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**Special issue :** "Hybrid organic-inorganic materials for sustainable applications"

## **Class II hybrid organic-inorganic membranes creating new versatility in separations**

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### **Abstract**

Membrane technology is becoming more important as a low energy separation process that can replace or enhance the efficiency of currently often costly and energy-consuming separation processes. After an introduction on the potential of hybrid materials for membranes, we highlight and categorize the wide diversity of hybrid organic-inorganic membranes. In this review, we focus on the preparation and application of class II hybrid organic-inorganic membranes with mechanically stable inorganic supports. Class II points to the presence of covalent bonds between organic and inorganic moieties. The variety of synthesis approaches applied to prepare such separation layers can be divided into 2 types, i.e. direct coating of a pre-formed hybrid solution, and post-synthesis grafting of organic groups. In the last part, we focus on strategies delivering hybrid organic-inorganic membranes that show promise for enhanced molecular separations in gas separation, hydrophilic and organophilic pervaporation and organic solvent nanofiltration. In addition, we will discuss the use of organically modified inorganic RO (reverse osmosis), UF (ultrafiltration) and MF (microfiltration) membranes for ameliorated pressure driven water filtration, membrane contactors, and low-fouling oil/water separation.

**Keywords:** gas separation, fouling, hybrid organic-inorganic membranes, membrane contactors, pervaporation, organic solvent nanofiltration, synthesis methods

## **1. Introduction**

### **1.1 Membrane separations**

Billions of barrels of oil equivalent are consumed yearly in molecular separations. For numerous chemical production processes, especially for cryogenic and azeotropic distillation, molecular separation is highly energy intensive. Replacing inefficient processes by molecular separation with membranes can save up to 50% of energy of specific processes [1]. Emerging applications are found in the fields of pervaporation of liquid mixtures [2-5], gas separation [6, 7] and organic solvent nanofiltration [8, 9, 10]. Appealing examples are the dehydration of wet bio-based fuels and olefin/paraffin separation in the petrochemical industry.

Membrane performance is generally defined by the selectivity to a specific mixture and the permeability (rate of mass transport through the membrane) of the permeating molecule(s). Separation can be based on differences in molecular size with respect to the pore size of the membrane, on differences in adsorption onto and diffusion into the membrane material, or on charge effects between solute and membrane. It should however be realized that, before considering any practical application, a membrane should also have high structural stability. Poor membrane stability cannot compensate for outstanding separation properties in view of the replacement cost and loss of production time. It is essential that a new membrane separation process is at least as reliable as a currently applied process before it can be implemented on any scale. A membrane life span of several years should be aimed at. Other factors to keep in mind are production cost and versatility. In terms of membranes, this means that they should preferably be prepared following a limited number of not-too-complex preparation steps, and that they should allow structure optimization to various processes and conditions.

### **1.2 Why hybrid materials?**

Hybrid materials can be defined in many different ways. Essentially, two classes exist, of which we will here only consider materials with a covalent link between organic and inorganic moieties, i.e. 'class II' hybrid materials. Class I materials are merely a physical mixture of organic and inorganic components [11, 12].

In general, the benefit of hybrid materials relies in the combination of a closely interacting organic phase with an inorganic phase, inducing new properties that cannot be achieved with only one of these phases separately. Organic materials typically allow for much larger diversity of functional properties than inorganic materials due

to the wide variety of organic moieties. This permits fine-tuning of interactions with the surrounding environment. Most inorganic materials only interact with the environment via the surface OH-groups (even though often present with different bond strengths) [13, 14] and the M-O-M groups (in which M is a metal), limiting their versatility. On the other hand, organic materials are characterized by a low stability (chemically, thermally and mechanically) in various operating conditions. For instance, polymers are often only stable in a narrow range of solvents, as they tend to dissolve, swell or tear locally. Similarly, sealing of e.g. polymer membranes is often inadequate due to lack of stability in a wide diversity of solvents or in harsh conditions (e.g. high temperatures, acids) [15]. Inorganic materials are often very stable under these conditions. In contrast to polymers, they show no swelling and allow for high temperature treatments, e.g. to induce crystallization to further enhance the chemical and mechanical stability, or to attach layers or highly inert glass or ceramic sealings. However, ceramic materials may have stability issues under hydrothermal, acid or basic conditions. For example, amorphous silicates, especially pure silica, are known to have a low hydrothermal stability, giving rise to limited applicability in contact with water. Many metal oxides are unstable in either acids or bases. It is generally accepted that amorphous metal oxides materials are chemically less stable than crystalline ones, although transition metal oxides are often more stable than silica. The crystallization processes itself however can also have drawbacks as uncontrolled crystallization may give rise to structural collapse. While methods exist to control this process for large pores, crystallization can affect the integrity of thin-film microporous and mesoporous structures. This limits the availability of inorganic membranes with subnanometer pores and makes the production of nanofiltration membranes expensive. Although silica materials are less chemically stable, their structure is much easier to shape as uncontrolled crystallization does not occur (with the exception of zeolite membranes that are a separate class of materials).

Another important factor is that a rigid pore structure can be more easily introduced in inorganic materials than in organic materials, making them better suited for sieving based on molecular size.

These benefits and drawbacks allow both inorganic and organic materials to be utilized in various applications, but limit their applicability as the result of their respective restrictions in adjusting their performance to specific applications. For this reason, hybrid materials are being developed that combine the benefits of both types of materials or even introduce new unique properties.

In this review, the emerging role of organic-inorganic hybrid materials in membrane-based separation processes is discussed. As will be further explained below, the structure of these materials is essentially inorganic, with the organic moieties acting as modifiers.

### **1.3 The potential of hybrid materials for membrane separations**

As membranes are more and more evolving from end-of-pipe separations to in-process use [16, 17], robustness to a wide diversity of conditions is required. Even though solvent-stable polymeric membranes are being developed [8, 10], inorganic materials are generally more suited for this purpose, as they are intrinsically more stable. Nevertheless, the inorganic matrix needs to be combined with organic moieties to induce the required diversity in their properties other than pore size and intrinsic surface hydrophilicity (related to surface OH-groups) to be able to tune their performance in many applications. Of particular benefit is the combination of robust materials with specific properties such as pore size and stability originating from the inorganic building blocks with the versatility of the organic moieties that allow fine-tuning of affinity interactions with the environment. For example, to further optimize/tune the filtration behavior in solvent separation applications, membrane-solvent, membrane-solute and solvent-solute interactions are being recognized as essential parameters in addition to the generally applied size exclusion effects (Fig. 1) [9, 13, 18-23]. Also in gas separation the interaction between the individual molecules and between the molecules and membrane surface are known to direct the separation performance [24].

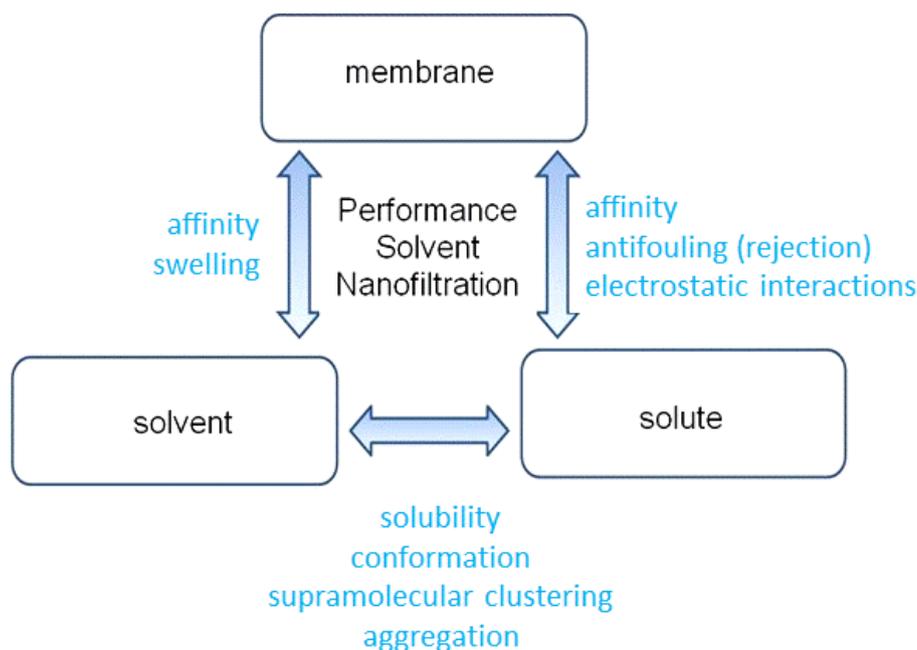


Figure 1: Membrane-solvent-solute interactions determining filtration behavior and performance. Swelling is only present in case of polymeric coatings or membranes. Adapted from [13, 18]

Indeed, as will be shown in section 3, membrane performance is often correlated with the interaction of the selective layer with the environment, i.e. with the solutes and solvents at a specific temperature and pressure. This specific interaction affects not only the flux/permeability and selectivity, but also membrane fouling. Clearly the triangular interaction scheme (Fig. 1) is very basic and the first reports on the respective contributions on membrane performance (specifically on organic solvent nanofiltration) have appeared only recently [18, 19, 22]. Also other properties remain important, including the size of the pores, concentration and size of the solute, physico-chemical properties of solvent and/or solute (including functional groups, polarity, induced dipolar interactions, charge etc.), operating conditions of the filtration process and the type of filtration process itself. Still, the scheme shows how the membrane properties change by tuning of the surface interactions and how insight in the role of the interactions advances applicability.

In this review, we aim to give an overview of the various methods that exist to prepare class II hybrid organic-inorganic membranes, with a focus on surface-grafted membranes and hybrid silica membranes. Furthermore, the unique behavior and opportunities of these hybrid membranes in sustainable separation processes are exemplified in various applications, spanning gas separation, pervaporation (organophilic and hydrophilic), organic solvent nanofiltration (OSN), membrane contactors, pressure-driven water filtration, and reducing fouling behavior in membrane filtration. We thus hope to demonstrate the potential of hybrid materials in influencing the triangular interactions shown in figure 1, as well as in opening new applications.

## 2. Synthesis methodologies of hybrid organic-inorganic membranes

The term ‘hybrid membranes’ encompass a very wide range of materials that needs a more detailed description to fully describe the type that is involved here [11]. Materials can be mainly polymeric with embedded inorganic nanoparticles, ceramic with an organic phase grafted onto the surface, or even consisting of a network structure with both organic and inorganic moieties built-in. The difference between these classes of materials is very large with respect to the materials synthesis, properties and behavior. Also the structure of the support system can be very different, ranging from intrinsically asymmetric in several polymeric systems, or asymmetrically built up of different layers in ceramic ones. It is therefore important to clearly stipulate the dominant phase of the membrane being inorganic-organic or organic-inorganic hybrid materials in which the last word stipulates the dominant phase.

