Ultrafiltration Membrane Made with Mesoporous MSU-*X* Silica

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A new membrane synthesized onto a commercial tubular support was prepared by the directed synthesis of ordered mesoporous MSU-type silica through an interfacial reaction between a silica condensation catalyst (NaF) and new hybrid micellar building units made of silica precursors and nonionic surfactants. This membrane exhibits a specific permeation behavior toward PEO polymers that can be explained by the porosity morphology and silica charge pH dependence.

I. Introduction

Inorganic membranes are semipermeable barriers that prevent two phases from getting into contact. They must be permselective in order to allow only some components of one phase to diffuse into the other, which explains why their transport properties depend on their microstructure, especially the pore size distribution and connectivity.[1] An additional requirement lies in the effective separation layer thickness, which must be as thin as possible to allow a proper steric separation without decreasing the diffusion flow below unacceptable values. To overcome the mechanical strength requirement for easy handling, the actual separation layer is always deposited onto one or several stacked macroporous layers and the successful synthesis of an inorganic membrane requires the ability to build thin, continuous, homogeneous, and defect-free layers onto porous rough supports. These membranes are usually prepared by coating the porous substrate with a colloidal oxide solution. The colloidal particle size defines the interparticle (textural) porosity size, thus the retention capacities.

Micelle templated structures (MTS) were first synthesized by two research groups who almost simultaneously described assembly mechanisms between surfactants and silica species; this led to ordered mesoporous silica identified as MCM-41, MCM-48, and FSM-16.[2−6] These materials attracted considerable attention due to the fact that they offer large surface areas (1000 $m^2 \cdot g^{-1}$) and pore volumes (1 $cm^3 \cdot g^{-1}$) with a narrow mesoporous pore size distribution, which can be mainly adjusted between 2 and 10 nm. Though these materials have been developed mainly for catalytic applications, their specific structure, especially the narrow distribution of pore size, led many authors to suggest that they should be developed as filtration membranes. However, the useful porosity of MTS materials is the structural (intraparticle) porosity, which requires avoidance of any additional textural porosity in the filtration layer. This condition prevents use of any of the usual synthetic pathways for membrane preparation where mesoporous particles are synthesized first. Preliminary results reported the synthesis of supported or unsupported MCM-41-type oriented mesoporous films,[7,8] or the preparation of mesoporous films prepared on dense substrates.[9] However, oriented materials such as MCM-41, which exhibits a hexagonal honeycomb porous framework, appear to be hardly suitable for membrane preparation because the porous network tends to align parallel to the support.[10,11] Therefore, compounds with a 3D porosity such as MCM-48 silica (cubic symmetry) prepared with cationic alkyltrimethylammonium or Gemini surfactants,[3,12] or MSU-*X* silica (3D wormhole

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porsity) prepared with nonionic poly(ethylene oxide)-based (PEO) surfactants,[13,14] seem better candidates. Compared with the wide field of thin layers supported onto nonporous flat supports, for photonic or dielectric applications, only a few studies describe the synthesis of membranes. A MCM-48-based membrane for gas separation was first reported, but it led to an unacceptably thick additional layer on top of the porous substrate that had to be mechanically removed prior to use.[15,16] The deposition of a surfactant-templated silica (STS) intermediate layer on top of a commercial γ-alumina support sublayer by dip-coating was also reported, but it was used only to improve its "surface finish" and to prevent a subsequently deposited microporous overlayer from penetrating into the support.[17] The permeability of a composite membrane made of a polysulfone membrane containing mesoporous MCM-41 particles was also reported.[18]

II. Experimental Section

MSU-*X* (*X* = 1 to 4) (MSU for Michigan State University) refers to the mesostructures formed from surfactant molecules that can be alkyl-PEO (1), alkylaryl-PEO (2), polypropylene-oxide-PEO block-copolymers (3), or ethoxylated derivatives of the fatty esters of sorbitan (Tween) (4). Tergitol 15S12 ($CH_3-(CH_2)_{14}(EO)_{12}-OH$), a linear nonionic polyoxyethylene-based surfactant provided by Union Carbide Chemicals, was used as the structure-directing agent. The silica source was a silicon alkoxide (TEOS: $Si(OEt)_4$ from Avocado). Sodium fluoride (Fluka), sodium hydroxide (SDS), and hydrochloric acid (SDS) were analytical grade compounds. All reagents were used as received. We used a tubular alumina membrane with a 200-mm length and an internal diameter of about 6.25 mm (Société des Céramiques Techniques, France). This membrane is made of three concentric layers of alumina particles with decreasing textural pore sizes from 10 μm (the external thicker layer) to 2.0 μm and finally 0.8 μm, onto which is synthesized the MSU-1 silica membrane. Polyoxyethylene polymers (PEO) solutions of molecular weight from 600 to 10 000 (Aldrich) were used as filtration solutes to determine the membrane cutoff.

