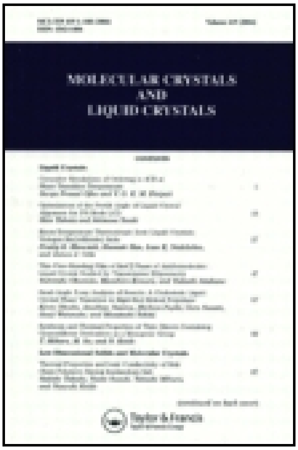

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Organic-Inorganic Hybrid Materials with Specific Solute and Gas Transport Properties for Membrane and Sensor Applications

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Organic-Inorganic Hybrid Materials with Specific Solute and Gas Transport Properties for Membrane and Sensor Applications

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This paper is concerned with synthesis of hybrid materials for membrane applications. Examples of hybrid nanocomposites (*type I*) and hybrid polymers (*type II*) are presented. Dealing with *type I*, molecular sieves such as microporous silica beads or zeolite crystals were added to polymer matrices as an attempt to increase gas and vapor separation membrane performance. Also, specific organic molecules were inserted in a silica matrix as the active part of chemical sensors. Regarding *type II* materials, the arrangement at the molecular level of the organic and inorganic parts as well as their chemical composition have been investigated for facilitated transport of heavy metal ions or aminoacids in aqueous media, but also for separation of oxygen/nitrogen or volatile organic compounds from air. Processing of *type II* membranes is mainly based on the sol-gel method for which the synthesis of hybrid materials is undoubtedly one of the major advances. The specific advantages of this "chimie douce" method (low temperature chemical process, large variety of material precursors, material structure adaptability, and good film forming ability) are described here as a very suitable way to design and synthesize synthetic membranes with improved performance.

Keywords: hybrid material; membrane; facilitated transport; gas separation; sensor

INTRODUCTION

Hybrid organic-inorganic materials have been developed in the past 20 years as an interesting alternative to limitations of conventional organic or inorganic materials. Composite materials formed by the combination of nanoscale inorganic and inorganic domains are attractive for the purpose of creating new materials with new or enhanced properties compared to the single organic or inorganic material. These new or enhanced properties principally arise from two synthesis approaches. The first one deals with the formation of nanocomposites in which the domain size of the inorganic phase is of about 100 nm and often much less, leading to enormous interfacial areas. In the second case the hybrid structure is obtained at the molecular level and results in hybrid polymers with specific properties. Originally studied for their enhanced mechanical properties, applications areas for hybrid materials have considerably expanded with current generation of materials in optoelectronic, ion-conduction, biology, catalysis and membrane separation [1-4].

As far as technological advances in membrane materials are considered, a first period, still under commercial development, dealt with membranes and processes adapted to separation of liquid media. Microfiltration (MF) of particles and microorganisms, utrafiltration (UF) of macromolecules and colloids, artificial kidney and hemodialysis (HD), and water desalting by reverse osmosis (RO) or electrodialysis (ED) can be mentioned as the major technologies developed during this period. Membranes adapted to the above listed applications discriminate particles or solutes according to the following mechanisms: a size effect for MF, UF or HD, an anionic or cationic exchange for ED and a preferential water solution in the membrane for RO. For all these techniques, only a marked difference of behavior (size, electrical charge, activity coefficient) allows the separation of two solutes.

Regarding membrane developments on the current period, much more severe selectivity criteria are required for membrane materials. Indeed, recent membrane processes under industrial development (gas separation (GS), nanofiltration (NF), facilitated transport (FT)) deal with the separation of very small entities (ions or molecules) in gas, vapor or liquid phases. In certain processes, membranes are at the interface of two different phases (pervaporation (PV), membrane distillation (MD)). In others, a reaction is coupled to the separation (catalytic membrane reactors (CMR)). Differences between entities to be separated are not so marked than for membrane processes developed during the first period. As an example, the small difference between kinetic diameters of nitrogen (3.64 Å) and oxygen (3.46 Å) render separation of one component very difficult by a simple size effect. Extraction of one specific aminoacid from a mixture of several aminoacids is another example of separation which cannot be attained by simple molecular sieving.

