the cyclohexane oxidation, cyclohexanol and cyclohexanone were found in both phases. In

the *n*-dodecane oxidation, since dodecanol and dodecanone products are not soluble in water they are completely recovered in the organic *n*-dodecane phase, demonstrating the possibility of the integrated reaction separation in one single unit.

In addition, the oxidation of cyclohexane was recently investigated by Gotardo et al. [55]. They studied the catalytic activity of representatives of the three generations of ironporphyrins, namely [5,10,15,20-tetraphenylporphyrin]iron(III) chloride (Fe(TPP)Cl), [5,10, 15, 20-tetrakis (2,6-dichlorophenyl) porphyrin]iron(III) chloride (Fe(TDCPP)Cl) and [5-mono(pentafluorophenyl) 10, 15, 20-tris(2,6-dichlorophenyl) 2, 3, 7, 8, 12, 13, 17, 18, octachloroporphyrin]iron(III) (Fe(PCl<sub>8</sub>)Cl), occluded in a polymeric film based on PDMS. The catalytic results show the influence of the polymeric support on the reactivity of the three generations of metalloporphyrins: the hydrophobic polymeric environment concentrates the substrate close to the catalytic sites and preserve the catalyst against auto-oxidative destruction.

Knops-Gerrits et al. [56] reported a composite catalyst for the *cyclohexene and styrene epoxidation*. The catalyst contains manganese diimine complexes (*cis*-Mn bis-2,2'-Bipyridyl), occluded within a NaY zeolite, incorporated in a polydimethyl siloxane membrane (*cis*[Mn(bpy)<sub>2</sub>]<sup>2+</sup>-NaY-PDMS). The three step synthesis consists of a Mn<sup>2+</sup> exchange of NaY, ligand sorption to form *cis*[Mn(bpy)<sub>2</sub>]<sup>2+</sup>-NaY and incorporation of the latter in a PDMS membrane.

The major differences between [Mn(bpy)<sub>2</sub>]<sup>2+</sup>-NaY as such and occluded in PDMS are observed in the sorption and catalytic characteristics. With the membrane system, the use of a solvent becomes obsolete. Cyclohexene and styrene were epoxidised with the oxidants H<sub>2</sub>O<sub>2</sub> or TBHP in presence and absence of solvents. Whereas optimal cyclohexene oxidation with [Mn(bpy)<sub>2</sub>]<sup>2+</sup>-NaY occurs with hydrogen peroxide in acetone, *t*BuOOH proves to be a better oxidant for [Mn(bpy)<sub>2</sub>]<sup>2+</sup>-NaY-PDMS. The reactions carried out in a 10 ml batch and 100 ml fed-batch reactors (membrane area = 6 cm<sup>2</sup>).

Selective oxidation of benzyl alcohol to benzaldehyde without any over-oxidation to benzoic acid is a key technological process that requires challenging synthetic routes. Ke et al. [57] prepared a rugged lead ruthenate pyrochlore (Py) catalyst incorporated Nafion 417 membrane (|NPy|). Surface morphological analysis shows the active Py catalyst mainly exposed in the outer surface and hence quite suitable for catalytic applications. Solid state UV–vis absorption spectroscopy study reveals the availability of free sulfonic acid sites even after the incorporation of Py in Nafion.

Hundred percent selective benzyl alcohol oxidation to benzaldehyde without any over oxidation to benzoic acid was observed. The catalytic membrane was 100% recovered from the reaction mixture without any marked loss of the Py activity even after four continuous runs.

Licini et al. incorporated Ti(IV) catalyst bearing C<sub>3</sub>-symmetric trialkanolamine ligands in different polymeric membranes for the oxidation of secondary amines and sulfides [58]. The selected polymers such as PEEKWC, PVDF and PAN with good thermal and chemical stability were used to prepare

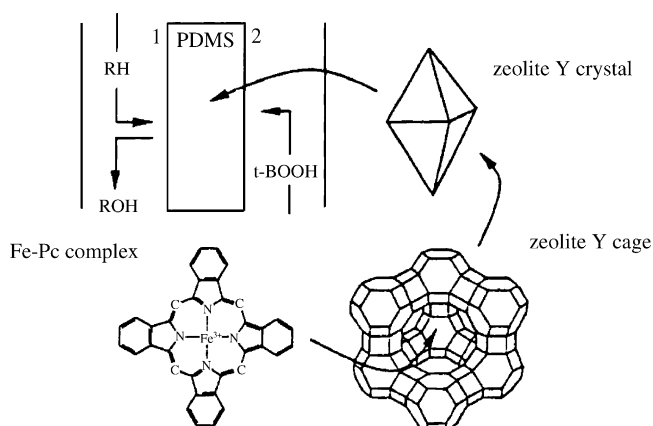


Fig. 7. Structures of FePcY–PDMS [53].



