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Preparation of templated mesoporous silica membranes on macroporous α-alumina supports via direct coating of thixotropic polymeric sols

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Abstract

A simple method for depositing mesoporous silica films directly on macroporous α-alumina supports is reported. A polymeric silica sol was prepared by hydrolysis of tetraethylorthosilicate in acid propanol in presence of hexadecyltrimethylammonium bromide as template. The rheology of the sol was changed by a modified urea-based thixotropic agent, which was used in a concentration range between 2% and 10% on volume. The dynamic viscosity of the sol was measured as a function of shear rate. The rheology modifier was found to increase the viscosity of the sol and confer at the same time a thixotropic behavior to it. Long range order in the unmodified and modified materials was analyzed by XRD on powders after calcination at 500 °C. It was found that the pore size increased with increasing concentration of additive, while the degree of order decreased until eventually, at high concentrations, the ordered porous structure collapsed completely. The gradual pore size increase at lower concentration is thought to be caused by swelling of the surfactant micelles by the rheology modifier.

The modified sols were deposited via dip-coating on α-alumina disks. The morphology of the silica top layers was characterized by SEM. Pore size distributions and permeances of the prepared membranes were assessed by permporometry and single gas permeation measurements, respectively. The membranes had narrow pore size distributions, with an average diameter of about 2 nm. Permeabilities of H_2, He, CH_4 and O_2 were compared. Hydrogen permeances up to 6×10^{-7} mol s^{-1} m^{-2} Pa^{-1} were measured at 473 K. The gas flux across the membrane follows a Knudsen-type mechanism, as shown by the permselectivities.

Keywords: Mesoporous silica; Membranes; Thixotropy; Rheology modifier; Sol–gel

1. Introduction

Templated silica is one of the most attractive materials for those applications in which a high specific surface area and a narrow pore size distribution in the mesoporous range are required [1,2]. Among all the organic molecules that can be used to tailor the pore structure of the silica matrix, surfactants are the most flexible ones. Silicon oxides with lamellar, hexagonal or cubic pore structure can be obtained under different synthetic conditions by using non-ionic or cationic surfactants as templates [3,4]. The interest in this new class of materials grew when it was discovered that glasses with regular porous structure were formed in the presence of quaternary ammonium surfactants (M41S materials) [5–7]. It was directly recognized that these materials may be applicable in a large number of fields beside heterogeneous catalysis; for example as membranes, sensors and in nano-electronics [8,9]. The two main requirements for a membrane, for instance, are high selectivity and high permeate flux [10]. Thus, templated glasses, which have a high porosity and a regular pore structure, are really attractive materials for the preparation of selective ceramic membranes [11].

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Nomenclature

η	dynamic viscosity [$\mathrm{mPa \cdot s}$]	γ_s	gas-solid interfacial tension [$\mathrm{J \cdot m^{-2}}$]
τ	torque [%]	Φ	flux [$\mathrm{mol \cdot s^{-1} \cdot m^{-2}}$]
u	cylinder velocity	θ	contact angle of the condensed phase on the pore wall
R	gas constant [$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$]	ε	porosity
T	temperature [K]	τ	tortuosity
r_k	kelvin radius [nm]	A_{tot}	total area [$\mathrm{m^2}$]
l_t	t-layer thickness [nm]	M	molecular mass [$\mathrm{g \cdot mol^{-1}}$]
V_{mol}	molar volume [$\mathrm{m^3 \cdot mol^{-1}}$]		

In the first report in which a surfactant templated silica layer was applied in a stacked membrane, it was applied as a spacer [12] between the mesoporous sub-layer and the microporous top layer of a ceramic gas separation membrane. The spacer prevented penetration of the top layer into the sub-layer during deposition. In later works templated silica has also been used to replace the conventional mesoporous intermediate layers [13–15]. However, the application of templated silica films directly on a macroporous support is not trivial. Indeed both sol synthesis and membrane coating procedure are critical steps.

In the first years after the discovery of ordered mesoporous oxides the focus was mainly on the preparation of powders and thin films on dense substrates [5,16]. However, the recipes that were developed for these cases are often not suitable for preparing membranes. Only a stable silica sol, with polymeric particles in the nanometer-size region, can yield a gas-selective membrane. Highly ordered M41S powders can be prepared easily at basic pH via strong electrostatic interaction between the cationic ammonium salt (S^+) and the negatively charged silica particles (I^-) [17,18]. The S^+I^- type interaction is commonly used for making powders. However, in order to synthesize a stable polymeric sol, a high degree of control over the condensation reaction is required. At basic pH the rapid condensation of silica particles would lead to fast precipitation or gelation. But when the pH is slightly below the silica isoelectric point at pH 2–2.5 [19], the condensation rate is at a minimum and it is possible to obtain transparent sols that are stable for many days even at room temperature. Nevertheless, under such conditions the interaction between the cationic surfactant and the slightly positively charged silica particles (I^+) is weaker and it is mediated by the surfactant counterion (X^-). Under such conditions, which are generally described as $S^+X^-I^+$ interactions, it is more difficult to obtain an ordered structure [17]. Furthermore, coating the sol onto a porous support is far more difficult because of the perturbing effect of the substrate on the drying film. Substrate roughness and capillary forces exerted by the substrate pores can easily result in film cracking or distortion of the ordered mesostructure [20]. The coating of a templated silica gel on a macroporous substrate such as α-alumina differs from the coating of traditional colloidal sols like boemite [21], titania [22] or zirconia [23]. In the latter cases the sol is formed by dense particles that have a size between 20 and 50 nm. Large quantities of binder such as polyvinyl alcohol (PVA) are added to change the rheological properties of the sols and the viscoelastic properties of dried uncalcined films. The coating of polymeric silica sols onto α-alumina supports is complicated by the fact that the polymeric silica sol is formed by particles that are far smaller (only a few nm [24]) than the pores of the support, which are often larger than 80–100 nm diameter. Furthermore, binders can be used only in small concentrations in order not to affect the supramolecular ordering of the surfactant micelles. The necessity to work in a restricted range of synthetic conditions, the difficulty to coat a polymeric sol onto a macroporous support, and the impossibility to use ordinary binders makes the coating of mesoporous silica films on porous substrates a challenge.