On a material point of view, since the development of asymmetric cellulosic membranes for water desalting in 1960, a number of breakthroughs in membrane applications have been achieved first with the development of synthetic polymers then with the utilization of advanced ceramic materials. Most of the existing industrial polymers have been applied to membrane preparation. An exhaustive list of these polymers cannot be listed here but one can mention the extensive utilization of polysulfone or polyamide for liquid filtration or polyimides for gas separation [5]. At this time the design of new polymers for membrane application is still in progress. A similar evolution can be noted with inorganic membrane materials including, porous metal oxides, carbon molecular sieves and more recently zeolites [6].

Taking into account the above considerations on current development of synthetic membranes, an interesting category of advanced membrane materials should be those combining certain of the basic properties of organic and inorganic membranes.

STRUCTURE OF MEMBRANE MATERIALS IN RELATION TO MEMBRANE TRANSPORT PROPERTIES

Basic properties of organic and inorganic membrane materials

The ability of a membrane to accomplish a desired separation depends on the relative permeability of the membrane for the feed phase components. The rate at which any compound permeates a membrane depends upon two factors: an equilibrium effect (partitioning of components between feed phase and membrane phase) and a kinetic effect (for example, diffusion in a dense membrane or surface diffusion in a microporous membrane). Hence the choice of a given membrane material is not arbitrary but based on very specific physical and chemical properties. These properties are different depending on the organic (polymeric) or inorganic (ceramic, metallic) nature of the membrane.

The most important class of membrane materials are organic and a number of criteria in designing a polymer membrane refer to the physicochemical nature of the permeants (gas, vapor, liquid, solid; dispersive, polar, ionic; reactive, inert; physical size and shape). Polymer membranes involved in the separation of single molecules or ions exhibit dense or almost dense structures. Polymers for gas and vapor separation are selected following criteria summarized in figure 1 which are different from those applied for polymer selection in the case of liquid separation applications.

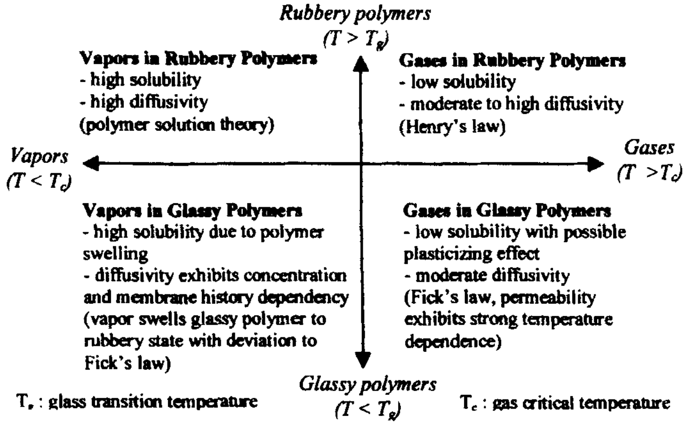

FIGURE 1. Criteria for gas and vapor separation with polymer membranes.

The physicochemical effects which influence permeation in liquid phase separation and how they can be used to assist in polymer membrane material selection are given in table 1. All these effects have not the same intensity in influencing component partitioning and transport across the membrane. It is noteworthy to mention that these effects can have a positive effect on membrane performance but also a negative one when they are exacerbated.

TABLE 1 Physicochemical effects involved in solute permeation across polymer membranes.