Inorganic-organic hybrid materials (e.g. polymeric membranes with embedded inorganic nanoparticles, or polymer membranes containing polysiloxane or organosilane precursors) are widely applied and combine the benefits of both inorganic and organic phases. However, the dominant phase in these materials is organic and their preparation is very different from those of the organic-inorganic materials. Therefore, we will not describe these so-called mixed matrix membranes (physical mixture of organic and inorganic and thus class I hybrid) [25] further in this review. Other materials that can be classified as hybrid membranes are MOF (metal organic

frameworks) [26] and ZIF (zeolitic imidazole frameworks) [27]. However, as generally no covalent bond exists between the metal and the organic moieties, we will also not discuss these types of hybrid membranes. In this review, we will specifically focus on membranes with a mechanically stable inorganic pore structure that is further modified, either by grafting organic groups onto the pore surface or by applying a separate selective hybrid top layer (see below). The resulting membranes are class II hybrid organic-inorganic materials, i.e. with organic functional groups covalently bound to metal atoms in the selective layer.

These class II hybrid organic-inorganic membranes can thus be divided in two types depending on the synthesis method (Figure 2), in which (1) dip-coating or (2) post-synthetic grafting is applied. The dip-coating method (1) consists of dip coating a sol containing pre-condensed monomeric (pre-polymerized polymeric) species onto the surface of a ceramic support. The sol has a hybrid character, i.e. it contains both inorganic and organic moieties that are covalently bound. An extra selective top layer is thus formed in which the hybrid top layer and the (inorganic) support layer are clearly visible separately. This category also encompasses other possible application methods of a separate top layer such as spin coating. In the post-synthetic method (2) organic functional groups are grafted onto the pore surface of the inorganic porous support. Specific individual precursor molecules (e.g. organoalkoxysilanes, organohalosilanes, organophosphonic acids, Grignard reagents, complexing agents like sulfates or carboxylic acids etc.) form a covalently bound (partial) monolayer or in some cases thin multilayers on the pore surface of the membrane. The post-synthetic method and the dip-coating method induce distinctly different properties at both the nanometer scale and at the macroscale. Both are explained in more detail below.

A general comparison of benefits and drawbacks of the dip-coating and post-synthetic methods can be found in a previous publication, in which also more details are comprised on the principles of organosilane and organophosphonic acid grafting [13].

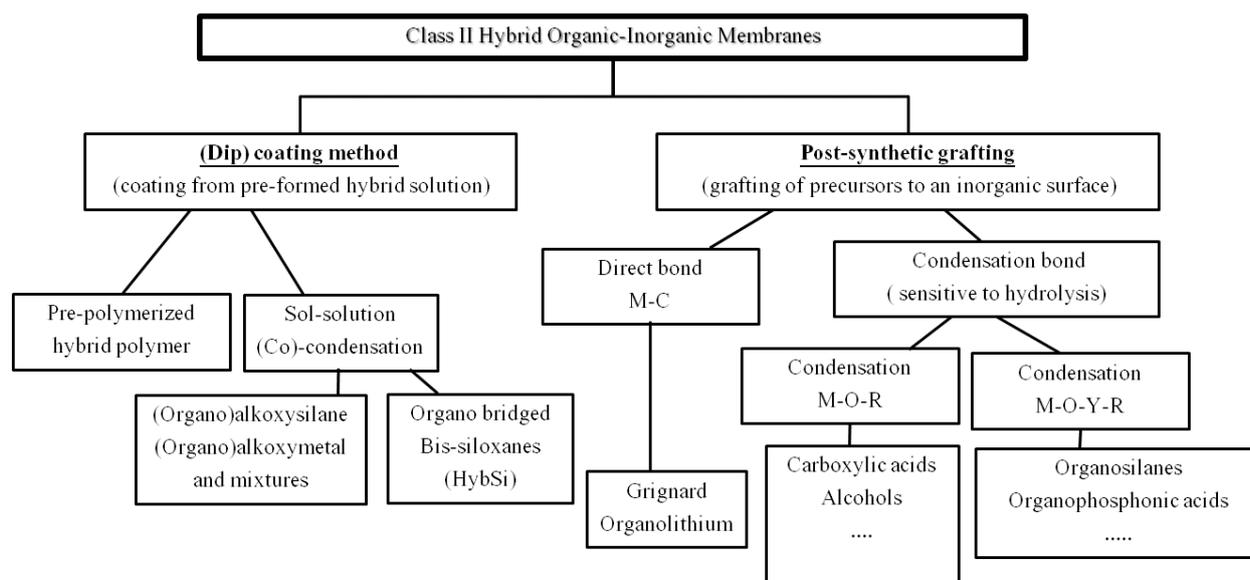


Figure 2: Schematic overview of the different synthesis approaches resulting in class II hybrid organic-inorganic membranes. M represents the metal of the metal oxide support, R the functional organic group and Y the bridging heteroatom.

## 2.1 Dip-coated organic-inorganic hybrid membranes

Dip- or spin-coated sol-gel hybrid organic-inorganic membranes are mostly applied as gas separation or pervaporation membranes as they are usually microporous (pore diameter < 2 nm). A low-viscosity preformed hybrid sol or polymer solution is applied onto a porous ceramic membrane support. As a separate layer is coated, typical problems can arise that generally also occur in other coated layers. Therefore, the quality of the sol solution is very important and needs to be adjusted to every specific material and desired pore structure. While aiming at a specific pore size and top layer thickness, other crucial macrostructural requirements are a good attachment of the top layer onto the support, prevention of infiltration of the coating sol into the underlying ceramic support and crack-free deposition. These are all related to the physico-chemistry of the dip-coating solution, i.e. the concentration and sol structure, and can be further optimized by control over the dip-coating process. For dip-coated membranes, high permeability and high mechanical, chemical and thermal stability are provided by the open inorganic support, while the denser thin hybrid top layer allows selective transport of molecules from a gas or liquid [28, 29].

The precursors for these dip-coated synthesized membranes can be very different in nature (Figure 2), and are basically either (1) polymeric with two reactive groups (e.g. silicon oils such as polydimethylsiloxane, PDMS), (2) organosilane monomers with three reactive groups and one pendant organic group (e.g. organoalkoxysilanes, organohalosilanes, organoalkoxymetals, organohalometals) or combinations with different organo-tri-/tetraalkoxysilanes, or (3) organically bridged bisilyl monomers with multiple reactive groups [30]. From the latter type HybSi® membranes are produced, which is a class of membranes with outstanding stability [31]. In (2) and (3), oligomeric species are produced by condensation or co-condensation of the precursors in a solvent. This sol is subsequently dip-coated onto the support.

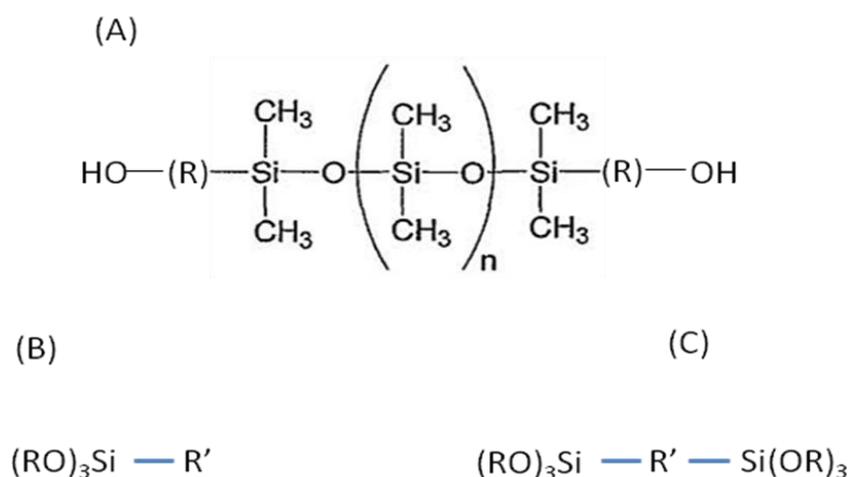


Figure 3: Schematic representation of the different precursors. (A) Hydroxy-terminated PDMS polymer (with  $n$  the number of monomer repetitions and (R) an optional organic hydrocarbon chain), (B) classical sol-gel precursors (example of monofunctional precursor with 3 reactive alkoxy groups), (C) bridged organic bisilyl precursor.

While the materials from all precursors are essentially based on Si-C and Si-O-Si bonds, the synthetic procedure can be quite different. The polymeric membranes are formed by dissolving already polymerized -often commercial- silicon oils. This gives little further synthetic control to change the properties except for the dip-coating procedure and the molecular weight of the silicon oil. In the sol-solution based dip-coated materials (3 or more reactive groups), the sol solution is synthesized starting from much smaller monomer building blocks (Fig. 3B/C). This allows more control over the synthesis procedure and the sol properties. Irrespective of the specific subclass, dip-coating of the one-pot pre-synthesized sols results in a homogeneous distribution of the organic groups throughout the top layer. This differentiates them from the post-synthetic membranes.

In general, apolar organic groups induce hydrophobicity and can thus also enhance the hydrolytic stability of the silicate structure. Hydrolysis of Si-O-Si bonds may lead to disintegration of the homogeneous porous thin-film structure, either by densification, coarsening or crack formation. Specifically the bisilyl precursors applied in the preparation of the HybSi membranes have been shown to greatly improve the hydrothermal stability in molecular sieving applications [31]. This enhanced stability has been evaluated and described by G. Smeulders *et al.* for PMO (periodic mesoporous silicate) powders, built-up by similar bisilyl precursors [32]. They concluded that the improved stability was caused by the homogeneity of the organic hydrophobic parts in the structure, making them more stable than organosilane-grafted silica materials. Additional factors are the mechanical properties, i.e. a higher fracture resistance and Young's modulus [33-35]. This results in a lower propagation rate of nanoscale cracks, while the flexibility of the bridge allows the Si-O-Si bonds to relax to their optimal conformation. This has been linked to a lower sensitivity to hydrolytic attack [36, 37]. A final factor that contributes to improved hydrolytic stability is the large number (6) of network-siloxane bonds of the minimum hydrothermally stable unit of hybrid silica as compared to other moieties, and its larger size, which result in a lower surface diffusion coefficient [38].

### 2.1.1 Polymer (PDMS) coated ceramic membranes

As a separate selective hybrid layer of polymeric material on the support is formed, these membranes show a similar behavior and interactions at the molecular level as purely organic polymers. One of the most extensively

studied polymer-coated ceramic membranes are PDMS/ceramic nanocomposite membranes made by dip-coating dissolved silicon oil on ceramic membrane supports. To prevent infiltration in the support layer, the dip-coating solution needs to have a sufficiently high PDMS concentration [28].