The general synthesis process was performed according to the MSU-*X* two-step synthesis pathway.[19] A 0.02 M solution of surfactant was prepared by the dissolution of 1.47 g of Tergitol 15S12 in 95 mL of deionized water. The acidity was adjusted to pH 2 by the addition of 5 mL of 0.2 M hydrochloric acid. A 3.33-g portion of TEOS was then added under magnetic stirring. Stirring continued until appearance of a clear microemulsion containing the hybrid micelles previously reported.[20] The final SiO_2/surfactant molar ratio was equal to 8. The solution was left to stand 24 h at room temperature. An 18-cm length of alumina support was first soaked with a (0.2 M) NaF aqueous solution. A protective film covered the outer surface of the alumina tube in order to avoid any reaction, and the support was then immersed into the microemulsion vessel for 24 h where the fluoride initiated the MSU-*X* formation onto the internal surface of the support. The silica layer synthesized on the alumina support was then dried at 75 °C for 12 h and calcined in air at 620 °C during 6 h with a 6 h preliminary step at 200 °C (heating rate of 3 $°C\cdot min^{-1}$).

Due to the small amount of silica deposited onto the alumina support, neither nitrogen adsorption nor X-ray diffraction measurements could help to characterize its nanostructure. The membrane was characterized by SEM, TEM and filtration tests. TEM was performed using a Philips CM30 T electron microscope with a LaB_6 filament as a source of electrons and operated at 300 kV. The TEM sample was prepared from a membrane thicker than those used for filtration tests: the alumina tube with the membrane was split so the internal surface became exposed. They were impregnated to saturation with Gatan G-1 epoxy and hardener. After hardening at 100 °C, half a matching cylinder of Al metal was glued onto the internal surface using the same Gatan G-1 combination. A cross section was sawed from the ensemble with a diamond saw. This slice was first prethinned by mechanical polishing with sand and emery paper, and subsequently with diamond paste. Finally, the specimen was ion-milled using 4.5 kV Ar ions at an angle of 6° over a section of 60°. During mechanical polishing the thin flake of Al metal was detached from the sample and was discarded. SEM micrographs were obtained on a Hitachi S-5400 FEG microscope. Filtration tests were performed on a homemade filtration bench-test. Standard 15-cm-length membranes were used to separate poly(ethylene oxide) solutions (3 $g\cdot L^{-1}$) with increasing molar weights from 600 to 10 000 $g\cdot mol^{-1}$. Their hydrodynamic radius was calculated according to the following empirical relationship: $Rg = 0.178\ (Mw)^{0.635}$.[21]

III. Results

The synthesis, based on PEO (poly(ethylene oxide)) nonionic surfactants, of MSU-*X* silica powders has been improved by introducing a two-step process with a first assembly step that leads to a stable solution of 8−10-nm hybrid micelles where a low reticulated silica shell surrounds the spherical nonionic micelle.[22] A condensation step is further induced by the addition of a fluoride salt, a well-known silica condensation catalyst.[19,23] This approach provides several advantages, among them being accurate control of the reaction kinetics, as the hybrid micelle solution is stable for days until it comes into contact with fluoride ions. This approach allowed us to direct the membrane synthesis by confining the catalyst at a specific point during the reaction, namely on the surface of the porous ceramic substrate. Silica is then synthesized only onto the surface of this support through an interfacial reaction between the catalyst impregnated in the porous support and the hybrid micelles present in the surrounding solution. Further drying and calcination to remove the surfactant opened the porosity. Such an interfacial reaction mechanism had been explored by Liu et al. for the preparation of continuous mesoporous films onto porous substrates.[24]

Figure 1 displays the SEM observation of a cross-section of the silica membrane after calcination. Surprisingly, no cracks appeared during calcinations. Two conditions may explain this phenomenon. First, the shrinkage of MSU-*X* (prepared according to our two-step synthesis) is rather low because the silica walls are

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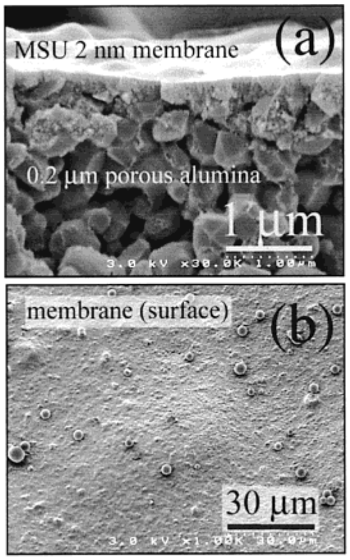

Figure 1. SEM observations of the 2-nm MSU-1 membrane synthesized onto a 0.8-μm alumina sublayer: (a) cross section; (b) surface. SEM micrographs were obtained on a Hitachi S-5400 FEG microscope.