Debye forces	Dipole-induced dipole interaction (1-2 kcal/mole) in the case of polar molecules in presence of a polar matrix.
London – van der Waals dispersive forces	Attraction forces (0.1 - 2 kcal/mole) between permeant and membrane material or between polymer segments in the membrane.
Hydrogen bonding	Usually stronger than polar and dispersive forces (2 - 10 kcal/mole), important in the case of aqueous media with possibility of clustering effect.
Electrical charges: - ionic exchange - charge interaction	Ionic exchange between ions in the feed phase and the charged sites of the membrane. Charge interaction between charged sites and charged permeants
Selective complexation	Selective complexant sites in the membrane. Increase of partitioning for one specific component in the membrane.
Steric effects	Related to the effective size of the permeating components and the effective size of the permeation corridor in the membrane. Depend on polymer physical state (glassy, rubbery) and chain mobility.

In general polymeric membranes have good film or fiber forming ability and can be processed as very compact systems offering large surface/volume ratio. They are not expensive and can be applied indifferently to large or small fluid volume treatment. In other respects they have a limited chemical and thermal resistance, and do not offer sufficient flux and selectivity for certain applications.

Selection of inorganic membrane materials in view of membrane preparation obeys to specific criteria different from those applied to polymeric membranes. Inorganic dense membranes principally used for gas separation are based on either metallic materials exhibiting a solution/diffusion transport mechanism or ceramic materials with a ionic or mixed ionic/electronic conductivity [7]. Inorganic porous membranes can be used indifferently for component separation in gas, vapor or liquid phases. The porous structure and the pore dimension (*d*) are classified, according to the IUPAC recommendation: macroporous ($d > 50$ nm), mesoporous ($50 \text{ nm} > d > 2$ nm) or microporous ($d < 2$ nm) material. Latest developments in inorganic membranes concern microporous materials for the separation of small molecules and ions. Up to now, three categories of material have been investigated for this purpose: nanophase ceramic oxides with textural microporosity [8], molecular sieves with structural microporosity [9], and more recently MCM like materials with ordered micro and mesoporosity [10]. Offering very good and chemical resistance, these membranes exhibit high permselectivity for some applications. Unfortunately they are still expensive and cannot be easily processed as compact systems like polymeric membranes.

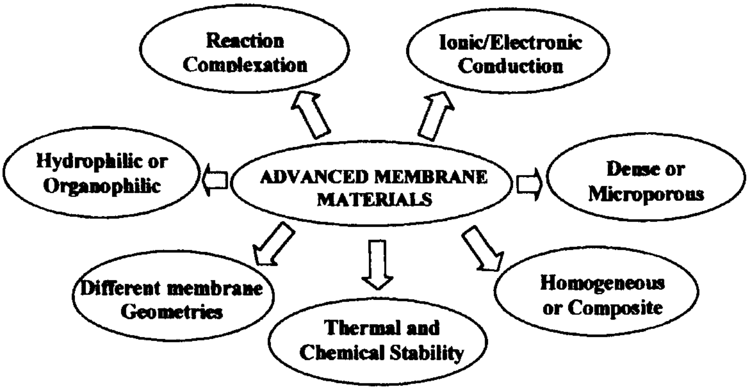

FIGURE 2 Required basic properties for advanced membrane materials.

Hybrid organic-inorganic materials offer unique opportunities to combine the specific transport properties of organic and inorganic materials (figure 2) in order to produce highly permselective membranes.

Transport in membranes.

Actual description of transport through membranes is generally given by flux equations derived from irreversible thermodynamics [11]. Unfortunately in this description the membrane is considered as a black box and no information is obtained or is required about the structure of the membrane. This is of no help for the design of membrane materials for which a physicochemical view on how the components permeate through the membrane must be considered. Although it is not possible to provide an extensive description of local transport mechanisms in membranes, some of the basic aspects of passive and active transports are described hereafter which will serve as vectors for the design and the preparation of new membranes based on organic/inorganic materials.

