Some aspects in inorganic membrane

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From 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 polymer membranes, then with the utilization of advanced ceramic materials.
At present, 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 and more recently zeolites [1].

The membrane is the key of the membrane process and the transport properties of the inorganic membrane systems depend, to a large extent, on the microstructural features (pore shape, size, tortuosity, …) as well as the architecture of the membrane.

Two main classes of membranes can be distinguished: dense (they are made of metals, hybrid organic-inorganic or mixed conductive oxides) and porous membranes. Pores can be an inherent feature of crystalline structures (zeolites, clays minerals, …) or be obtained by packing and consolidation of small particles.

The inorganic membranes can be described as an asymmetric porous material formed by a macroporous support with successive thin layers deposited on it. The support provides mechanical resistance to the medium.

Materials formed from nanoparticulate sol-gel systems

The sol-gel process is one of the most appropriate methods for the preparation of microporous and mesoporous oxide layers.

The first stage in the sol-gel process consists of the preparation of a sol using molecular precursors, either metal organics or metal salts. In both cases, condensation reactions occur at the sol stage with formation of clusters or colloids which collide at the final stage to form the gel. In the case of membrane formation, coating of the active layer has to be carried out at the sol stage with a rheological behavior adapted to the porous substrate chosen as membrane support.

During sol-gel processing of inorganic membranes, sols and gels evolve in a different way depending on the category of the precursors used. This evolution has a great influence on the porous structure of final membrane materials.

Zirconia Nanofiltrer

A supported microporous zirconia layer has been obtained from a nanoparticle organic sol using chelating agents as blocking functional groups in metal alkoxide condensation [2]. Zirconium isoproxide was used as the ceramic precursor to synthesize the organic particulate sol [3].

The supported zirconia layer obtained after sintering at 500 °C exhibited a tetragonal crystalline structure and revealed a very fine structure. Powder X-Ray diffraction (Scherrer's formula) was used for the determination of an average individual crystal sizes. In this membrane, packing of the nanoparticles results in mean pore diameters of 1,4 nm and a porosity of 18%.

γ-Alumina nanofiltration membrane

The colloidal method is used in this example and the choice of the precursor is primordial. If commercial boehmite is used [4], pore diameters are not smaller than 5 nm and the lower sintering temperature is 540 °C. Aggregates were not completely broken during the peptization, whereas for the peptization of the precipitated boehmite no or smaller aggregates were formed because of the electrostatic repulsion takes place before drying [5].

Hafnia nanofiltration membrane [6]

The sol precursor of the membrane was elaborated by nitric

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acid peptization of the hydrous hafnium oxide precipitated by complete hydrolysis of hafnium alkoxide. The sintering temperature was equal to 450 °C for 1 h. At this temperature, the monoclinic hafnia phase appears. Pore diameters are equal to 1,4 nm and the cut off was evaluated at 420 Da. The water permeability is 2,5 $lh^{-1}m^{-2}$ bar^{-1}.

Membranes for catalytic applications

The classical synthesis methods for conventional catalysts often start from salts or oxide precursors and involve precipitation, impregnation or even solid/solid reactions. These methods are usually not adapted to the homogeneous casting of catalysts on supports and may lead to limited specific surface areas and to heterogeneous distributions of active species. The sol-gel process, starting from the homogeneous distribution of precursors at the molecular level, often improves these specific criteria for obtaining powders or film-shaped materials either as pure phases or homogeneous doped or dispersed in a matrix.

The following examples show the potentialities of the sol-gel process for catalyst synthesis and applications to catalytic membrane preparation.

Lanthanum oxychloride catalytic membrane from metal salt precursors

An attractive approach for the conception of a membrane reactor for oxidative coupling of methane is the preparation of a catalytically active membrane. The sol-gel process has been investigated in order to prepare LaOCl inorganic membranes supported on commercial alumina tubular supports. Both mesoporous and microporous LaOCl membranes were prepared, through a precise monitoring of the fundamental phenomena occurring during the sol preparation and thermal treatment [7-8].

VMgO catalytic membranes prepared form original metallo-organic precursors

The synthesis of original metallo-organic molecular precursors has been attempted in order to obtain a homogeneous liquid phase, adapted to casting and being a precursor of pure VMgO catalysts with a controlled V/Mg ratio, a high S_{BET} and a high catalytic activity.

A functional magnesium alkoxide $Mg(OCHCH_3CH_2\text{-}OCH_3)_2$ has been synthesized. The derived sol can be cast on a support, dried and fired at 600 °C to obtain VMgO catalyst.