catalytic membranes by dry and wet phase inversion method. Two different reactions have been studied: the stereoselective sulfoxidation of aryl alkyl sulfides and the oxidation of secondary amines. With the first reaction type, the catalyst enantioselectivity in the new polymeric environments has been evaluated; by means the second one, the chemoselectivity in the ratio nitrone/immine products was related to the different polymers used and in particular as function of their different hydrophobicity, valuated by means of contact angle measurements (CAM). A fast screening of the catalytic membranes and a first evaluation of the influence of the surrounding polymer phase on the catalyst activity have been carried out in a batch reaction.

Bonchio et al. [59] have carried out heterogeneous photooxidation of alcohols in water with oxygen, by novel polymeric catalytic membranes, PVDF and PDMS based, incorporating decatungstate ( $W_{10}O_{32}^{4-}$ ). These photocatalytic membranes gave proof of their complete stability under near UV irradiation and their good recycling with no loss of activity. Membrane induced discrimination of the substrate results from the oxidation of a series of alcohols, through comparison with the homogeneous reaction. Further research work will be focused to a better understanding of the membrane based structure–reactivity trend in order to improve the synthetic potential of the method.

## 6. Pervaporation

The concept of using Pervaporation (PV) to remove by-product species from reaction mixtures was proposed in the early stage of pervaporation research. The coupling of pervaporation with an equilibrated reaction has gained considerable interest in 1980s. In this process, pervaporation is used to extract continuously one of the formed products in order to achieve complete conversion of the reactants. In particular, the esterification reaction combined with pervaporation received attention. In esterification processes, both inorganic and polymeric membranes have been used to increase the yield using pervaporation or vapor permeation arrangements. Pervaporation membrane reactors have been studied for esterification of oleic acid and ethanol [60], propionic acid and propanol [61], erucic acid and cetyl alcohol, tartaric acid and ethanol, oleic acid and butanol, and valeric acid and ethanol [62] with various acids or lipases as catalyst. This can be explained by the industrial importance of esters, the well-known reaction mechanisms and the availability of hydrophilic membranes which allow selective extraction of

the produced water. Pervaporation enhanced reactors are expected to provide a promising alternative due to the following considerations [62]:

1. PV is a rate-controlled separation process, and the separation efficiency is not limited by relative volatility as in distillation.
2. In PV only a fraction of feed that is permeated by membrane undergoes the liquid- to vapor-phase change, and thus energy consumption is generally low as compared to distillation.
3. With an appropriate membrane, PV can be operated at a temperature that matches the optimal temperature for reaction.

PV is often applied in combination with another technology as a hybrid process. Of these, PV-distillation and PV-reaction hybrid processes are already finding industrial applications [64].

For PV-membrane-based reactive separations, the membrane either removes the desired product or the undesired product (water for esterification reactions).

In Table 12, some examples of PV coupled to chemical reactions are summarised.

### 6.1. Membrane preparation

#### 6.1.1. Bifunctional membranes prepared with polymer blend


In the study of David et al. [61] paratoluenesulfonic acid is used as an esterification catalyst and a hydrophilic membrane (GFT membrane) based on PVA was used to achieve the separation. It was observed that although the membrane was perfectly selective to water, after several runs, the flux increased while the selectivity decreased due to esterification of some OH groups carried by the PVA chains by the acid. This was explained as the presence of an homogeneous catalyst which catalysed both the reaction in the liquid phase and in the membrane. The use of catalytically active membranes may avoid this problem. The target membranes should have high selectivity toward water and contain catalytic sites.