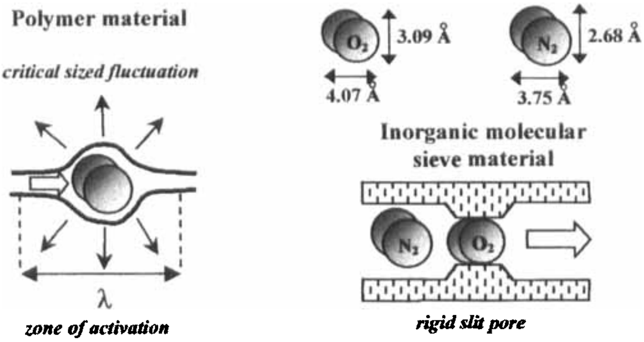

FIGURE 3 Comparison of simple transport for gas molecules in dense polymeric materials and microporous inorganic materials.

Comparison of gas transport in polymeric membranes and in molecular sieve membranes is a good example of passive transport under a pressure driving force in which limitation of a dense polymeric material can be surpassed by using a microporous inorganic material. Schematization of molecular diffusion in figure 3 shows that displacement of a gas molecule can be considered as an activated transport with temperature based on chain motion in the case of a polymeric matrix and on a jump through a rigid pore corridor in the case of a microporous inorganic matrix. When two gas molecules like nitrogen and oxygen are considered, their relative rate of diffusion (permeability and selectivity) in the polymer matrix depends on the size λ of the zone of activation and the local critical sized fluctuation of the matrix for each molecule. Up to now, attempts to produce polymer structures in which diffusion rate can be notably increased and well differentiated between these two molecules failed because of the trade-off: one parameter, permeability or selectivity, is improved while the other is simultaneously affected negatively. On the contrary a fixed pore dimension for molecular sieve materials (carbon or zeolite) induces a selectivity based on small geometrical differences and rotational effect of molecules passing through a pore constriction. Selectivity of 10-14 and permeability of 100-1000 Barrer were measured for O_2/N_2 separation with carbon molecular sieves. With an outstanding polymer category such as polyimides, the permeabilty did not exceed 1 Barrer when the selectivity was kept as high as 8-9. (1 Barrer = 10^{-10} cm.cm^3/cm^2.s.cmHg)

Facilitated transport is another interesting concept in advanced membrane development. Very selective mass transfers of gases, ions or molecules can be achieved with these membranes. They have first been developed as liquid membranes in which transport is facilitated by the presence of a carrier. Such a carrier molecule should possess a high affinity for one of the components in the feed phase and it should accelerate in this way the transport of this specific component across the liquid membrane. Up to now the most efficient way to use this category of membrane has been to immobilize the liquid membrane in a macroporous polymer support by capillary forces. Because they exhibit a high permselectivity, important applications are expected for these supported liquid membranes. Unfortunately the utilization in industry is restrained by a poor stability. An alternative concept to supported liquid membranes is to fix selective complexant sites in a dense polymer matrix (figure 4). Described in the literature as fixed site carrier membranes, the complexant sites in these membranes do not play the role of carriers but bind selectively a component from the feed phase. The role of the complexing sites is to increase partitioning of one component selectively in the membrane and then to facilitate diffusion of this specific component to the strip phase. The main advantage is to provide membranes with long lifetime compatible with industrial applications.

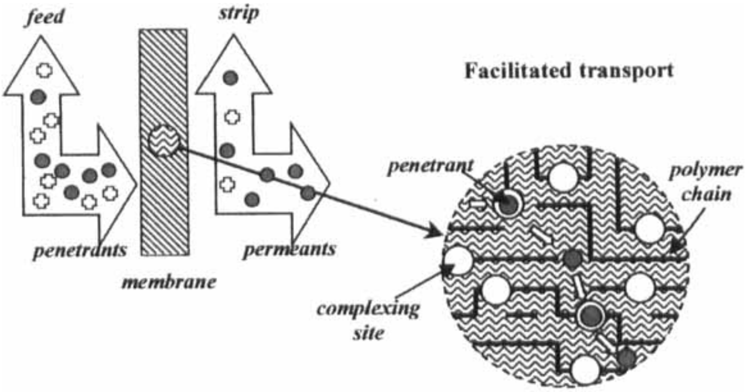

FIGURE 4 Schematic representation for facilitated transport using a fixed complexing site membrane.