Even though pure PDMS membranes are widely studied, combinations with other polymeric units are being developed as well. Su *et al.* coated a Polyurethane-polydimethoxysiloxane top layer on a tubular ceramic support [39]. In a first step, polyurethane was pre-polymerized with hydroxyl-terminated polydimethoxysiloxane. Subsequently the ceramic tubular support was immersed in an ethyl acetate solution containing 1 wt% of polyurethane-polydimethoxysiloxane. The dip-coating PU-polydimethoxysiloxane top layer introduced superhydrophobicity and superoleophilic behavior.

### 2.1.2 (Co)-condensed membranes based on sol-gel chemistry

While polymer-coated membranes are simply produced by coating of a polymer solution onto the support, co-condensation of precursors with 3 or more reactive groups allows much wider control over the materials properties as more variation is possible during preparation of the sol-solution.

(Co)-condensed membranes can be formed in different ways. The general principle is the condensation of one type of precursor or co-condensation of 2 or more different precursors (e.g. organoalkoxysilane and TEOS) to form a sol, which is then dip-coated onto the ceramic support. After drying, the coated sol gives rise to a hybrid top-layer. The intrinsic properties of the sol (controlled by the synthesis conditions of the sol-solution) in combination with the dip-coating conditions and subsequent drying and thermal consolidation procedures determine the specific character and performance of the selective hybrid top layer. While most applied precursors for the sol-gel hybrid membranes are silane-based, this method can also be applied with precursors based on other metals, such as alkoxymetals, organoalkoxymetals and tetrahalometals.

The first silica-based membranes were prepared from tetraethylorthosilicate (TEOS) [40-43] by sol-gel methods. Nanoporous structures are formed as a result of the mild synthesis conditions of sol-gel [44], while defect-free layers  $< 1 \mu\text{m}$  can be coated onto a porous support system. To obtain the micropores (pore diameter  $d_p < 2 \text{ nm}$ ) needed for molecular separation, the hydrolysis and condensation reactions must be acid-catalyzed, usually in alcohol-based (e.g. ethanol, isopropanol) mixtures with water and nitric or hydrochloric acid. This implies that the pH is below the isoelectric point (IEP), which is at  $\text{pH} \sim 2.2$  for  $\text{SiO}_2$  [45]. Methylated silica membranes with somewhat higher stability in water were produced by co-condensation of TEOS with methyltriethoxysilane [46, 47]. However, the use of silsesquioxane precursors with bridging organic moieties has led to substantial improvement of the hydrothermal stability as compared to that of inorganic silica (cf. Section 3.3). Organically bridged membranes were first studied at the universities of Twente and Amsterdam by Castricum *et al.*, and long-term hydrothermal pervaporation tests were carried out in collaboration with the Energy research Centre of the Netherlands (ECN) [31]. Other groups have also started investigating this special class of materials, and much work is currently also being carried out in Nanjing [48], Beijing [49] and especially by Tsuru *et al.* in Hiroshima [50, 51]. While the first organically-linked silica membranes were prepared from 1,2-bis(triethoxysilyl)ethane (BTESE,  $(\text{C}_2\text{H}_5\text{O})_3\text{-Si-C}_2\text{H}_4\text{-Si-(OC}_2\text{H}_5)_3$ ) [38], the separation properties may be adapted by using other bridging groups than  $\text{C}_2\text{H}_4$  [52-54]. A great variety of organic bridges in precursors is nowadays commercially available, including alkane, alkene, alkyne, aromatic and functionalized moieties [30]. The surface properties can be further modified by applying mixtures with other precursors. The organic content can be tuned by adding pendant groups via alkyl- or amino-trialkoxysilanes [55-57]. Adding TEOS increases the inorganic content [58], while other metal oxides have also been incorporated in hybrid silica. Following reports that Nb doping results in a decreased  $\text{CO}_2$  permeance in  $\text{SiO}_2$ -based membranes [59], several studies have been carried out for mixtures of Nb alkoxides and BTESE [48, 60, 61].

Variation of the preparative conditions leads to a great variety of membrane properties. The internal pore structure is essentially determined by the concentrations of the hybrid silica precursor, water and acid or base (including concentration and type), the reaction temperature and time [44, 62, 63]. Other preparation parameters that require control are the choice of solvent, the drying rate and the structure and pretreatment of the porous multilayer system.

Oligomeric colloidal structures are formed during sol-gel synthesis as the result of condensation reactions. While these would ultimately condense to a continuous network gel with high viscosity, thin-film coating of defect-free layers requires a sol with low viscosity. At the same time, a certain minimum degree of condensation is required to prevent extensive infiltration of the oligomers into the substrate upon coating [55]. Dynamic light scattering [64] is a straightforward method to assess the oligomer mean hydrodynamic diameter, which should be larger than the pore size of the support. Careful tuning of the condensation time and/or of the reactant concentration is required to obtain optimum coating conditions, which depends largely on the structure of the precursor molecule

[53]. For example, while NMR studies indicated condensation rates of the same order for BTESE and TEOS [65], BTESE exhibited much faster colloidal growth than TEOS due to its larger size and larger network-forming ability.

Sol synthesis has been reported under several conditions, including at 60°C with ethanol as a solvent [38], and at room temperature with only water [66]. For practical reasons, reaction times (several hours) are usually orders of magnitude longer than coating (minutes). This guarantees easy handling of the coating sol, as ongoing condensation is relatively slow. Considering that dust particles may adhere to the drying surface and create defects, coating is preferably performed in a cleanroom [67].

The support system for hybrid silica membranes is usually ceramic, and consists of a macroporous support of e.g.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [68] and a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [69] or Si/Zr oxide [70] layer with typically 2-5 nm pore diameter. While flat disks are often applied for research purposes, tubular membranes are more suitable for scaling up. In recent work, deposition of hybrid silica onto organic polymers has been studied. Polymeric supports are generally cheaper than ceramic ones, and may provide greater flexibility in application. For example, spiral-wound membranes, suitable for e.g. nanofiltration, require deposition onto a flat polymeric support. Solvent-free synthesis of a BTESE-derived organosilica membrane by means of expanding thermal plasma chemical vapor deposition (ETP-CVD) on a polyamide-imide substrate was recently reported [71]. However, partial decomposition of the organic bridges occurred during the deposition process. BTESE sols were successfully spin-coated on polysulfone films [72] and selective membranes were prepared on porous ultrafiltration (UF) membranes from the same material [73]. Some limitations that have to be taken account when using polymers are the low glass transition temperature (185 °C for polysulfone), which restricts the maximum consolidation and operating temperatures, and the limited stability in some solvents.

Further condensation of silanol groups after coating is required to obtain a polymeric network structure that is sufficiently dense [44] to exhibit adequate separation selectivity. This involves thermal consolidation of an as-dried membrane at 200°C or higher, which is often done in an inert atmosphere such as nitrogen [38,48]. Lower temperatures result in membranes with lower selectivities and permeances in both pervaporation and gas separation [74]. Post-treatment with HCl can be applied as an alternative or additional consolidation method [66, 75]. FTIR analysis confirmed condensation by a decrease in the number of Si-OH groups and an increase in the number of Si-O-Si groups after HCl exposure, which was accompanied by a decrease of the pore size. Considering that the organic bridge appears to be essential for the high hydrothermal stability of hybrid silica [32], calcination at high temperatures and/or under oxidative conditions should be avoided, as these may lead to pyrolysis and loss of the organic bridging groups. A significant reduction of Si-C and C-H groups was observed with FTIR after thermal treatments at 300°C under oxygen [76] or 450°C under nitrogen [60], along with a reduced stability of the membranes to steam [77].

Different names are being used in the literature to describe the organically-linked or -bridged membranes, such as hybrid (organo)silica membrane, membrane with controlled silica network size [50], organosilica membrane, ethylene-bridged silsesquioxane molecular sieving membrane [78], “PMO-type” [13] and HybSi [79]. The latter term is also used in commercialization. The Dutch company Pervatech currently produces these membranes under this name. The common property of these membranes is that they are produced from a precursor with an organic bridging group between two silicon atoms that is related to high hydrothermal stability.

## 2.2 Post-synthetic organic-inorganic hybrid membranes

Post-synthetic grafting is also known as surface modification. A covalent bond is formed between the precursor molecules and the pore surface of the membrane. Ideally, this results in the formation of a (sub)monolayer or of only a few layers in case of polymerization. The small dimensions make it more difficult to image the organic layer separately in comparison to the coated hybrid layers. In surface-modified membranes, all organic groups are only situated on the pore surface of the selective layer, making them fully accessible. Grafting can be done on commercial ceramic membranes. The membranes thus are already size selective and free of cracks, while sealing can be already in place. The grafting will thus only change the physico-chemistry of the surface and sometimes reduce the pore size. This is a clear advantage compared to the dip-coating method.

The method also has limitations, as the pores of the inorganic supports are relatively large compared to those obtained by the coating method. Nearly all commercially available inorganic membranes (except for zeolites) have pore sizes of 0.9 nm or larger [13, 80], and diffusion limitations restrict grafting of membranes with smaller pores. This makes the operation window of post-grafted membranes distinctly different. Therefore, they are mainly applied in nano-, ultra- and microfiltration unless a severe pore size reduction is obtained by grafting large organic groups. Moreover, as the functional groups are only present at the top layer, the stability towards

chemical attack (e.g. hydrolytic stability) is very important. The loss of already a small fraction of the surface-grafted groups can create hydrophilic sites that enhance water adsorption. Adsorbed water can then cause hydrolysis of more M-O-(Y)-R bonds, inducing further leaching of grafted groups. This will thus result in an increasingly rapid decline of the performance due to degradation of the organic layer [32, 81]. For hydrolytically sensitive groups (e.g. organosilanes [82-84]), degradation of the grafted layer can be diminished by grafting long, very hydrophobic functional groups and by assuring full surface coverage. High hydrophobicity however limits applicability in more polar solvents. When hydrolytically stable bonds are applied (e.g. organophosphonic acid or Grignard modification), sub-monolayer coverage and small hydrocarbon or even hydrophilic groups can be deposited, allowing applicability in a much broader range of solvents.

At small pore size, functional groups that have similar sizes cannot always be deposited at high surface coverage [18, 62, 85, 86]. For example, Rezaei Hosseinabadi *et al.* showed a lower surface coverage of a C<sub>12</sub> aliphatic hydrocarbon deposited in a 1 nm pore compared to the smaller C<sub>8</sub> hydrocarbons and appointed this to diffusion limitations [18].