Polymer blending was considered to be a very convenient method for preparing “bifunctional” (catalytic and separative) membranes. One component of the blend should have the catalytic property while others should provide the separation properties to the blend. David et al. [61] prepared ionic membranes by blending PVA with an ionic polymer (P). The ionic polymer was chosen in such a way that specific properties were imparted to the membrane. Poly(styrenesulfonic) acid

Table 12  
Several applications of the pervaporation for chemical reactions

Kind of reaction	Membrane type	Catalyst/membrane material
Propanol and propionic acid esterification [61]	Catalytic	PSSA/PAN, PVA
<i>N</i> -Butyl alcohol–acetic acid esterification [63]	Catalytic	PVA/PAA–Zr(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
<i>N</i> -Butyl alcohol–acetic acid esterification [64]	Catalytic	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /PVA
Hydrogenation of 4-chlorophenol [9]	Catalytic	PEBA–Pd
Epoxidation of propene to propene oxide [66]	Inert	Mn(TPP)Cl/nonpolar pervaporation membranes

Table 13  
Conditions of preparation of the films [61]

Polymers	Monomer unit	Solvent	Support	Evaporation conditions
PAN	$-\text{CH}_2-\text{CH}-$   CN	DMSO	Teflon	15 h at 100 °C
PSSA	$\text{CH}_2\text{CH}-$   			
PVA	$-\text{CH}_2-\text{CH}-$   SO <sub>3</sub> H	H <sub>2</sub> O	Glass plate	12 h at 20 °C and 4 h at 40 °C

(PSSH) was chosen for the pervaporation-assisted esterification process. The sulfonic acid groups of PSSH catalyse the ester formation. The hydrophilic matrix helps in water extraction from the reaction medium in the pervaporation-assisted reaction. Different ionic membranes using PVA with ionic polymers such as sodium poly(styrene sulfonate) (PSSNa), poly(acrylic)acid (PAA) or poly(dimethyl dimethylene piperidinium) chloride (PDMEDM-PCl) were prepared to design ion-exchange membranes.

Polymer blending was performed by the solution method, in which the polymers to be blended were dissolved separately in an appropriate solvent. Then, films of different compositions were obtained by mixing the solutions containing 12 wt.% of polymer, and casting them by using “Gardner blade” onto suitable support. Solid films are obtained after complete evaporation of the solvent. The average thickness of the membranes was about 80 μm. In Table 13, the membrane preparation conditions and supports are summarized.

#### 6.1.2. Bifunctional membranes prepared by catalyst entrapment in polymeric matrix

Another way of preparing catalytically active dense polymeric membrane is to immobilize the solid catalyst necessary for the esterification reaction into the polymeric membrane. The main feature of the “bifunctional” membrane is to combine permselectivity for water with catalytic activity for esterification. Addition of acidic catalyst into the dense active layer could reduce the separation difficulties caused by the introduction of the catalyst into the reaction mixture (especially the homogeneous catalyst).

Two shortcomings, the small amount and the spatial distribution of the catalyst, are major hurdles for the development of the catalytic membrane. To overcome these shortcomings the membrane structure could be improved through copolymerization, blending or grafting in order to promote selectivity between water and acid. Zhu and Chen [64] prepared both copolymerized catalytic PVA membrane and PVA/PAA blend catalytic membrane on porous ceramic plate. Both membranes have catalytic properties since an esterification catalyst of solid acid, Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O was immobilized on the dense active layer. The porous ceramic plates rather than porous polymer membranes were used as a support for the dense catalytic polymer layer due to weak strength, weak chemical and pressure resistances of porous

polymer membranes. However, the inorganic UF membranes have overcome these shortcomings. During membrane preparation the catalytic layer and the dense active separation layer were divided into two layers in one catalytic composite membrane to prevent the membrane being destroyed through esterification either by catalysts that diffuse from the solution into the active separation layer [63], or by catalysts that contact directly with the active sites in the polymer blend membrane [64].

Liu et al. [65] studied the effect of crosslinking of polymers for membrane preparation by preparing the catalytic membranes with and without crosslinking for the coupling of pervaporation with esterification of acetic acid by *n*-butanol. For this purpose catalytic membranes with H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (esterification catalyst acid) entrapped in PVA was prepared in two steps. First the PVA composite membranes crosslinked by glutaraldehyde on the porous ceramic plates were prepared. Second, phospho-tungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was immobilized on the dense active layer. Thus, catalytic and separative layers were also separated in this study. Catalytic activity and stability of the membranes which were prepared without crosslinking and crosslinked in different methods were tested by immersing the membrane in a different solutions including reaction components. It was found that, for the membrane prepared without crosslinking, conversion was decreasing continuously after each successive use for esterification (6 h for each esterification at 80 °C), probably due to the entrapped catalyst being washed away. In order to improve the catalytic membrane stability, first the ratio of moles of PVA to H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was increased, second, the crosslinking degree was increased or other crosslinking methods such as PVA crosslinked by glutaraldehyde, by just heating etc. were used.