STRATEGY AND EXAMPLES OF ADVANCED MEMBRANES USING HYBRID ORGANIC/INORGANIC MATERIALS

Taking into account local transport phenomena and membrane material requirements for advanced membrane developments, one can see that organic or inorganic materials are not able to fulfill entirely physicochemical and structural requirements for the preparation of highly permselective membranes.

Because they can combine basic properties of organic and inorganic materials, hybrid materials offer specific advantages for the preparation of artificial membranes exhibiting high selectivity and flux as well as good thermal and chemical resistance. Hybrid organic/inorganic materials are usually classified in two categories:

- *Type I* in which only interactions like van der Waals forces or hydrogen bonds exist between organic and inorganic parts. Hybrid materials can be described here as micro or nanocomposites in which one part (organic or inorganic) is dispersed in the other part acting as the host matrix.
- *Type II* in which covalent bonding exists between organic and inorganic parts, resulting in an homogeneous hybrid material at the molecular level.

The following examples from the literature and recent results from our group illustrate different approaches of membrane preparation using *type I* or *type II* hybrid materials.

Hybrid organic/inorganic membranes for gas and vapor separation

Potential application of *type I* hybrid materials for gas and vapor separation has been investigated by several authors. Microporous silica beads, mica, vermiculite as well as zeolite crystals were added to polymer matrices as an attempt to increase membrane permselectivity thank to the contribution of the molecular sieve material present in the polymer [12,13]. A major problem arose in the case of gas permeation which is the microporous cavities surrounding the mineral charge due to poor compatibility between the molecular sieve particles and the glassy polymers used as the host matrix. More successful have been some attempts with rubbery polymers and zeolite crystals for pervaporation membrane application. Recently, an interesting paper explained what are the reasons for unsuccessful attempts with gas separation [14]. The authors provide an analysis of hybrid (*Type I*) membrane material potential from a fundamental standpoint. According to them the performance of the so called mixed matrix composite (MMC) membranes can be predicted using various theoritical analysis. With this kind of membrane, expected performance can be estimated, based on volume fractions of the two phases present, for cases where the molecular sieve phase is assumed to be continuous or discontinuous, figure 5.

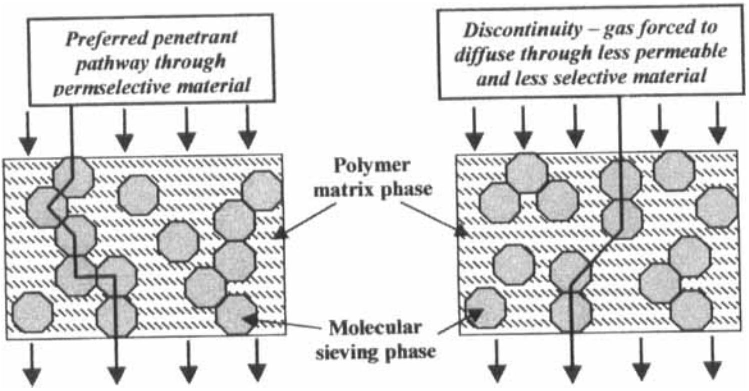

FIGURE 5 Effect of molecular sieve particles filling on gas and vapor diffusion pathway across an hybrid composite membrane.

More promising seem to be *type II* hybrid polymers. Up to now a large number of structural combinations in glassy polymers have been investigated with the aim of application in gas separation. In particular, polyimides have been widely regarded because of the good physical properties (high T_g value) and the tunable chemical composition of this category of polymer. Polyimides are synthesized by reacting a dianhydride molecule with a diamine. In order to improve permeability and selectivity of these membranes, several authors recommended the control of the dimension of the gaps between the chains as well as the extent and frequency of the segment motions which control the leap channels in the polymer material [15]. In our case we decided to replace the diamine by a silicon based coupling agent leading to a hybrid polymer network exhibiting an intermediate structure between a glassy polymer matrix and a fixed gap molecular sieve structure (figure 6). Preparation method and characterization of such hybrid membranes based on Kapton polyimide segments and crosslinked with silicon coupling agents were described elsewhere [16]. In very recent experiments we compared an Ultem polyimide membrane with an hybrid membrane containing the same polyimide segments but crosslinked with silicon coupling agents in order to form a three dimensional network with well defined gap dimension between the imide segments. In the case of oxygen/nitrogen separation it has been possible to increase the permeability of the hybrid membrane by a factor of 2.5 compared to the pure polyimide membrane and to keep the selectivity as high as 7.