The post-synthetic method can be further divided in subclasses (Figure 2). The organic functional groups can either bind directly to the surface (M-R) or via an oxygen bond by a condensation reaction. The latter may be further subdivided in a covalent bond of the organic group to either (1) the oxygen atom (M-O-R) or (2) to a heteroatom (e.g. P, S, Si), which is in turn bound to the surface metal atom via oxygen (M-O-Y-R), in which M is the metal atom of the ceramic top layer and Y is the bridging heteroatom. The formation of a direct M-R bond via organometallic chemistry (3) is the most recently developed method. The latter membranes are published under the name 'Grignard functionalized membranes' or 'FunMem ® membranes'. Each class, of which synthesis details will be further explained below, gives rise to hybrid top layers with specific properties, as will be shown in section 3.

### **2.2.1 Grafted organic-inorganic membranes with a direct oxygen bond**

M-O-R bonds are typically made via etherification reactions between alcohols or carboxylic acids and the hydroxyl groups of the inorganic membrane top layer. The method is easy, straightforward and warrants high surface coverage of the organic functional groups [87]. Nevertheless, it is not widely applied. The main reason is the fast hydrolysis of the M-O-R bond in the presence of water or substitution reactions of other alcohols or carboxylic acids with the surface-grafted groups. While stability and applicability depend strongly on the functional group (hydrophobicity, branching degree, surface coverage) and the operating conditions, they are usually limited compared to the other grafting methods.

### **2.2.2 Condensation via a heteroatom**

By far the most applied method for grafting of ceramic membranes is condensation via a heteroatom to produce a M-O-Y-R bond. Different types of precursors are applied, including organoalkoxysilanes, organohalosilanes and organophosphonic acids, which will be further detailed below.

#### *Organosilane-modified membranes*

The best-known method is the use of organosilanes. Typically, a chemically stable Si-C bond is attached to the surface via a reaction with an organosilane with one, two or three reactive groups, resulting in the formation of M-O-Si-C bonds. Organosilanes constitute the most versatile type of coupling agents with a broad range of organic functionalities commercially available. The choice in type of functional groups in combination with the type and number of reactive groups is enormous, exceeding that of all other coupling agents (e.g. phosphonic acids) with an order of magnitude. A virtually unlimited variety of hybrid membranes can be synthesized by applying this type of precursor.

Adaptation of the applied synthesis conditions may further tune the properties of organosilane-grafted membranes. While the organosilanes have similar structures (Fig. 3B) as those used in dip-coating via co-condensation (section 2.1), no stable sol needs to be obtained that may limit the length of the hydrocarbon chains. This broadens the choice of organosilanes provided that the pores are sufficiently large, in view of possible diffusion limitations. The choice of the type (often short alkoxy groups or halogens) and number (between 1 and 3) of the reactive groups has a direct effect on the synthetic control and the resulting properties of the hybrid layer. For example, if only one reactive group is present, polymerization reactions with the surface grafted groups are excluded, while anchoring of the functional group to the membrane surface is only via a monodentate bond, i.e. one bond to the surface. One bond may be more susceptible to hydrolysis and leaching, and a larger number of reactive groups can give rise to more robust e.g. tridentate bonds (three bonds with the surface), but at a much higher risk of polymerization reactions and multilayer formation. They therefore require much better synthetic control (e.g. water content).



dip-coating synthesis methods. The grafted hybrid layer however differs in the orientation of the PDMS dip-coated layer as the result of multiple bonds between each individual molecule and the surface [96]. This gives rise to materials with properties that resemble both the dip-coated hybrid layer and the post-synthesis grafted layer, forming an intermediate class. Except the chemical nature, also the pore size of the membranes can thus be altered.

Via a similar “click” approach, other polymers or functional groups can be anchored to a pre-grafted layer, giving rise to a wide diversity of hybrid membranes. The organosilanes are grafted as reactive anchoring groups on which specific monomers can polymerize under the right conditions. The grafted group serves as a cross-linker between a polymer layer and the inorganic support [12, 91, 97]. Cot *et al.* describe a method to crosslink a polyimide layer to an inorganic support. The specific benefit of the silicon coupling agent is the formation of a three-dimensional network with a well-defined gap size between the imide segments [12]. Similarly, Zhou *et al.* created poly(N-isopropylacrylamide) chains on the surface of zirconia membranes with a method they denoted as chemical graft polymerization [91]. In a first step  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS) was grafted on the surface via a liquid-phase reaction by filtration at 80°C in toluene, followed by drying. Subsequently, NIPAAm (poly(N-isopropylacrylamide)) was polymerized onto the surface-grafted MPS groups in an aqueous solution initiated by  $K_2S_2O_8$  (0.15 wt%). Another example of a multi-step approach is 3-aminopropyltrimethoxysilane (APDMES) grafting followed by the growth of dendrimers on the amine functional groups via multiple follow-up reactive steps [97]. These membranes were reverse-selective to the removal of small hydrocarbon species (propane) from light gas (nitrogen).

#### *Organophosphonic acid-modified membranes*

As organophosphonic acids bond strongly onto transition metal oxide surfaces, the modification is fast and cheap. Modification can be done in organic solvent or water, depending on the solubility of the chosen precursor. The most applied phosphonic acids have 3 reactive groups (P-OH, P-OR and/or P=O depending on the applied phosphonic or phosphinic acid). Similar to organosilanes with 3 reactive groups, multiple bonds can be formed with the surface but polymerization reactions are generally not occurring.

Mono-, di- and tridentate bonds on metal oxides have been reported, with additional bonding variants depending on which type of reactive group (P-OH or P=O) interacts with the surface [83, 98-100]. The control over the bonding type, grafting density, etc. depends on the type of phosphonic acid, the support and the synthesis conditions applied [83, 98, 101, 102]. It is important to note that in most cases a dangling P-OH or P=O bond is left, which is not attached to the surface. The presence of this dangling bond can substantially influence the membrane separation properties [103].

Despite the benefits of using organophosphonic acids, the method is not widely applied in membrane modification. Randon *et al.* have successfully modified  $\gamma$ -alumina, titania and zirconia membranes with alkyl phosphonic acids (methyl-, ethyl-, n-butyl- and phenyl phosphonic acid, and n-dodecylphosphate) resulting in an increase of the hydrophobicity [104]. They observed clear benefits (improved permeability and selectivity) of the alkylphosphonic layer in propane/nitrogen gas separation and in ultrafiltration of aqueous Bovine serum albumin (BSA) protein separation [101]. Ghulam Mustafa *et al.* have modified ceramic nanofiltration membranes with methyl-, hexadecyl- and phenyl phosphonic acids with the purpose of studying their performance as an anti-fouling layer [103]. Membranes modified with methylphosphonic acid were still sufficiently hydrophilic to allow economic water fluxes while the two other membranes became too hydrophobic for water filtration.

Caro *et al.* compared modification of  $\gamma$ -alumina ultrafiltration membranes modified with organosilylation with alkyl/aryl phosphonic acid modification. They concluded that coating of the  $\gamma$ -alumina with a Si-OH rich film to provide more anchoring sites is beneficial for efficient silylation. Phosphonylation on the other hand could be done in one step on the same support, giving rise to Al-phosphate [105].

The stability of phosphonic acid grafted metal oxides towards hydrolytic attack is higher than for organosilanes on titania and zirconia surfaces [83, 84, 106]. However, on silica supports, the opposite has been observed, which could be explained by the weak Si-O-P bond [83]. Similarly, on alumina surfaces, phosphonic acid grafting results in a higher density of the functional groups but with a lower hydrolytic stability [84]. Degradation of the hybrid layer is strongly influenced by the accessibility of water to the M-O-Y-R bond [32, 81]. The stability is however determined by various factors, including the hydrophobicity of the organic groups, branching, density of the grafted layer, self-assembling properties, number of bonds to the surface, horizontal or vertical polymerization (organosilanes), type of precursor and type of support material [32, 81]. As any other membrane, the stability is also strongly dependent on the application conditions itself. A recent study on the long-term stability of hydrophobic perfluoroalkylsilane (FAS)-modified membranes correlated the loss/leaching of FAS after 1 or 2 years with the type of interacting chemicals (air, water, hexane, chloroform), the type of support (titania and alumina) and pH [81].

More details on organosilane and organophosphonic acid modification and stability can be found in a previously reported open-access book chapter [13] as well as in several other reviews and books [14,83,84].

### **2.2.3 Organometallic-modified hybrid membranes**

The use of organometallic chemistry for the preparation of surface-modified hybrid membranes has only recently been developed. This method applies organometals such as Grignard reagents or organolithium to directly form a M-C bond without an intermediate oxygen nor a heteroatom [107, 108]. As organometallic reagents are highly reactive, the modification has to be done in dry ethers as solvents, on pretreated supports and under an inert atmosphere [18, 107, 108]. The obtained side product MgBr salt needs to be washed off via an appropriate washing method. The membranes are subsequently dried at slightly elevated temperature under vacuum to remove the solvents or loosely bound volatile molecules from the surface.

As it is a fairly recent method, much research is still needed to fully understand the synthesis mechanism and the properties of these materials. Nevertheless, basic characteristics of the grafted layer (e.g. thermal stability, typical bonds via infrared and  $^{13}\text{C}$ -CP/MAS-NMR, contact angle, cleanability, sorption characteristics, flux and retention measurements) have been reported [18, 103, 107, 108]. On titania powders and membranes the Grignard modification typically resulted in submonolayer coverages. In contrast, organosilane graftings rather give typically full monolayer coverage, require to warrant stability towards water [18, 103, 107, 108]. The submonolayer coverage has been shown by IR (powder) and micro-ATR/FTIR (membrane top layers) and by contact angles and filtration tests. As only partial surface coverage is obtained, membranes possess amphiphilic properties induced by both remaining OH-groups on the surface and the hydrophobic aliphatic or aromatic hydrocarbons grafted onto the surface. This amphiphilic nature results in a unique performance of these membranes in various applications that can span the whole range of polar up to apolar solvents.

Currently, only little information on stability is yet available, as this grafting method has been developed only recently. However, a recent study on the antifouling properties showed that both the methyl Grignard and methyl phosphonic acid-modified membranes fully retain their original performance after chemical cleaning to remove the irreversible fouling of humic acid. The cleaning process was repeatedly done at 50°C and a pH of 10 during 30 min [103]. More details are given in section 3.7.

As a wide variety of Grignard reagents is commercially available, this method is very flexible. It allows the synthesis of a broad range of functional membranes, giving rise to the name FunMem.