The membrane stability was expressed in the evolution of the molar ratio H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> extracted from the membrane to the initial H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in the membrane (R) as a function of time. Increasing PVA amount from 0.2 to 0.5 g decreased the R from 50% to 40%. However, the increase of PVA was limited since the membrane surface would crash in the process of drying if there was too much PVA in solution. The reason for H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> washed away from the membrane was thought to be the decrease in the bond force of PVA to H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> due to interaction of acetic acid with PVA when the membrane was swollen. It was also found that R value decreased to 30% with a membrane prepared by heating. However, since the surface of the catalytic membrane may also crash during heating, this way was not found to be suitable for catalytic membrane preparation. The membrane prepared with PVA crosslinked by GA showed the best performance having R values less than 20%. Thus, only this membrane was used for esterification–pervaporation experiments. It was found that pervaporation enhanced esterification moderately and the conversion was increased from 70% to ~85%.

Catalytically active membranes with effective catalysis in hydrodechlorination of 4-chlorophenol containing palladium nanoclusters of 3–5 nm were prepared from polyether-*b*-amide (PEBA) [9,10]. The elastomer poly(ether-*b*-amide) (PEBA) is

known as a polymer effectively concentrating slightly polar chemicals such as phenols, higher alcohols from water. PEBA membranes with various concentrations of different catalytically active metal nanoclusters were prepared. These membranes were used to simultaneously concentrate and react organics by catalytic pervaporation (see Section 6.2.2). However, during the process a considerable amount of educt passes the membranes without any reaction [9]. Because the tested compound exhibits no specific affinity to Pd, the reaction can take place only by statistical contact. Contrary to the educt chlorophenol, the  $H_2$  revealed high interaction with the Pd-nanocluster, e.g. firstly solved in the metal before leaving the membrane. To improve the statistical contact of the non-interacting educts with the catalyst during pervaporation, various membrane configurations were suggested, prepared and tested.

## 6.2. Applications

### 6.2.1. *N*-Butyl alcohol–acetic acid esterification

The membranes prepared both copolymerized catalytic PVA membrane and PVA/PAA blend catalytic membrane on porous ceramic plate (as above reported in Section 6.1.2) were characterised and used for *N*-butyl alcohol–acetic acid esterification reaction coupled with pervaporation to separate by-product water [63]. Different reaction parameters (temperature, catalyst concentration and initial reactant molar ratio) were studied experimentally. Among the all studied parameters the temperature had the strongest influence on the performances of the pervaporation–esterification reaction coupling. The second effective factor was the initial reactant molar ratio (only kinetics affected). Catalyst concentration was the last factor.

In Fig. 8, the diagram of pervaporation and pervaporation–esterification coupling is shown. It was found from binary pervaporation experiments that, selectivities of crosslinked PVA catalytic membranes were higher than those of PVA/PAA blend catalytic membranes, and the permeation flux increased as the temperature increased while separation selectivities decreased. Since the composite catalytic membrane with better separation selectivity was preferential (if its flux was not very low), the cross-linked PVA composite catalytic membrane was used in the pervaporation–esterification experiments. In

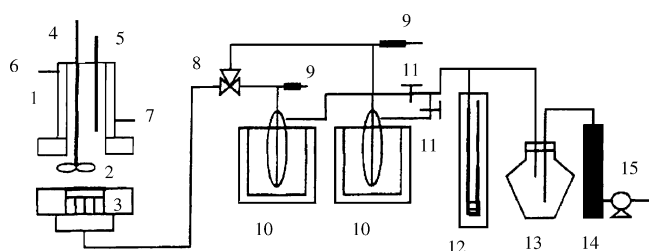


Fig. 8. Diagram of pervaporation and pervaporation–esterification coupling: (1) reaction cell, (2) membrane, (3) porous support steel plate, (4) stirrer, (5) thermometer, (6) input of thermalstated water, (7) output of thermalstated water, (8) three way cock, (9) vent to atmosphere, (10) cold trap, (11) two way cock, (12) barometer of U type, (13) buffer tank, (14) drying column, and (15) vacuum pump [63].

comparison, by pervaporation conversion is increased from 65% to 95%.