The specific characteristics of the alkoxide derived catalyst, attributed to a high homogeneity of V and Mg species distribution in the molecular precursor, induce attractive catalytic properties for the oxyde-hydrogenation of propane. Some preliminary results have been reported recently [9]. VMgO powders with various V/Mg ratio are currently being investigated in detail and this will give a better understanding of the nature of the catalytic sites active for the oxydehydrogenation of propane.

Tailoring of the mesoporous and microporous membranes by templating effects

The porosity of sol-gel derived ceramic layers can be tailored by incorporation of templating units during their synthesis. These templates can be further removed to generate corresponding pores in the final materials. The choice of the removable units depends on the required pore size and shape. They can be small individual organic, inorganic or metal-organic molecules, molecular aggregates like lyotropic liquid-crystal phases, organic polymers or solid particles [10-12].

The synthesis method of mesoporous molecular sieves using the templating effect of lyotropic liquid crystal mesophases was first proposed in 1992 [13]. Aluminosilicate and silica particles were prepared by hydrothermal synthesis in presence of cationic surfactants. The synthesis of silica networks in ordered amphiphilic media was then obtained by sol-gel routes at room temperature and atmospheric pressure. It was also extended to the use of other kinds of amphiphilic molecules: neutral surfactants [14-15] and block-copolymers [16]. Investigations were carried out in order to enlarge these synthesis methods to the preparation of layers.

Mesophase templated silica layers exhibiting lamellar, hexagonal and cubic structures were obtained. The resulting porous layers are not always continuous and extra-porosity can be observed at a larger scale than the ordered porosity produced by the templating mesophases [17-18].

4-1. Preparation of hexagonal silica layers

The preparation of hexagonal silica films from silicon alkoxides (tetramethoxysilane (TMOS) for sols M and tetraethoxysilane (TEOS) for sols E and alkyltrymethylammonium bromides ($C_nH_{2n+1}{}^-(CH_3)_3NH_4{}^+$, Br^- with n=8, 10, 12, 14 or 16, labeled Cn) was investigated. This study enabled to develop continuous hexagonal porous layers on porous or dense substrates [19].

The porous texture of the layers obtained from sols M and E was characterized by nitrogen adsorption using specific analysis conditions. A precise tailoring of the pore size in the thin layers can be obtained by modifying the surfactant chain length or the sol composition [19-20].

Extension to other oxides

Aluminum and transition metal alkoxides are too-reactive precursors to directly extrapolate the synthesis methods applied in the case of silicon alkoxides. Studies were carried out in the laboratory on alumina or titania using halogenides or alkoxohalogenides as precursors. Ordered hybrid wet gels were prepared, but the ordered structures usually disappeared during the thermal treatment applied for the surfactant elimination. The fact that the inorganic network produced in the wet gels was too tenuous can explain these results.

Zeolite membranes formed by hydrothermal synthesis

The inherent attractive properties of zeolites explain why the preparation and application of zeolite membranes is the subject of intensive research [21]. Such attractive properties include regular pore sizes with molecular dimensions, a high thermal stability, acid or basic properties, possibility of ion exchange, dealumination-relaumination, isomorphous substitution and insertion of catalytically active guests (transition-metal ions, complexes or chelates, basic alkali metal or metal oxide clusters and enzymes). By combining their

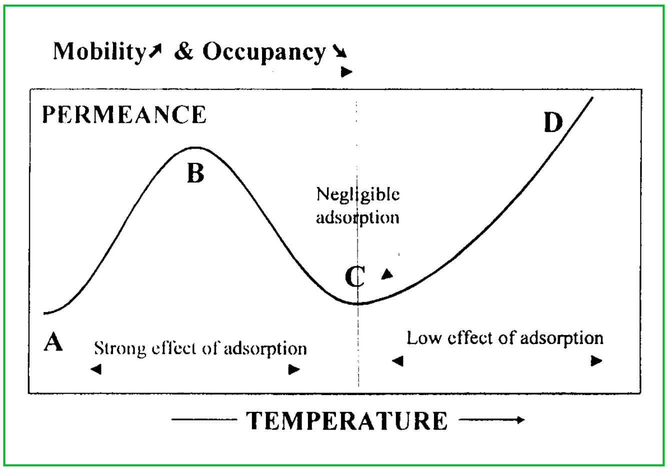

Figure 1 - Schematic evolution of the permeance of single gas through MFI Membranes, as a function of temperature. ABC: activated configurational diffusion; AB: the mobility of adsorbed species increases and the occupancy decreases; B: the increase in mobility cannot compensate the decrease in occupancy; C: adsorption is negligible; CD: activated transport through micropores

adsorption and molecular sieving properties, zeolite membranes have been used for the separation of mixtures containing non-adsorbing molecules, or different organic compounds, or permanent gases/vapors or water/organic.