## **3. Applications of hybrid organic-inorganic membranes**

Since the 1990s, many groups have been working on the development of high-quality class II hybrid organic-inorganic membranes for a variety of applications. All synthesis routes described in the previous sections have been utilized with a multitude of organic functional groups on different inorganic membranes. The hybrid organic-inorganic membranes obtained showed a clear enhancement of the performance in the applications of interest, as described below. In each case, they combine the high thermal, chemical and mechanical stability of the inorganic membranes with the surface or structural functionality of the incorporated organic groups. They owe their ameliorated properties to the combination of the advantages of both of the organic and inorganic assets. Compared to the purely inorganic, non-hybrid versions of the membranes, they can profit from a changed surface affinity, an altered surface charge, and/or an adjusted microstructure, such as a decreased pore size.

As will become clear in the sections below, in several cases the organic groups are used to create hydrophobicity on/in the intrinsically hydrophilic inorganic membrane support. This logically also leads to reduced membrane charge (electronic contrast), due to the lower density of surface OH-groups, although this effect has hardly been utilized. In most cases of grafting with long organic groups, the pore size of the membranes is also clearly reduced.

The flexible platform technologies FunMem<sup>®</sup> and HybSi<sup>®</sup>, extensively described above, also lead to membranes that can be tailored to the specificity of the application envisioned, thus creating versatility in separations.

The sections below give an overview of the literature on membrane applications in which the use of hybrid organic-inorganic membranes has proven advantageous. The FunMem<sup>®</sup> and HybSi<sup>®</sup> technologies will be described in somewhat more detail, as the authors were involved in the technology development and application screening of the resulting flexibly tunable membranes.

### **3.1 Gas separation**

The first incentive for creating hybrid organic-inorganic membranes was an increase in the gas separation performance of existing mesoporous metal oxide or glass membranes [101, 104, 105, 109, 110]. Grafting introduced gas transport mechanisms other than the low-selective Knudsen diffusion of the mesoporous supports. Both silanation and phosphonic acid grafting using primarily apolar long alkyl or perfluoroalkyl groups were applied for this purpose. Depending on the groups grafted, surface diffusion or solubility of a particular gas could be enhanced. The research in the 1990s resulted in an only modest selectivity increase [101, 104, 105, 109, 110]. More recently [94, 111] much better results were obtained. Javaid *et al.* [94] produced good propane/N<sub>2</sub> selective membranes by grafting of long chain alkyl trichlorosilanes on 5 nm alumina membranes. They obtained a propane/N<sub>2</sub> permselectivity of around 25 and permeance of about  $5 \cdot 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ . The group of Montpellier [111] grafted TiO<sub>2</sub> mesoporous membranes with long perfluoroalkyl chains, resulting in a strong increase of the CO<sub>2</sub>/N<sub>2</sub> permeabilities (up to  $5 \cdot 10^{-12} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ ) and permselectivities (up to 12). Similar treatment of Al<sub>2</sub>O<sub>3</sub> membranes was less successful. In both cases [94, 111], the enhanced properties were attributed to an enhanced solubility of the preferred gases in the chemically modified membranes. As a result, the hybrid organic-inorganic membranes have become competitive to the best polymeric membranes for these applications [112], and especially to the best solubility-selective polymeric membrane PDMS (for CO<sub>2</sub>/N<sub>2</sub> permselectivity of 8 combined with a permeability of  $10^{-12} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ ) [113]. Consequently, the grafted membranes can be considered as inorganic alternatives for PDMS, combining the high free volume (the remaining pore volume) of the inorganic support with the desired hydrophobic/fluorinated membrane surface properties of the organic groups.

The narrow pore structure of inorganic silica allows for high gas separation selectivity based on the size of the molecules relative to the pore size of the membrane material. For H<sub>2</sub>/CH<sub>4</sub>, values above 4000 were reported [67, 114], but substantially (two orders of magnitude) lower permselectivities were found after introducing terminating methyl groups [67]. The size-based gas selectivity of HybSi is of similar order as for methylated silica [46, 50, 115]. The lower gas permselectivity was ascribed to a more open pore structure than for inorganic silica as the result of the larger size of the organic ethylene bridge, which was also demonstrated in computer simulations [116]. The organic bridge however also allows for tuning of the structure and of the interaction with the permeating gases. For a series of membranes with different size, flexibility, and shape of the organic bridging group, the highest H<sub>2</sub>/N<sub>2</sub> single gas permeance ratios were observed for materials with the shortest, CH<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> alkylene, bridges (~15 at 250°C) [53]. Short bridges therefore seem to be most suitable for size-based molecular sieving. A specific interaction of CO<sub>2</sub> with (likely the silanol groups of) hybrid silica, appears as a negative apparent activation energy of CO<sub>2</sub> permeance. This resulted in increased CO<sub>2</sub>/H<sub>2</sub> permeance ratios for octane- and benzene-bridged organosilica (~1.6 at 50°C). Considering that CO<sub>2</sub> has a larger kinetic diameter than H<sub>2</sub>, transport through these materials is affinity-dominated. For the octane-bridged material, strongly temperature-dependent gas transport was observed. The flexibility of this longer organic bridge results in a material with a polymeric character, while the network backbone structure of an inorganic (silica) material is retained. Unlike most organic polymers, neither of the hybrid silica membranes showed plasticization under the applied conditions.

Shorter CH<sub>2</sub> bridges generally show somewhat enhanced size-selectivity than C<sub>2</sub>H<sub>4</sub> ones [117], which also resulted in higher propene/propane separation factors [118]. C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of up to 30 were attributed to both size (propene has a smaller kinetic diameter than propane), and to the specific interaction between the  $\pi$ -bond (C=C double bond) of C<sub>3</sub>H<sub>6</sub> and silanol groups in hybrid silica. For hybrid silica with ethylene C=C bridges, a similar  $\pi$ -bond interaction was suggested to increase the adsorption of and selectivity towards CO<sub>2</sub> [54]. Independent variation of the pore structure by adapting the sol-gel synthesis procedure allows for further tuning of the gas separation selectivity. It was found that the membrane pore structure can be adapted by adjustment of the acid-to-Si ratio immediately before the onset of physical drying, while the rheological properties required for thin-film coating are retained [62]. After thermal consolidation, exposure to HCl rather resulted in an increase in the number of Si-O-Si groups and a smaller pore size [66].

The incorporation of pendant methyl groups in the structure resulted in lower overall gas permeances. This was observed both in membranes prepared from MTES/BTESE, and from a 1,1,3,3-tetraethoxy-1,3-dimethyldisiloxane (TEDMDS) precursor [119]. Addition of pendant amino groups to BTESE-based membranes similarly resulted in reduction of the H<sub>2</sub> permeability with increasing amino content [57]. With an increasing length of incorporated pendant groups, the CO<sub>2</sub>/H<sub>2</sub> selectivity increased along with a reduction of the size-based H<sub>2</sub>/N<sub>2</sub> permselectivity [56]. This indicated a lesser molecular sieving character, and as a consequence a stronger effect of the CO<sub>2</sub>-membrane interaction.

### 3.2 Organophilic pervaporation

As organic modification of inorganic membranes typically changes the polarity of the membranes from intrinsically hydrophilic to more hydrophobic, different groups have studied the possibility to change the pervaporation (or vapor permeation) behavior of microporous metal oxide membranes [120-123]. The objective was to obtain membranes that preferentially permeate the more apolar component of a solvent mixture, altering the typical dehydration behavior of the native microporous metal oxide membranes. The first attempts around the year 2000 applied silanation of relatively small organic groups on microporous alumina membranes (pore size of ~1 nm) [120, 121]. However, these did not deliver the effects aimed for, as pore clogging caused by the grafted groups did severely decrease the permeability, while the selectivity showed no or only a slight change [120, 121]. To solve the problems encountered, later studies started to graft on open membranes and used more hydrophobic perfluoroalkylsilanes (FAS) [122, 123]. Song *et al.* worked on open porous alumina membranes (pore size ~0.1  $\mu\text{m}$ ) and used long-chain FAS [122]. This resulted in strongly hydrophobic membranes (water contact angles ~160°) tested for aroma recovery from diluted aqueous solutions (model aroma compounds: ethyl-, propyl- and butyl acetate in concentrations of ~0.5 wt%). The vapor permeation performance was characterized by high permeabilities (typically 0.5  $\text{kg}/\text{m}^2\text{h}$ ) and high selectivities (typically 100 to 200), much better than the performance of the alternative polymeric PDMS membrane. The absence of membrane swelling of the hybrid organic-inorganic membrane guarantees a constant selectivity at various temperatures, unlike the PDMS membrane. Kujawski *et al.* grafted FAS groups on ceramic tight or open ultrafiltration membranes (pore size ~5 nm or ~30 nm) [123]. Also this development was successful, especially on titania membranes, and resulted again in membranes with clear organophilic pervaporation behavior. Selectivity factors of up to 6 for water/ethanol mixtures, and up to 95 for water/MTBE, combined with high fluxes of 2 to 5  $\text{kg h}^{-1}\text{m}^{-2}$  (for a concentration of 1 wt% of the organic in the feed) were realized. The grafted FAS groups showed a conformation change from tangled to straight as the result of a polarity decrease of the liquid mixture in contact. The superior results of grafted titania membranes over grafted alumina membranes were also found in gas separation studies [111] (see 3.1).

Selective pervaporation of organic compounds can also be carried out with inorganic silica-based membranes by incorporation of pendant groups using sol-gel dip-coating methods. One example is the recovery of ethyl acetate, methylethyl ketone and isopropanol from aqueous solutions with phenyl-functionalized silica [124]. When elevated temperatures are required, the enhanced stability of HybSi-based membranes would however be preferred. Organophilic properties of HybSi membranes were first reported for octane- or biphenyl-bridged materials, which showed an increased *n*-butanol flux in 5%  $\text{H}_2\text{O}/n$ -butanol pervaporation [53]. The large size of the organic bridging group made the material more hydrophobic than  $\text{CH}_2$ - or  $\text{C}_2\text{H}_4$ -bridged materials. The incorporation of pendant alkyl groups however results in an even more hydrophobic material. By combining  $\text{C}_2\text{H}_4$  bridging- and terminating alkyl moieties, HybSi membranes changed from preferentially water permeating to butanol permeating (from a 5% *n*-butanol/ $\text{H}_2\text{O}$  feed) when the number of carbon atoms in the organic tail increased to 10 (Figure 5) [56]. This was accompanied by an increase of the 3-phase water contact angle from 65° to 111°. The separation factor towards *n*-butanol was higher than for a purely evaporation-based process, demonstrating the role of affinity in the separation process.