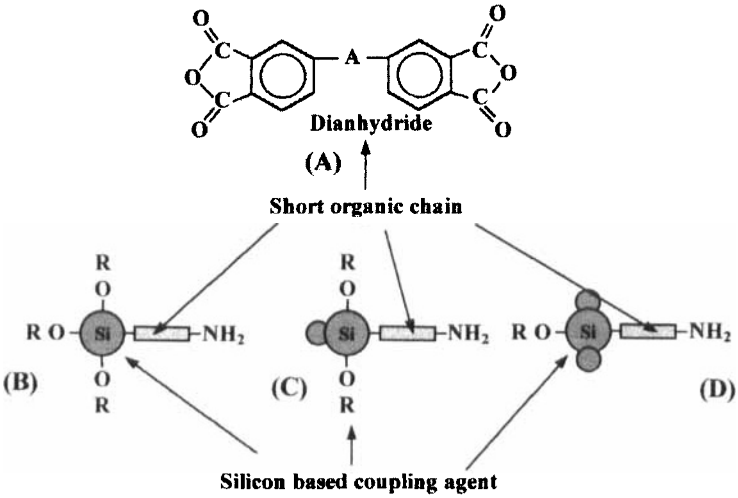

FIGURE 6 Precursors used in the preparation of hybrid poly(imide/siloxane) membranes for gas separation.

Hybrid organic/inorganic membranes applied to facilitated transport in liquid media

In fixed site complexant membranes, monotopic fixed complexant sites, with a single interaction point with solute allowed a facilitation in the solute transport, but usually the selectivity was lower [17,18]. Recently we proposed to use polytopic receptors which present different interaction types with the solute (hydrogen bonding, electrostatic interactions, van der Waals forces) [19]. Thank to the versatility of hybrid material chemistry, such polytopic receptors were chemically linked to an heteropolysiloxane host matrix and thin supported membranes were prepared from this material (figure 7).

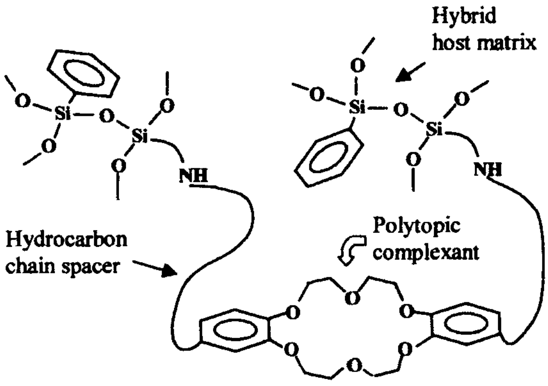

FIGURE 7 Example of polytopic complexant incorporated in an hybrid host matrix used as facilitated transport membrane.

By using polytopic receptors in a membrane, facilitated transport of organics can be obtained with the selective separation of a specific molecule from a mixture. An increased selectivity can be expected due to the synergetic and more specific supramolecular complexation of the solute in the hybrid matrix. This concept was proved with molecules of biological interest [20]. The separation of a mixture of seven aminoacids showed that multiple molecular recognition can be transferred in dense solid materials by anchoring the macrocycles in the crosslinked siloxane matrix. A good selectivity was also obtained in facilitated transport of organic acids (Succinic, Tartaric, Aspartic) by the same membrane due to the combination of non-covalent interaction type (hydrogen bonds and ionic interactions) with the polytopic receptor sites.