It was also shown that increase in temperature accelerated both esterification and pervaporation. The water content in reaction mixture was decreased abruptly when membrane permeation flux was increased due to increase in temperature. As a result, the esterification was stimulated and the rate was increased. However, when separation difficulties were taken into account, operating the system with an equimolar mixture, pervaporation may create the optimum performance conditions. Increasing the catalyst content may be alternative way to accelerate the ester production since much water was produced and the permeation flux of water was increased due to high amount of water in reaction mixture.

### 6.2.2. Hydrogenation of 4-chlorophenol

The reaction produced phenol and, in smaller yield, cyclohexanone and cyclohexanol. Membrane thickness, feed temperature, metal composition and concentration were varied to study the effects on the reaction. At different membrane thickness the flux density decreases and the enrichment factor increases e.g. from  $\beta = 82$  (53 mm) to  $\beta = 95$  (115 mm) at 57 °C. Fig. 9 depicts the possible hydrogenation products of 4-chlorophenol. Depending on the catalyst, besides the dechlorinated product phenol, also cyclohexanone and cyclohexanol may result (Fig. 9).

The production of phenol and cyclohexanone decreased with increasing temperature: phenol/cyclohexanone 12%/0.06% (28 °C), 2.4%/0.006% (42 °C) and 1.4%<0.005% (57 °C).

The increase of temperature corresponds with a counter-current behaviour of  $H_2$  supply (degreasing with temperature) and amount of 4-chlorophenol to react (increasing flux with temperature). Comparison of different catalysts in the membrane (Pd, Pd/Rh (9/1), Pd/Rh (1/1), Rh) demonstrated that pure Pd preferentially yields phenol. With increasing amount of Rh the yield of the secondary products cyclohexanone and cyclohexanol increases relative to phenol.

### 6.2.3. Epoxidation of propene to propene oxide

Heijnen et al. [66] proposed the use of relatively nonpolar pervaporation membranes for the epoxidation of propene to propene oxide based on micellar catalysis (Fig. 10). This is an example of inert pervaporation membrane: the homogeneous catalyst has been incorporated in micelles and the membrane is only separative.

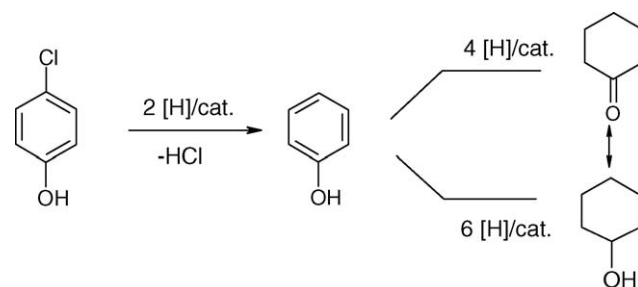


Fig. 9. Reaction products of the 4-chlorophenol hydrogenation [9].

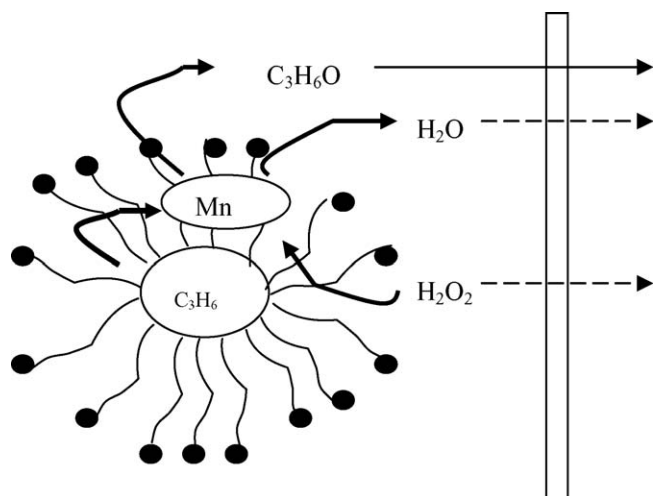


Fig. 10. Pervaporation coupled to micellar catalysis (modified from Heijnen et al. [66]).