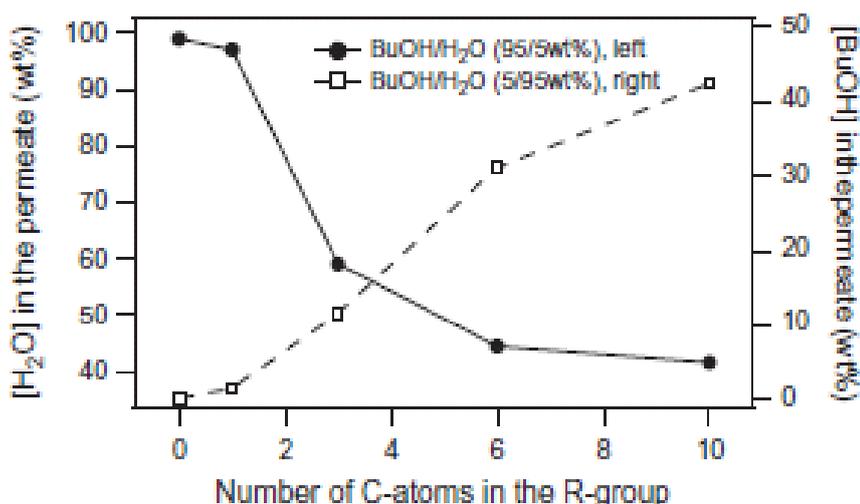


Figure 5: Permeate concentration as a function of the number of C atoms in the terminating R-group incorporated in  $C_2H_4$ -bridged HybSi membranes. Pervaporation experiments involved butanol/water feed mixtures of 95/5 and 5/95 wt% at 95°C [56].

### 3.3 Hydrophilic pervaporation

Of notable relevance is the substantial hydrothermal stability of HybSi membranes. While silica membranes show high performance as dehydrating pervaporation membranes, long-term exposure to water leads to pore size changes even at temperatures as low as ~70°C [47]. Consequent permeability and selectivity changes result in substantial decrease of the pervaporation performance. While methylated silica, prepared by in-situ incorporation of pendant methyl groups, was shown to have improved stability up to 95°C for more than 1 year, higher temperatures similarly led to a fast decline in selectivity [47]. Considering that many dewatering applications require substantially higher operation temperatures, the development of organically bridged silica, or HybSi<sup>®</sup>, membranes that showed stability up to at least 150°C for several years raised new interest in inorganic membranes for pervaporation.

Several reports have appeared discussing the separation properties and stability of hybrid silica under pervaporation. Most tests involved dehydration of a feed containing 5 wt.% water in *n*-butanol. While in the first reports,  $C_2H_4$ -bridged membranes from mixtures of BTESE and MTES have been described [38, 55], membranes prepared from only BTESE showed both a higher water flux and a higher separation factor [31]. The adverse effect of methyl groups on the separation properties was also observed for gas permeation and is discussed in section 3.1. In pervaporation, a twice faster decline in water flux was even observed with methyl groups present in the structure [31]. Even then, in a continuous testing period of 1000 days with a BTESE/MTES membrane [125] (Figure 6), the permeate water purity remained well above 96 wt.%. Purely BTESE-based membranes have also shown stability at 190°C applying a 3 wt.%  $H_2O/n$ -butanol feed. The permeate contained about 99 wt.% water during the full 36 day testing period. High temperatures up to 160 °C were shown to be advantageous for the dehydration of viscous  $H_2O$ /glycerin mixtures, as they induce a drop in viscosity, leading to a substantial increase of the flux [126].

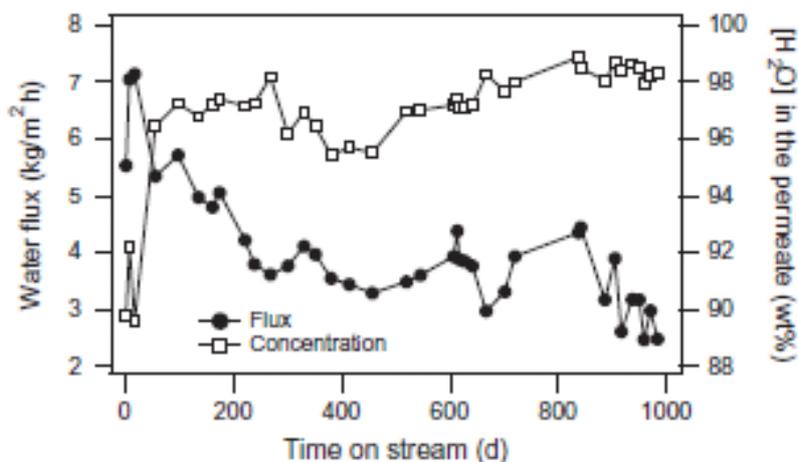


Figure 6: Separation performance (water flux and water content in the permeate) for the dehydration of 5 wt% water from *n*-butanol at 150°C of HybSi membranes from BTESE and MTES [125].

Higher separation factors were found for water/alcohol mixtures with a shorter organic CH<sub>2</sub> bridge [52]. This was especially advantageous for the dehydration of smaller alcohols, with a separation factor of over 20 from a 5 wt% H<sub>2</sub>O/methanol feed. This type of separation is relevant for biodiesel applications. The high selectivity was explained by the presence of a smaller number of larger micropores (1–2 nm). Several other water/solvent separations have been reported with HybSi, including *N*-methyl pyrrolidone (NMP). While NMP is one of the strongest aprotic solvents and for that reason frequently used in polymer manufacturing, a stable performance was reported during the 50 days of measurement [125]. Typical applications in which pervaporation membranes may be applied are reactions in which water is eliminated, such as in esterification or acetal production, to assist in shifting the reaction equilibrium. For the latter, long-term stability under the relevant conditions has been validated in the presence of an ethanol – butyraldehyde – 1,1 diethoxybutane – water mixture [127].

Acid stability is relevant in various processes. To purify products from fermentation reactions, membranes should be resistant to organic acids such as HAc. Only a very limited selectivity decline was observed for periods between 50 and 350 days with up to 15% of acetic acid added to a mixture of 5 wt.% water in ethanol [125]. In experiments that lasted several days, indications were found that dehydration of acetic acid is feasible for BTESE-based membranes [119]. While stable membrane performance in 0.05 wt.% HNO<sub>3</sub> was observed in a mixture with 5 wt.% water and *n*-butanol, HNO<sub>3</sub> concentrations of 0.50 wt.% showed a gradual decline in permeate purity from >99% to ~95% over a 30-day period. Addition of 1 wt.% methanesulfonic acid led to a rapid loss of selectivity [125]. Considering that post-test analysis showed that both the selective layer and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sub-layer had disappeared [79], it can be suggested that the stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rather than of the hybrid silica layer is limiting under these conditions.

While HybSi membranes are generally highly stable in the sense that they retain their selectivity, a gradual decline in flux is observed in the course of several months to years of continuous operation [31, 125]. The flux decline is generally undesired, but it may easily be overcome in many practical applications by gradually increasing the operation temperature.

### 3.4 Organic solvent nanofiltration

Modification of tight mesoporous membranes in order to specifically enhance their flux performance in apolar solvent filtration was first studied in this century using post-synthesis organosilane grafting (silanation) [85, 128–131]. From this research it is clear that for a correct modification inside the small mesopores, it is important to carefully choose the size and amount of reactive groups of the organosilanes. Polymerization reactions are preferably avoided, and, in general, post-modification in the gas-phase leads to better and more reproducible results than in the liquid phase. In all the studies mentioned, hydrophobization of the inner membrane surface by the organoschlorosilane grafting was shown, most clearly by the enhanced permeation of apolar solvents as hexane, or toluene.

Tsuru *et al.* [93] have shown for the first time that the hydrophobic nature of a silanated membrane leads to solvent transport that fits viscous flow behaviour: the fluxes of all solvents vary according to their viscosities so that viscosity times flux is a constant, independent of the solvent. More recently, Buekenhoudt *et al.* [9]

measured the same behaviour for the silanated 3 nm ZrO<sub>2</sub> membrane of Voigt *et al.* [128]. In contrast, fully inorganic nanofiltration and tight ultrafiltration membranes show clear deviation from this behaviour, due to their especially low apolar solvent fluxes [9, 85, 93].

Voigt *et al.* [128] studied also the retention behaviour in apolar solvents. Their best silanated 3 nm zirconia membrane was fully hydrophobic (showing no water flux) at a cut-off value of 600 Da as measured with polystyrene oligomers dissolved in toluene. They also tested this membrane for homogeneous catalyst retention using the Pd-BINAP catalyst (~1000 Da) in toluene. The retention of the full catalyst was measured to be > 99%, while the retention of the BINAP ligand was about 65%. Economically high toluene permeabilities from about 6 Lh<sup>-1</sup>m<sup>-2</sup>bar<sup>-1</sup> (pure toluene) to about 1 Lh<sup>-1</sup>m<sup>-2</sup>bar<sup>-1</sup> (during catalyst rejection) were found.

Tsuru *et al.* studied the organic solvent filtration behaviour of methylated silica membranes produced by the dip-coating method. They compared the results to those of fully inorganic silica and titania membranes [132]. The hydrophilic inorganic membranes showed a drastic flux decline for hexane during the first minutes of filtration (up to 95% flux decline was measured). This loss of permeability was attributed to the presence of trace amounts of water in hexane, adsorbing onto the hydrophilic pore surface. In contrast, the methylated silica membranes revealed no flux decline owing to the low affinity of water to their hydrophobic surface. More recently, Tsuru also measured the retention performance of these membranes using polyolefin oligomers in hexane solutions. Using these mixtures, their methylated silica membranes with a pore size around 2 nm showed molecular weight cut-offs of 1000 to 2000 Dalton, correlating well with their pore sizes [133]. Permeabilities in the mixtures were similarly high as for the pure solvent (7.2 to 27 Lh<sup>-1</sup>m<sup>-2</sup>bar<sup>-1</sup>). With increasing oligomer concentration, no flux decline, and thus no fouling was observed.

Another alternative way of producing hybrid organic-inorganic membranes for organic solvent nanofiltration was developed by A. Pinheiro *et al.* [134, see also above]. The method consists of polymer grafting to attach preformed polymer chains, with one reactive end, to an anchoring site on a organosilane grafted inorganic support membrane. In [96] they used the amine reactive side created by silanation with APTES (3-aminopropyltriethoxysilane, preferably performed in the gas phase) to graft epoxy-terminated PDMS. The resulting membranes showed high permeability for apolar solvents following viscous flow behaviour (0.5 and 4.8 Lh<sup>-1</sup>m<sup>-2</sup>bar<sup>-1</sup> for IPA and hexane, respectively). A molecular weight cut-off value of 500 Da was measured using a mixture of polyisobutylene (PIB) in toluene. The PDMS-grafted membrane showed stable performance during testing periods of up to 170 days. Extensive swelling as occurring in the pure fully organic PDMS membranes was not observed. In a similar way, nanofiltration membranes with intermediate polarity were prepared by grafting polyimide-based polymers into the pores of mesoporous gamma-alumina membranes [134]. Similar fluxes and a slightly higher molecular weight cut-off (830 Da) were determined. The permeability of hexane however showed the flux decrease typical of the more hydrophilic membranes due to adsorption of traces of water present in the solvent [132]. This method clearly creates flexibility in synthesis, as many different polymers may be grafted in this way.