Hybrid organic/inorganic sensing layers used in chemical sensors

The characteristics of hybrid membrane materials defined for gas or liquid applications are also relevant for the design and the preparation of chemical sensors, in particular those based on an optical fiber device. Most of optical chemical sensors are very simple systems in which an organic molecule is trapped or grafted in a semipermeable matrix and this molecule is sensitive to the component to be sensed in the medium surrounding the fiber. For that, the sensing material is coated as a thin film on the fiber in order to transmit light signals from the excitation source to the sensing layer and/or from the sensing layer to the light analysis system.

To be attractive, a sensor must exhibit a short response time, a good reversibility, a long lifetime and a good chemical durability in the case of aggressive environment. The durability is not so important as far as cheap and disposable sensing material such as optical fibers can be used. Response time and reversibility relate to membrane problems as far as they depend in part on the diffusion rate in the sensing layer of the component to be sensed. Lifetime depends on the entrapment efficiency of the sensing molecule in the host matrix. An important additional point is the control of the refractive index in the sensing layer. All these aspects make hybrid materials prepared by the sol-gel process well adapted to optical chemical sensors

Two concepts were tested and compared, first the sensing molecules were physically trapped in an heteropolysiloxane matrix, then the sensing molecules were modified and grafted in a mesoporous silica matrix. In a previous work on the preparation of a pH sensor using fluorescein sodium salt as the sensing molecule, we showed that specific problems arose when this molecule was physically trapped in the hybrid matrix [20]. In order to prevent leaching of the sensing molecules, an almost dense microporous structure for the host matrix was prepared resulting in a slow diffusion of protons and a rather long response time for the sensor. In a subsequent work we proposed an alternative way in which the sensing molecule is chemically linked to a mesoporous matrix. This optical chemical sensor was designed for hydrazine concentration analysis in nuclear fuel reprocessing [21]. The 4-(dimethyl)aminobenzaldehyde (DMAB) was chosen as a sensing molecule able to react reversibly with hydrazine and to provide an optical signal. As reference sensing material, DMAB was physically trapped in a sol-gel derived matrix obtained from a mixture of tetraethoxysilane and methyltriethoxysilane as network modulating agent. In order to allow chemical grafting of DMAB in a mesoporous silica matrix, the molecule was chemically modified (DMABs) as shown in figure 8. Comparison of the two sensing materials showed that the response time was essentially governed by the diffusion of hydrazine whereas the lifetime was dependent on the retention of DMAB. The results were in favor of the sensing molecule chemically linked to the host matrix.

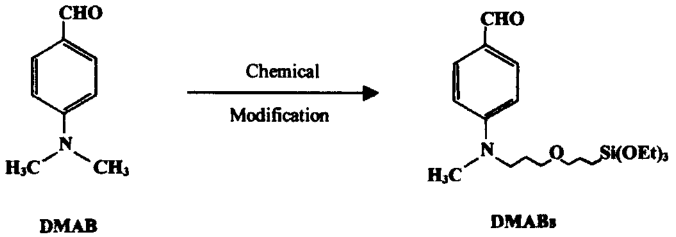

FIGURE 8 Sensing molecules used in the preparation of optical chemical hydrazine sensor. Physically trapped molecule (DMAB). Chemically grafted molecule (DMABs).

CONCLUSION

Organic-inorganic hybrid materials are expected to provide many possibilities as new membrane materials. Thank to the possibility to combine permselectivity and some of the physicochemical characteristics of polymer and ceramic membranes, hybrid membrane materials can exhibit very different properties from their original components (organic and inorganic materials). In addition, hybrid membranes can be processed indifferently as thin films or hollow fibers similarly to polymer membranes as well as thin supported films on porous ceramic supports. This is of a great advantage for industrial application as far as they can compete with existing membranes on an

economical point of view but with specific transport properties which lead to new opportunities in membrane separation technologies.

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