Coupling the reaction with pervaporation process, two goals can be realised: the more hydrophobic propene oxide preferably dissolves in membrane and diffuses through it, while the water and the oxidant will be retained to a larger extent; the micelle-incorporated catalyst can be reused.

## 7. Conclusions

The main advantage of polymer-based catalytic membranes in the field of fine chemical synthesis in contrast to inorganic membranes concerns their preparation: the control of the thickness, the large scale preparation and the crack-free membrane synthesis are much less problematic. Furthermore, a dense polymer phase can actively take part in the reaction influencing sorption and diffusion of reagents and products. For a given reaction, the best polymer material to realise reaction and separation in one step, strongly depends from the reaction species solubility properties.

In this paper a survey of the preparation methods and application of recently developed polymeric membrane for catalytic (non enzymatic) membrane reactor is given. These issues were discussed in the context of three general classes of Membrane Reactors: Gas Phase Reactors, Liquid Phase Reactors, Pervaporation Reactors.

Research in the gas phase membrane reactors is still limited; the most important reaction until now is the selective hydrogenation. In this field, membranes with nanosized ultrafine clusters uniformly distributed throughout the polymeric matrix constitute one of the main goals. In fact, preparation and handling of ultrafine clusters catalysts is crucial for high performance of the catalytic membrane in terms of turn over and permselectivity. In gas phase reactions the membrane also acts as a separator between the different gaseous molecules involved in the process. Therefore, the membrane should be not only highly selective, but it should also be permeable enough to give a sufficient separation.

For liquid phase reactions, two different kinds of catalysts can be incorporated in the polymeric membranes: inorganic

(metal, zeolites, polyoxometallates) and metallorganic complexes. In most cases, PDMS has been the polymer material chosen, because it combines mechanical, chemical and thermal stability with high permeability and affinity for the reagents. The inorganic catalysts entrapped in polymeric membranes can increase the catalytic activity by improving the sorption of the reagents, excluding other compounds from interfering. Selective reagent sorption and retention of the catalyst in the membrane make the catalytic performance of these membranes superior to their non-membrane resident counterparts. For example, in the alcohols photooxidation reaction, polymeric membrane entrapping peroxometallates gave “proof” of complete stability under near UV irradiation and good recycling with no loss of activity [59]. The membranes with homogeneous metal complexes occluded constitute a new way of heterogenation, without any chemical modification of the catalyst. The activity of the immobilized complexes remained constant in next runs, proving the absence of deactivation or complex leaching. In the oxidation reactions with aqueous oxidants, the hydrophobic catalytic membrane, as an interphase between the two immiscible reagent phases, organic and aqueous phases, renders a solvent redundant and excludes the water molecules, from competitive sorption at the catalytic sites.

In pervaporation reactors, the membrane combines in situ the reaction with the products separation; moreover, it gives the possibility of feeding reagents from different sides of the membrane to the catalyst. These two combinations should be adjusted to a specific reaction. The esterification reaction combined with pervaporation received attention. Increasing the catalyst content may be an other way to accelerate the ester production, in alternative to a temperature increase. In fact, much water is produced and consequently permeation flux is increased giving a shift of the equilibrium reaction. For preparing “bifunctional”, catalytic and separative membranes, polymer blending was considered to be very convenient method. One component of the blend has the catalytic property whereas others have the separation properties. High separation factors are possible by selecting opportunely the two polymers for the blend.

## Acknowledgement

Authors thank Dr. Bart Van der Bruggen from the Katholieke Universiteit Leuven for his useful suggestions and discussion, in structuring this review.

## References

- [1] T.T. Tsotsis, A.M. Champagnie, R.G. Minet, P.K.T. Liu, in: Becker, Pereira (Eds.), Computer aided design of catalysts, Marcel Dekker Inc., New York, 1993 (Chapter 12).
- [2] G. Saracco, H.W.J.P. Neomagus, G.F. Versteeg, W.P.M. van Swaaij, Chem. Eng. Sci. 54 (1999) 1997.
- [3] J.N. Armor, Catal. Today 25 (1995) 199.
- [4] J.A. Dalmon, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Catalytic Membrane Reactors in Handbook of Heterogeneous Catalysis, Weinheim, Germany, VCH, 1997, p. 1387 (Chapter 9.3).