Recently, a new type of post-synthesis grafting on metal oxide supports using Grignard reagents was developed with organic solvent nanofiltration in mind [107] (see also section 2.2.3). The main driver for this development was the relatively low stability to rehydroxylation of organosilanes grafted on transition metal oxides as titania or zirconia (low stability of the R – Si – O – Ti/Zr bond, see previous sections). The resulting innovative FunMem<sup>®</sup> membranes show economically interesting fluxes for both apolar solvents and water [18]. This is due to their amphiphilic character caused by the partial surface coverage of organic groups. The FunMem<sup>®</sup> membranes show again viscous flow behaviour for a variety of solvents (including water), when grafted with sufficiently long alkyl chains. The retention behaviour for native and grafted membranes was measured in 4 test mixtures [135]. Two different solvents and two different solutes, both with varying polarity were used (acetone/toluene with intermediate/low polarity, and polyethylene glycol/polystyrene with high/low polarity). In all cases superior performance of the hybrid membranes was shown. The best retentions were achieved in the acetone plus polystyrene mixture. All results can be elegantly explained by taking into account the relative affinities of the solvent, solute and membrane surface, as visualised in figure 1 and 7. Hansen solubility parameters can be used to quantify some of the affinities. To show the potential of using these affinity effects in real separations, filtration was performed with a phosphine metal ligand (molecular weight 688 Da) in isopropanol. Except the pure phosphine, this mixture also contains the mono- and dioxide impurities. Despite the fact that the three solutes have similar size, they can be separated based on differences in their polarity, using a modified membrane. More specifically, the hybrid membrane retained the pure phosphine and the mono-oxide for > 99% and 89% respectively, while the dioxide impurity showed negative retentions (-160%) meaning that it is preferentially permeating through the membrane. The retention of the pure phosphine for a native, ungrafted membrane is too low to perform a similar purification. Many more affinity-based separations are currently being investigated using a next generation of FunMem<sup>®</sup> membranes with functional grafted groups other than hydrophobic ones. The versatility of the Grignard grafting technology will even allow to really tune membranes towards specific separations.

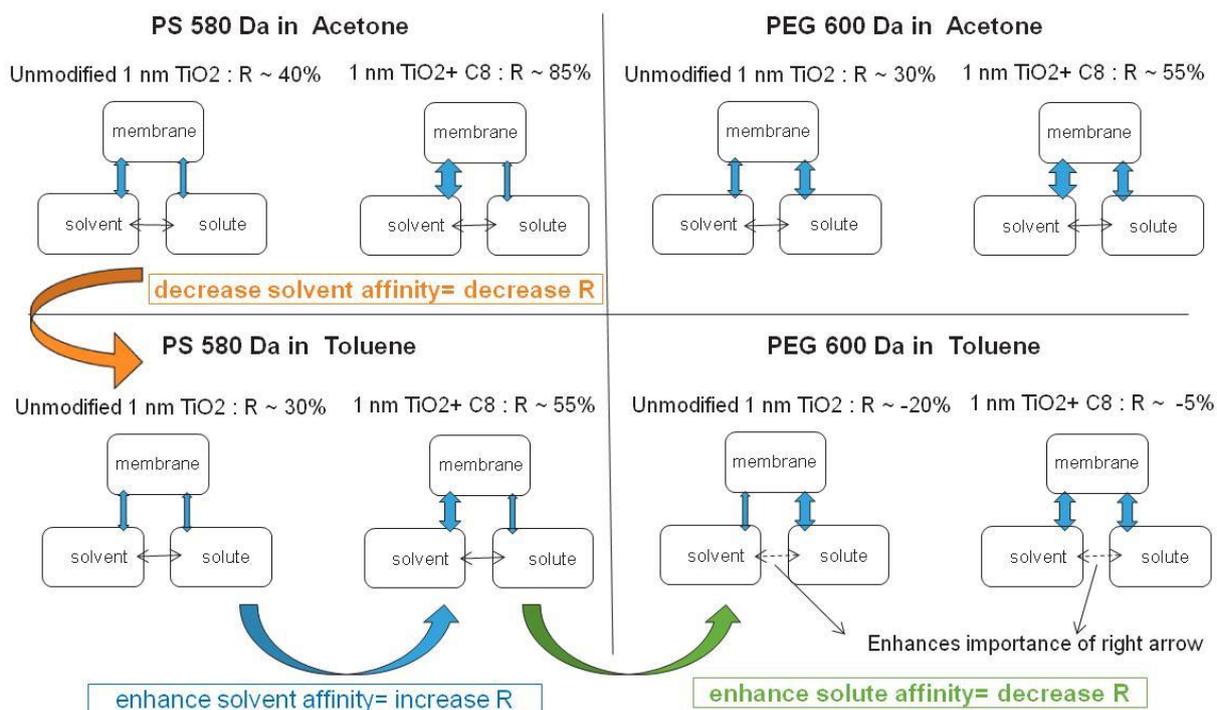


Figure 7: Representation of the membrane–solvent–solute interactions in different solvent-solute mixtures on unmodified and Grignard modified membranes. The thickness of the arrows reflects the importance of the interaction.  $R$  = rejection. Adapted from [18,135]

For membranes based on organically bridged silica (HybSi), organic nanofiltration has been explored for membranes based on combinations of (C<sub>2</sub>H<sub>4</sub> and octane) bridges and pendant alkyl groups [57]. In this initial study, the hybrid silica membranes showed one order of magnitude lower acetone and toluene fluxes than for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support system, i.e. without the HybSi top layer. Not all membranes showed a detectable toluene flux, and no clear trend was observed between the flux and the length of the pendant alkyl group. Unlike for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, no decline of the flux in time was observed for the hybrid silica-based materials. In the presence of Bengal Rose and Sudan Blue dyes, no detectable solvent flux was measured for either of the membranes. More work is envisaged to result in improvement of the performance of the hybrid silica membranes in organic nanofiltration.

### 3.5 Membrane contactor applications

Membrane contactor applications typically require macroporous membranes (for high flux) that are non-wetted by the mainly aqueous liquid feed. Moreover, for easy operation, wetting should be avoided also at a trans-membrane pressure of a few bar. Larbot *et al.* started to develop hybrid organic-inorganic membranes for this application [136, 137]. To this end they grafted open zirconia MF/UF membranes (typical pore size 50 à 200 nm) using perfluoroalkylsilanes (FAS). This resulted in strongly hydrophobic materials with contact angles of 140 to 150°. These contact angles are similar to the contact angle of water on the highly hydrophobic polypropylene (PP) and PTFE materials that are typically used for contactor applications. As a consequence, despite the large pore size of the native membranes, water permeabilities remained zero until at a pressure of 2 to 3 bar. In this work, bubble-free ozonation (transfer of ozon into water without making bubbles, which could lead to foam formation) was mentioned as the envisaged contactor application. The application typically needs an inorganic membrane, as polymeric membranes are insufficiently chemically stable. However, no test results were shown. A few years later, in collaboration with Kujawski, similar hybrid organic-inorganic zirconia and titania membranes were actually tested in membrane distillation using NaCl solutions [138]. The tests successfully showed salt retentions of 99 to 100% combined with high water fluxes (6 l h<sup>-1</sup>m<sup>-2</sup> for a feed at 95°C, and the permeate at 5°C). Similar good results were obtained in air-gap and vacuum membrane distillation [139, 140]. At high salt concentrations at the feed side, evidence of only limited fouling of the membranes was noticed [34]. All the positive results prove that the FAS-grafted inorganic membranes can compete with the polymeric PTFE or PP membranes typically used for these contactor applications.

Recently, phosphonic acids and more specifically bisphosphonic acids (two reactive groups giving bidentate reaction with the surface), were used to develop highly hydrophobic ceramic microfiltration membranes for contactor applications (contact angles  $> 110^\circ$ ) [141]. The membrane consisted of macroporous  $\alpha$ -alumina; the functional group of the bisphosphonic was a perfluoropolyether, which is known for its chemical inertness. It was shown that the bisphosphonates spontaneously form self-assembled monolayers (SAMs) that resist harsh conditions [142]. Dupuy *et al.* used this type of hybrid organic-inorganic membranes for membrane-intensified extraction of oxygenated terpenes from citrus essential oils [143]. These oxygenated terpenes are highly valuable molecules in the flavour and fragrance industry, and are typically extracted using ethanol/water stripping solutions. Use of the membrane can eliminate the difficult phase separation step after extraction (time-consuming decantation). Tests with a commercial polypropylene module of Liqui-Cell<sup>®</sup> revealed unworkably low breakthrough pressures of  $< 0.1$  bar for the hydro-alcoholic mixture. On the contrary, both PTFE membranes and bisphosphonic acid-grafted alumina membranes showed non-wetting at pressures up to about 0.5 bar, making the process industrially feasible. Tests on hollow fibre modules of both materials showed similarly good mass transfer results. However, the grafted alumina module showed a clear fractionation of limonene and citral, which was not observed for the PTFE module [144].

### 3.6 Pressure-driven water filtration

Back in 1995, Randon *et al.* [101] already applied grafting of butyl phosphonic acid to decrease the charge of the membrane and thus the adsorption of proteins such as BSA (Bovine Serum Albumin). This leads to an extensive increase of the protein retention in ultrafiltration from 48 to  $> 99\%$ . However, the grafted titania UF membrane was strongly hydrophobic, and required pre-wetting with an ethanol-water mixture before use. The resulting process flux of the hybrid membrane was about of factor of 2 lower than that of the unmodified titania membrane.

More recently, grafting of ceramic tight UF membranes (5 and 10 nm  $\gamma$ -alumina membranes) was applied to increase their heavy metal ion removal performance [89]. In particular, the low-cost biopolymer alginate, which has high heavy metal adsorption capacity, was grafted. A 2-step method was developed that resulted in the formation of a relatively stable bond with the membrane surface, leaving the  $-\text{COOH}$  metal-binding groups of the alginate available for metal adsorption. The  $\text{Cd}^{2+}$  retention measured increased by a factor of 1.5 to 2 compared to the unmodified membrane. This performance was conserved in a second run after acidic regeneration. While this is one of the rare examples to date in which the electronic charge (electronic contrast) of the pore surface was intentionally increased to alter the adsorption properties of hybrid organic-inorganic membranes, this strategy is more intensively used in other types of hybrid materials for ameliorated ion-exchange [see e.g. 150].