In spite of the progress made in the field of supported zeolite membranes during the last 10 years, a number of points still need to be explored or further studied such as:

- improve synthesis control and reproducibility;
- control of membrane quality, detection of micro-defects and influence on membrane performance;
- control zeolite crystal orientation;
- extension of membrane synthesis to zeolite structures with smaller pores (e.g. 3 Å);
- clarify transport mechanisms.

Starting from the synthesis method developed in [22], it has been possible to prepare “composite MFI/α-Al_2O_3 zeolite membranes” in which most of the zeolite material was grown *in situ* by hydrothermal treatment, inside specific pores of a commercial α-Al_2O_3 support.

The synthetic method is currently extended to the synthesis of composite MOR (mordenite) zeolite membranes [23].

Concerning the gas transport of single gases in zeolite membranes, the results we obtained with gases able to enter the zeolite channels can be described by (or by a part of) the ABCD curve represented in Figure 1. The region ABC corresponds to a transport by configurational diffusion (decreasing effect of adsorption).

Concepts for advanced membranes using hybrid organic/inorganic materials

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

Type I in which only interactions like van der Waals forces or hydrogen bonds exist between organic and inorganic parts.

Type II in which covalent bonding exists between organic and inorganic parts, resulting either in an homogeneous hybrid material at the molecular level or in high surface area inorganic materials modified through surface grafting of inorganic groups.

Hybrid organic/inorganic membranes for gas separation

Schematization of molecular diffusion in Figure 2 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.

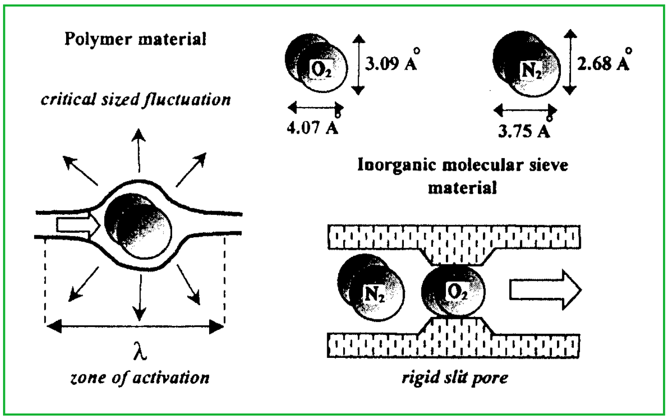

Figure 2 - Comparison of simple transport for gas molecules in dense polymeric membranes and microporous inorganic materials

A fixed pore dimension for molecular sieve materials (carbon or zeolite) induces a selectivity based on small geometrical 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 sieve membranes.

In order to improve permeability and selectivity of these membranes, 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. Such hybrid membranes based on Kapton polyimide segments and crosslinked with silicon coupling agents were described elsewhere [24-25].

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 with the pure polyimide membrane and to keep the selectivity as high as 7.

Hybrid organic/inorganic membranes for facilitated transport

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. An alternative concept to supported liquid membranes is to fix selective complexant sites in a dense polymer matrix (Figure 3). The role of the complexing sites is to increase parti-

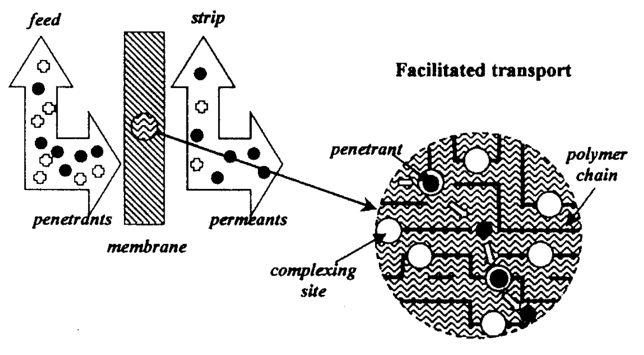

Figure 3 - Schematic representation of facilitated transport using a fixed complexing site membrane

tioning of the component selectivity in the membrane and then to facilitated diffusion of this specific component to this strip phase. The main advantage is to provide membranes with a long lifetime compatible with industrial applications.

Recently, we proposed to use polytopic receptors which present different interaction types with the solute (hydrogen bonding, electrostatic interactions, van der Waals forces) [26]. This new concept of facilitated transport membrane can benefit by using supramolecular chemistry in particular for the transport of charged and solvated solutes with miscellaneous geometry such as molecules of biological interest. Recently, we have grafted such polytopic receptors in a polysiloxane host matrix and prepared thin supported membranes from this material by a sol-gel process.