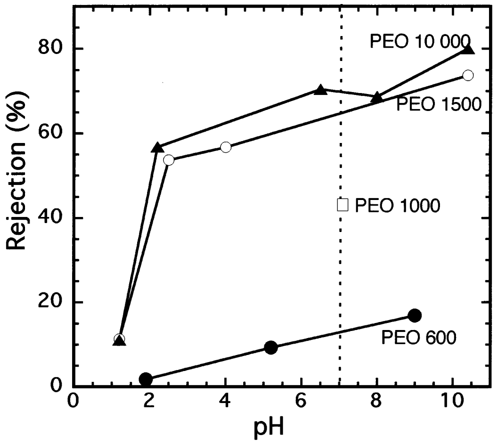

Figure 2. Evolution of the rejection rate of the silica mesoporous membrane as a function of the pH, for different polymers. At pH 7 (dotted line), the cutoff of the silica membrane can be assigned between PEO 1500 and PEO 1500. The test was performed in water with the filtration pressure ΔP set at 4 bar.

much thicker than those of MCM-41 silica. Second, the main parameter for the preparation of crack-free inorganic membrane is its thickness. By obtaining a thin-enough continuous film (200 nm), cracks were avoided (when thicker membranes are prepared, they crack upon calcination). A closer observation of the membrane−support interface shows that the membrane bottom layer is embedded into the top layer of the porous support, which prevents it from being easily pulled off the porous support (Figure 1a). The membrane surface is continuous, and it exhibits only a small amount of defects mainly made up of residual silica particles adsorbed onto the surface (Figure 1b).

The rejection efficiency of the membrane was tested in water ($\Delta P = 4$ bar) with hydrophilic PEO polymers of molecular weights 600, 1000, 1500, 4000, and 10 000, as a function of the solution acidity. The rejection rate as a function of the pH, for the different PEO polymers, is displayed in Figure 2. The general behavior appears to be much more complex than a simple steric rejection mechanism. First, for neutral pH, one observes a steep increasing of the rejection rate between PEO 600 and the higher-MW polymer (see dotted line), which confirms that the silica layer exhibits a narrow pore size distribution with a cutoff at −2000 Da. The pore diameter can thus be estimated, from this cutoff, to lie between 2.0 and 3.0 nm. What is more surprising is the rejection plateau at 80%, even for PEO 10 000 whose size is by far bigger than the expected pore size. This permeability cannot be explained by leaks resulting from membrane defects that would go along with higher water permeation flow than observed (7.5 L·m^{-2}·bar^{-1}·h^{-1} at $\Delta P = 1$ bar to 2.5 m^{-2}·bar^{-1}·h^{-1} at $\Delta P =$ 10 bar). This provides the first clue that the membrane topology could be different from that of membranes formed from colloidal stacked particles layers. One may also remark that one does not reach a full permeability with PEO 600. Indeed, the hydrodynamic radius of PEO 600 is 14 Å.[21] When pH becomes basic, the negative silica charge increases and the effective pore radius (unaffected by the double water layer on silica) decreases, which may tend to decrease the permeability of PEO, even the smallest.

This preliminary observation is confirmed by the behavior of the membrane as a function of the pH. Indeed, from pH 10 to pH 2, only a slight decrease in the rejection capacity is observed. For PEO 10 000 (mean diameter 6.8 nm), however, a total rejection efficiency loss is observed below pH 2. This rejection loss cannot be explained by a membrane deterioration (no flow increase detected), or a configuration change of the polymers shape in solution with pH (checked by light scattering). We undertook TEM analyses of a membrane slice (Experimental Section). Because of the required thickness, only the outer surface reveals details of the microstructure. The TEM analysis confirms the homogeneity of the membrane and the lack of textural porosity. It reveals also an unexpected parallel alignment of 30-nm thick mesoporous silica columns (Figure 3). This specific orientation, with pores that seem almost orthogonal to the support surface, could be assigned to a columnar growth of silica building blocks, induced by the diffusion of fluoride ions out of the support pores. From these observations, one may expect that the pores within these silica blocks will be mostly oriented along their main dimension, hence normal to the substrate surface.