Another example of pressure-driven water filtration is reverse osmosis (RO), which is a widely used technique to produce high-purity water, e.g. to make drinking water from seawater. Large-scale RO is currently carried out with polymeric membranes. The applicability of ethane-bridged HybSi membranes in reverse osmosis was investigated with 2000 ppm NaCl, and with 500 ppm of  $\text{MgSO}_4$ , various alcohols and glucose [145]. Permeabilities between 0.9 and  $3.2 \cdot 10^{-13} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  were found at salt rejection factors between 93.8 and 99.4% at  $25^\circ\text{C}$ . The permeability was a factor of 8 higher at  $90^\circ\text{C}$ , and a moderate increase of the rejection was observed.

While the overall permeability of HybSi membranes is rather low, they retained their separation properties after prolonged exposure to sodium hypochlorite solutions ( $\text{NaClO}$ , at  $\text{pH}=7$ ), which was measured up to 35000 ppm-h. This agent is the most widely used disinfectant in water treatment for biofouling control. Commercial polyamide membranes suffer from poor resistance to these conditions. Even a few parts per million of chlorine in feed water could lead to significant membrane degradation [146]. Ethane-bridged HybSi lacks the amide linkages that are sensitive to attack by aqueous chlorine. Moreover, it allows high-temperature RO, which is required in several industrial applications [147]. The maximum operating temperature of most commercial polyamide membranes is normally below  $55^\circ\text{C}$ . Thus, for applications in which the process mixture is already at a high temperature, HybSi membranes may also be advantageous. A continuous increase of the water flux with the transmembrane pressure was observed (i.e., the permeability remained constant, in line with the solution-diffusion model), while ion permeation was independent of the pressure. This led to an increase in salt rejection [54].

Application of ethylene instead of ethane bridges gave a twice higher water permeability and a similar high NaCl rejection ( $>98.5\%$ ). The higher water permeability was explained by the presence of more polarizable  $\pi$ -bond electrons in the  $-\text{CH}=\text{CH}-$  bridges, which increases the affinity of the membrane to polar water molecules. Modification by an ozone treatment led to higher permeability and lower NaCl rejection [54].

Recently, grafting of organic groups has also been applied to reduce fouling of membranes in pressure-driven filtrations involving water. As the application aim is essentially different from improving the intrinsic separation properties of the membrane (section 3.1 to 3.6), this will be described in a separate section below.

### 3.7 Reduction of membrane fouling

Organic modification has been applied to reduce the fouling of the intrinsically hydrophilic native inorganic membranes [90,91,95,148]. Gao *et al.* grafted 0.2  $\mu\text{m}$  zirconia microfiltration membranes with organosilanes with long alkyl chains in order to avoid water adsorption during the filtration of water in oil emulsions [95]. The grafting resulted in a flux increase of about a factor 2, combined with an improved water rejection from 90 to about 100%. It was concluded that the organic membrane modification efficiently mitigated flux decline during filtration. Similar positive anti-fouling effects were also found when grafting with perfluoroalkylsilanes (FAS) [148].

Also in water filtration, grafting has recently been explored as a way to sustainable fouling mitigation [103, 149]. In this study, fouling reduction of commercially available titania nanofiltration membranes has been envisaged. Compared to the intrinsically more hydrophobic polymeric nanofiltration membranes, the titania membranes show relatively low fouling due to their high hydrophilicity, and therefore strong adsorption of water. However, the abundant OH-groups on the pore surface cannot only interact with water but also with many different polar foulants, leading to remaining fouling issues. To avoid these unwanted adsorption effects, and simultaneously keep sufficient hydrophilicity and thus water flux, grafting with short relatively inert groups (such as methyl and phenyl groups) has been performed. Two methods delivering hybrid organic-inorganic titania membranes stable to hydrolysis, were compared: grafting with phosphonic acids, and with Grignard reagents (FunMem<sup>®</sup> technology). These two methods avoid unwanted polymerization reactions in the small micropores of the nanofiltration membranes, which can occur with organosilane reagents. The grafting efficiency was evaluated by measuring irreversible fouling with typical surface and ground water foulants (humic acids with and without calcium, meat peptone and laminarin gum). Figure 8 summarizes the flux decrease due to irreversible fouling in different fouling situations by plotting the normalized water fluxes (fluxes divided by the water flux of the fresh membrane) for 4 membranes (an ungrafted membrane with a pore size of 0.9 nm membrane, methyl- and phenyl FunMem, and a membrane grafted with methyl using the phosphonic acid method) [103]. The figure shows that every grafting method is effective in reducing fouling in all conditions. However, the methyl Grignard modified membrane (FunMem) shows unparalleled low fouling. All results can be qualitatively understood taking into account the physico-chemical properties of the foulants and of the grafted and ungrafted membrane surfaces. The unique bond created by the Grignard grafting strongly reduces the possible interactions between foulants and membrane surface, leading to a rather “inert” membrane. The best performing membrane remained unfouled (no irreversible fouling) in a wide variety of studied fouling conditions, including pulp and paper effluent streams, and olive oil waste waters [103, 149]. Moreover, in olive oil waste water filtration it shows not only superior flux, but also remarkably higher COD retention (increased from 11 to 48%) [149]. In filtration of real surface water, the retention of humics was similarly high for both grafted and ungrafted nanofiltration membranes [149].

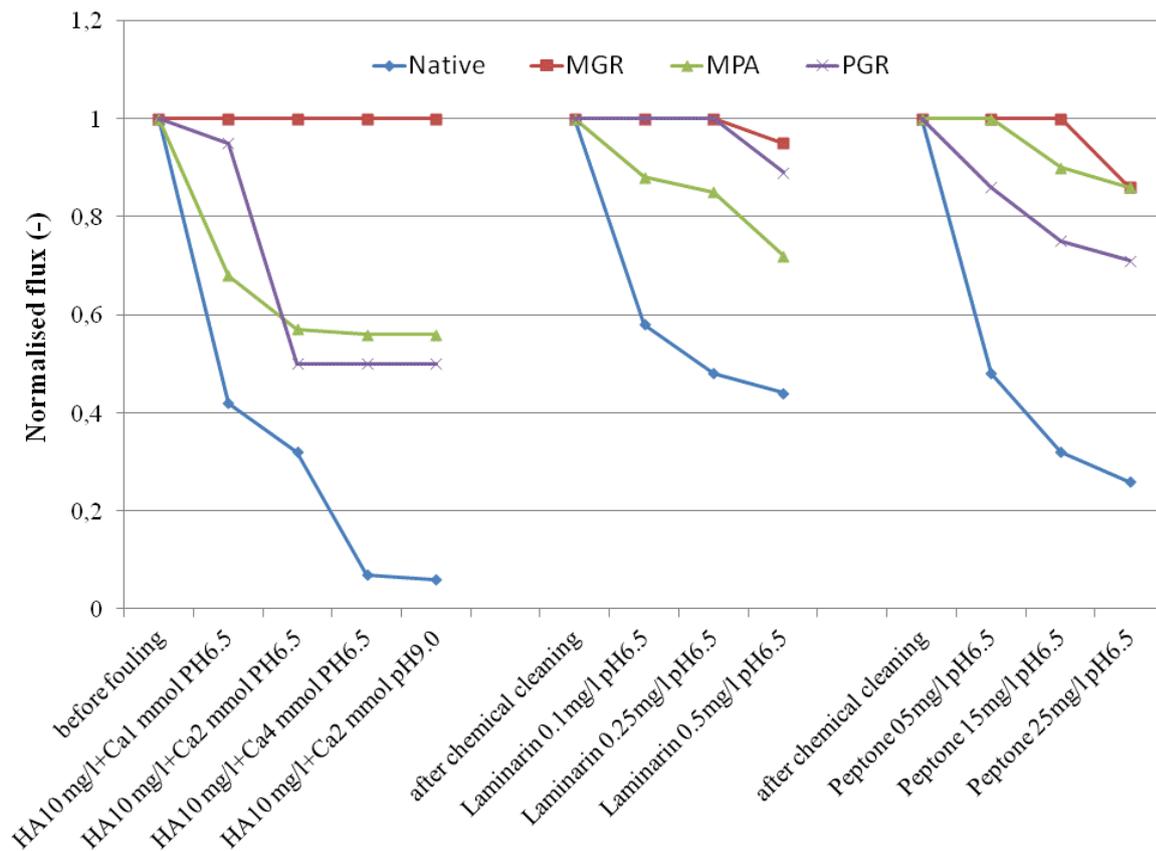


Figure 8: Normalized water fluxes of Grignard (GR; MGR = methyl Grignard, PGR = phenyl Grignard) and phosphonic acid (PA; MPA = methyl phosphonic acid) grafted titania nanofiltration membranes and unmodified membranes before and after exposure to different foulants. The applied foulants are Humic Acid (HA) in a concentration of 10 mg/L in combination with  $\text{Ca}^{2+}$  concentration of 1, 2 or 4 mmol/L and two pH levels; laminarin gum in concentrations of 0.1, 0.25 or 0.5 mg/L; meat peptone in concentrations of 5, 15 and 25 mg/L. In between the measurements with the different type of foulants the membranes were chemically cleaned (pH 10, 50°C, 30 min). Adapted from [103,149].

## Conclusion

The development of hybrid membranes and their use in separation applications have evolved strongly in the last decade. This opens new opportunities to replace current energy-intensive separation processes or convert them into hybrid processes. The wide variety of methods to tune the selective layer of hybrid membranes to specific applications can carry membrane technology into a new era.

While interactions between the membrane and the individual components of a mixture (solute and solvents) are increasingly understood on a qualitative level, much research is still required to fully control and comprehend all specific interactions in separation processes. This also includes the correlation between the precursors and synthesis conditions to produce the various hybrid membranes with their stability under operating conditions.

We have evaluated the various types and subtypes of class II hybrid membranes. These consist either of homogeneous selective layers from dipcoated PDMS- or silica-based hybrid sols, or of inorganic porous structures grafted by ether bonds, with organosilane, organophosphoric acid or organometallic reagents. Especially the HybSi and FunMem concepts show great promise in producing membranes with both improved stability and versatility in molecular separation applications, including gas separation, (organophilic and hydrophilic) pervaporation and organic solvent nanofiltration, as well as in contactor, pressure-driven water filtration, and antifouling applications.

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