- [5] A. Julbe, D. Farrusseng, C. Guizard, *J. Membr. Sci.* 181 (2001) 3.
- [6] L. Paturzo, A. Basile, E. Drioli, *Rev. Chem. Eng.* 18 (6) (2002) 511.
- [7] L. Giorno, E. Drioli, *TIBTECH* 18 (2000) 339.
- [8] Marcan Sanchez, T.T. Tsotsis, *Catalytic Membrane and Reactors*, Wiley–VCH Verlag, 2002.
- [9] G. Bengston, H. Scheel, J. Theis, D. Fritsch, *Chem. Eng. J.* 85 (2002) 303.
- [10] G. Bengston, M. Oehiring, D. Fritsch, *Chem. Eng. Process.* 43 (2004) 1159.
- [11] I.F.-J. Vankelecom, *Chem. Rev.* 102 (2002) 3779.
- [12] H. Yamamoto, Y. Mi, S.A. Stern, *J. Polym. Sci., Part B: Polym. Phys.* 28 (1990) 2291.
- [13] B.D. Freeman, *Macromolecules* 32 (1999) 375.
- [14] M.S. McCaig, E. Seo, D.R. Paul, *Polymer* 40 (1999) 3367.
- [15] M.R. Pixton, *Macromolecules* 28 (1995) 8277.
- [16] J. Zhang, X. Hou, *J. Membr. Sci.* 97 (1994) 275.
- [17] I.W. Kim, K.J. Lee, J.Y. Jho, H.C. Park, J. Won, Y.S. Kang, M.D. Guiver, G.P. Robertson, Y. Dai, *Macromolecules* 34 (2001) 2908.
- [18] C.C. Hu, Y.C. Wang, C.L. Li, K.R. Lee, Y.C. Chen, J.Y. Lai, *Desalination* 144 (2002) 103.
- [19] R.E. Kesting, *Fritzsch, Polymeric Separation Membranes*, Wiley–Interscience, New York, 1993.
- [20] E. Drioli, G. Golemme, 1996. Private communication.
- [21] J. Shultz, K.V. Peinemann, *J. Membr. Sci.* 110 (1996) 37.
- [22] D. Fritsch, K.V. Peinemann, *Catal. Today* 25 (1995) 277.
- [23] J.F. Ciebien, R.E. Cohen, A. Duran, *Supramol. Sci.* 5 (1998) 31.
- [24] J.E. Castanheiro, I.M. Fonseca, A.M. Ramos, R. Oliveira, J. Vital, *Catal. Today* 104 (2005) 296.
- [25] J.E. Castanheiro, A.M. Ramos, I.M. Fonseca, J. Vital, *Catal. Today* 82 (2003) 187.
- [26] J. Vital, A.M. Ramos, I.F. Silva, H. Valente, J.E. Castanheiro, *Catal. Today* 56 (2000) 167.
- [27] I.F.-J. Vankelecom, N.M.F. Moens, K.A.L. Vercruyse, R.F. Parton, P.A. Jacobs, in: H.U. Blaser, A. Baiker, R. Prins (Eds.), *Heterogeneous Catalysis and Fine Chemicals, IV*, Elsevier, Amsterdam, 1997, p. 437.
- [28] I.F.J. Vankelecom, E. Scheppers, R. Heus, J.B. Uytterhoeven, *J. Phys. Chem.* 98 (1994) 12390.
- [29] M.J. Burk, *J. Am. Chem. Soc.* 113 (1991) 8518.
- [30] I.F.-J. Vankelecom, P.A. Jacobs, 2000. Recent developments in dense, organic, catalytic membranes, ICCMR, July 3–5, Zaragoza, Spain.
- [31] P.E.F. Neys, A. Severeys, I.F.J. Vankelecom, E. Ceulemans, W. Dehaen, P.A. Jacobs, *J. Mol. Catal.* 144 (1999) 373.
- [32] M.E. Rezac, B. Bayer, E.T. Sorensen, N. Karangu, in: *Proceedings of the Euromembrane 97 on Progress in Membrane Science and Technology*, June 23–27, University of Twente, The Netherlands, 1997, pp. 11–13.
- [33] M.T. Reetz, M. Zonta, J. Simpelkamp, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 301.
- [34] M.A. Harmer, W.E. Farneth, Q. Sun, *J. Am. Chem. Soc.* 118 (1996) 7708.