Using solid dense heteropolysiloxane membranes with grafted polytopic macrocyclic complexants, we obtained the facilitated transport of an amino acid (*L*-phenylalanine) and organic acids (succinic, tartric, aspartic) [26-27].

Thanks to the contribution of supramolecular chemistry, these hybrid membranes, which have an intermediate configuration between liquid membranes (selective complexation with a specific carrier) and ion-exchange membranes (charge interactions), have shown promising transport results. Other innovative separation methods can be expected by supramolecular and autoassembling aggregates in self-organized systems such as molecualr channels, built under control, and anchored in a crosslinked siloxane matrix.

CVD and PECVD and their application to inorganic membrane

Recently, CVD techniques have been explored to prepare microporous composites membranes and dense silica, zirconia or titania membranes. Gavalas and co-workers [28] studied the deposition of amorphous silica inside the porous wall of Vycor glass tube using SiH_4 and O_2 or $SiCl_4$ and H_2O gases.

Burggraaf and co-workers [29] have investigated the deposition of yttria-stabilized zirconia on a porous substrate with varying pore sizes from metal chloride and water vapor. The modified membranes have a potential application and advantages in the development of solid oxide fuel cells (SOFC). The surface modification of membranes by counterdiffusion CVD consists of the deposition of solid oxide in the internal walls of the substrate pore.

When a plasma is used, it is not necessary to heat the substrate. Moreover, it is possible to obtain deposits with the same composition as CVD, but at lower temperature. In this case, the membranes are usually amorphous.

Tungsten were deposited by reducing WF_6 with H_2 diluted with Ar.

The growth rate hardly depends on the WF_6/H_2 ratio and on the pressure of 40 Pa and $WF_6/H_2=1/20$, the growth rate is 3.5 nm min^{-1}, but only 2 nm min^{-1} at 100 °C.

The crystallite mean size is 8 nm when the deposition temperature is 375 °C.

The deposition of aluminum nitride membrane was performed in a capacitively coupled reactor with trimethylaluminum (TMA1) and ammoniac as precursors and N_2 or H_2 as carrier gas [30-31].

The last example concerns organic/inorganic membranes deposited on porous polymer substrates from siloxanes precursors. Two series of siloxane precursors were used for the deposition on porous polymer substrate (esters of cellulose):

- linear: hexamethyldisiloxane (M2) and octamethyltrisiloxane (M3);
- cyclic: hexamethylcyclotrisiloxane (D3) and octomethylcyclotetrasiloxane (D4).

The structure of the deposits is very dependent on the more or less energetic character of the plasma represented by V/P_pM (V=radio-frequency voltage, P_p=the monomer partial pressure and M=the monomer molecular weight), and can be, in fact, turned from SiO_2-like inorganic coatings (high values of V/P_pM) to silicone-like polymers (low values of V/P_pM) [32].

Conclusions

In the last decade, the development of new inorganic membrane materials has gained the advantage of an interdisciplinary approach integrating recent advances in the field of material science.

The sol-gel process is certainly the most appropriate way to produce purely inorganic or hybrid organic-inorganic membranes. CVD and PECVD are also very convenient techniques for the synthesis of ceramic and also metal carbide or nitride membranes on flat or tubular substrates. New material architectures recently developed in mesoporous molecular sieve systems have been successfully transposed to inorganic membrane preparation. Such materials result from the application of new concepts in porous materials, based on the templating effect of supramolecular arrangements. The preparation of supported continuous zeolite layers can also be considered as a major advance in inorganic membranes. They can work either at low temperature for gas and vapor separation or for applications in catalytic reactors. At high temperature, when adsorption is no more effective, they can be used for their molecular sieving or catalytic properties.

Pillared clays is another category of materials able to produce membranes with well-defied pore geometry and size distribution [33]. Carbon microporous membranes can be prepared by pyrolysis of selected polymer films on carbon supports. Dense ceramic membranes exhibiting a mixed ionic electronic conductivity have become of great interest as a means of separating oxygen from air or other oxygen-containing gas mixtures. Main applications for these membranes are in SOFCs technologies and in membrane reactors for partial oxidation of alkanes.

At present, perovskite-type oxygen conductors are one of the most investigated category of ceramic materials with the aim of applying them as dense oxygen separation membranes.

The development of ceramic hollow fibers and of high-tech multichannel supports with very small channel diameters is expected to considerably reduce the volume/surface ratio of modules and extend the competitiveness of ceramic membrane technologies.

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