IV. Discussion

These observations, along with the specific filtration behavior, led us to think that the membrane nanostructure brought by this in-situ synthesis, using the hybrid micelles precursors of mesoporous MSU-*X* silica, exhibits a new topology that provides a special behavior of the permeability process. This property should then allow, depending on the acidity, molecules bigger than the pore size to diffuse through the membrane.

We intended to explain these specific properties by two arguments: one regarding the nature of the membrane, that is, the silica; and the other taking into account the cylindrical shape of sparely connected pores. PEO polymer chains in solution behave like statistical spherical coils swelled with water whose shape is a

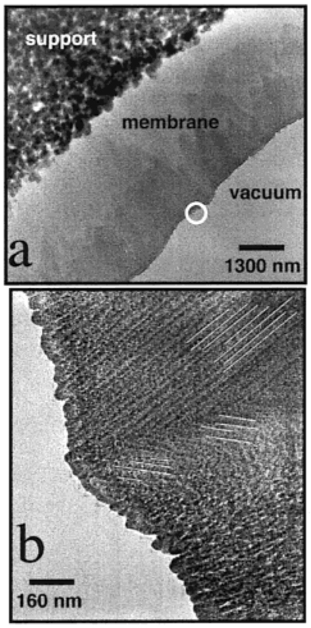

Figure 3. TEM observation of (a) the silica mesoporous membrane and (b) a magnification of its interface (white ring in (a)). White lines parallel to the silica columns were drawn for visual help. TEM was performed using a Philips CM30 T electron microscope with a LaB_6 filament as a source of electrons and operated at 300 kV.

result of an equilibrium between the EO groups elongating and an entropic string effect that tends to shrink these EO chains. This equilibrium leads to the usual ball-like shape, but it can be modified if an external parameter, such as an adsorption strength, is introduced. Interactions between PEO and silica depend on interactions between the oxygen atoms of the PEO chains and the silica surface.[25−27] At pH 7, the PEO oxygen atoms bear a significant negative charge (δ^- −0.44), the positive charge being spread out between carbon atoms.[28,29] This charge will interact attractively or repulsively with the silica, whose surface charge will depend on the medium acidity. Above pH 2, the silica isoelectric point, silica exhibits an increasing negative charge with $Si-O^-$ surface groups. These negative charges will prevent the PEO oxygen atoms from interacting with the silica. The rejection cutoff will thus depend only on a size-exclusion effect. Nevertheless, fractions of larger polymers will be distorted by the flow pressure and can enter the membrane and diffuse throughout, which could explain the limit of rejection rate at 80%, even for the biggest molecules coiled with diameters larger than the pore size. Below pH 2, silica exhibits a positive charge with $Si-OH_2^+$ surface groups. Electrostatic interactions with PEO chains will provide an additional strain term that will allow the polymer to stretch enough to enter the pore. The liquid flow will then allow it to slide into the pore.

This argument can work as far as one takes into account the specific geometry of the pore framework as deduced from the TEM observations. Studies of polymer adsorption in granular porous media have led to the proposal of bridging adsorption mechanisms based on a flow-induced elongation of polymers.[30] This elongation can allow the polymer to adsorb across pore necks formed between particles and to form kinetically stable bridges that will finally lead to the membrane fouling. This mechanism applies obviously to membranes prepared through a classical colloidal particle-stacking process, leading to a textural porosity with a tortuous and branched framework. The bridging mechanism described by Zitha, which explains perfectly the fouling mechanism in granular membranes, can help also to explain that the lack of connectivity of the MSU membrane does not allow the polymers to block the pores, once the pH allows them to enter the pore by the adsorption mechanism. The polymer will thus be confined within the cylindrical pore and will be pushed throughout by the flow pressure. We can compare these observations with HPLC chromatography results operated with MSU-*X* silica where a specific behavior was also assigned to nonconnected long cylindrical pores.[31]

In summary, the synthesis of a silica membrane made of mesoporous structured silica has been possible thanks to the initial preparation of stable hybrid micelles. An interfacial reaction between these micelles and a catalyst at the ceramic porous support surface has led to the synthesis of a homogeneous, defect-free thin (200−400 nm) layer. TEM observations provide the first clues that this silica layer may have grown in an unexpected way, with domains mainly orthogonal to the support surface. That helped to build a sparsely connected cylindrical porous framework that gave a new filtration behavior. This permeation, which depends on the medium acidity, is based not only on steric limits but also on electrostatic interactions. This opens the field to new processes where filtration membranes could allow the separation of ethoxylated polymers from nonethoxylated ones, regardless of their size.

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