- [35] U. Schubert, *New J. Chem.* 18 (1994) 1049.
- [36] J.W. Cho, D.R. Paul, *Polymer* 42 (2001) 1083.
- [37] J. Ren, A.J. Silva, R. Krishnamoorti, *Macromolecules* 33 (2000) 3739.
- [38] D.B. Lincoln, R.A. Vaia, Z.A. Wang, B.S. Hsiao, *Polymer* 42 (2001) 1621.
- [39] S. Llias, R. Govind, *AIChE Symp. Ser.* 85 (1989) 18.
- [40] H.P. Hsieh, *AIChE Symp. Ser.* 85 (1989) 53.
- [41] M.P. Harold, P. Cini, B. Patenaude, *AIChE Symp. Ser.* 85 (1989) 26.
- [42] A. Stankiewicz, *Chem. Eng. Process.* 42 (2003) 137.
- [43] J.M. Sousa, P. Cruz, A. Mendes, *J. Membr. Sci.* 181 (2001) 241.
- [44] H. Gao, Y. Xu, S. Liao, R. Liu, J. Liu, D. Li, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 106 (1995) 213.
- [45] C. Liu, Y. Xu, S. Liao, D. Yu, *Appl. Catal. A: Gen.* 172 (1998) 23.
- [46] C. Liu, Y. Xu, S. Liao, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 137 (1997) 139.
- [47] A. Bottino, G. Capannelli, A. Comite, R. Di Felice, *Desalination* 144 (2002) 411.
- [48] J.S. Choi, I.K. Song, W.Y. Lee, *Catal. Today* 67 (2001) 237.
- [49] J.K. Lee, I.K. Song, W.Y. Lee, *Catal. Lett.* 29 (1994) 241.
- [50] D. Fritsch, K.-V. Peinemann, *J. Membr. Sci.* 99 (1995) 29.
- [51] V.M. Gryaznov, M.M. Ermilova, N.V. Orekhova, *ICCMR 2000*. July 3–5, Zaragoza, Spain, p. 31.
- [52] D. Fritsch, I. Randjelovic, F. Keil, *Catal. Today* 98 (2004) 295.
- [53] R.F. Parton, I.F.J. Vankelecom, D. Tas, B.M. Janssen, P.P. Knops-Gerrits, P.A. Jacobs, *J. Mol. Catal. A: Chem.* 113 (1996) 283.
- [54] G. Langhendries, G.V. Baron, I.F.J. Vankelecom, R.F. Parton, P.A. Jacobs, *Catal. Today* 56 (2000) 131.
- [55] M.C.A. Gotardo, A.A. Guedes, M.A. Schavon, N.M. José, I.V.P. Yoshida, M.D. Assis, *J. Mol. Catal. A: Chem.* 229 (2005) 137.
- [56] P.P. Knops-Gerrits, I.F.J. Vankelecom, P.A. Jacobs, *Catal. Today* 32 (1996) 63.
- [57] J.H. Ke, A.S. Kumar, J.W. Sue, S. Venkatesan, J.M. Zen, *J. Mol. Catal. A: Chem.* 233 (2005) 111.
- [58] M.G. Buonomenna, E. Drioli, R. Bertoncello, L. Milanese, P. Scrimin, G. Licini, *J. Catal.* 238 (2006) 221.
- [59] M. Bonchio, M. Carraro, G. Scorrano, E. Fontananova, E. Drioli, *Adv. Synth. Catal.* 345 (2003) 119.
- [60] H. Kita, S. Sasaki, K. Tanaka, K.I. Okamoto, M. Yamamoto, *Chem. Lett.* (1988) 2025.
- [61] Q.T. Nguyen, C.O. M'Bareck, M.O. David, M. Metayer, S. Alexandre, *Mater. Res. Innovat.* 7 (2003) 212.
- [62] F. Lipnizki, R.W. Field, P.K. Ten, *J. Membr. Sci.* 153 (1999) 183.
- [63] R. Feng, R.Y.M. Huang, *Chem. Eng. Sci.* 51 (1996) 4673.
- [64] Y. Zhu, H. Chen, *J. Membr. Sci.* 138 (1998) 123.
- [65] Q. Liu, J. Peish, H. Chen, *J. Membr. Sci.* 159 (1999) 233.
- [66] J.H.M. Heijnen, V.G. de Bruijn, L.J.P. van den Broeke, J.T.F. Keurentjes, *Chem. Eng. Proc.* 42 (2003) 223.