Templated silica membranes applied directly on α-alumina substrates were successfully made by Roy Chowdhury et al. via dip coating [13,14], and by Huang et al. via casting [15]. Solvent transport through membranes prepared by Roy Chowdhury et al. showed behavior which is typical for truly mesoporous systems. On the other hand, the XPS depth profiles implied the absence of a real silica layer after calcination [13]. The concentration of aluminium at the surface of the membrane was larger than that of silicon, which suggests that the membrane was constituted by silica penetrated into the substrate [14,25].

In recent years two solutions to this problem have been proposed. The most common way for preparing templated silica membranes is via hydrothermal growth of the material on top of a substrate. The substrate is immersed in a mixture containing surfactant, solvent and an organic or inorganic silica precursor [26,27]. Water and a base are present to promote the hydrolysis and condensation reactions that lead to the formation of silica. Membranes obtained with this procedure were gas selective and applicable in nanofiltration processes [28]. In spite of that, silica grew both inside and on top of the support, forming a resistive thick layer. An alternative procedure has been introduced by Boissiere et al. [29]. A tubular support was impregnated by an aqueous solution of NaF. NaF catalyzes the condensation reaction of the silica precursor. In this way the growth of the selective silica layer was restricted to the area on top of the support. In order to be reproducible this procedure requires a high degree of control over all the parameters involved in the preparation.

In this work, we propose a different approach to deposit templated mesoporous silica membranes directly on macroporous supports. It involves tuning of the rheological properties of the sol to render it a thixotropic behavior, so that it can be coated directly on a macroporous substrate. We modified the rheological properties of a polymeric silica sol by adding BYK-420 (kindly provided by BYK-Chemie, Wesel, Germany), which consists of a modified urea solution. BYK-420 is a commercial additive used in aqueous coatings to improve anti-sagging properties or as anti-settling agent for pigments. This product is able to increase the viscosity of a suspension, conferring thixotropy at the same time. The thixotropy inhibits penetration into the pores of the α-alumina substrate during the drying stage of the silica film. This behavior can simplify the processing of polymeric sols in the preparation of silica membranes.

2. Experimental part

2.1. Sol synthesis

Aqueous nitric acid (0.05 N) was dropped under vigorous stirring in a conical flask containing a solution of tetraethylorthosilicate (TEOS, 98% purity, Aldrich), in 1-propanol (analytical grade, Acros). After 5 min the templating agent cetyltrimethylammonium bromide (CTAB, ⩾99% purity, Aldrich) was added. The molar ratio of the final mixture was TEOS/CTAB/1-propanol/H_2O/HNO_3 = 1:0.13:15:15.5:0.14. All reagents were mixed under nitrogen atmosphere in order to avoid the hydrolysis of TEOS before the reaction started.

The mixture was heated at boiling temperature for 2 h under reflux; then it was allowed to cool down. The transparent sol was kept at 5 °C for a few days until it was used for sample preparation.

2.2. Thin film deposition and powder preparation

α-Alumina disks were used as macroporous supports for film deposition. They were prepared by colloidal filtration of α-alumina powder (AKP30, Sumitomo, Tokyo, Japan) dispersed in acidic water, as described elsewhere [30]. After drying at room temperature, the green supports were calcined at 1100 °C (heating/cooling rates of 2 °C/min). Flat disks of 39 mm diameter and 2.0 mm thickness were obtained after polishing. The final porosity of these supports was about 30% and the average pore size was in the range of 80–120 nm [31].

Varying amounts of BYK-420 (BYK-Chemie, Wesel, Germany) were added to the aged silica sol and the mixture was stirred for a few hours. The alumina macroporous supports were then dip-coated in the solution under class-1000 clean room conditions. The samples were dried at 40 °C in air (60% relative humidity) for 3 h. The membranes were then fired at 500 °C for 3 h (heating/cooling rates of 0.5 °C/min). After deposition of the first layer macropores in the support could still be detected by permporometry in all samples, irrespective of BYK-420 concentration. In order to cover these defects a second coating layer was applied, followed by calcination.

Table 1
Coating solutions (S) used in this work for the preparation of powders (*P*) and membranes (*M*)

Coating solution	BYK-420 volume fraction	Name of unsupported sample	Number of layers	Name of membrane
S00	0.00	P00	*	*
S02	0.02	P02	2	M02
S06	0.06	P06	2	M06
S10	0.10	P10	2	M10

*No membranes were obtained without BYK-420.

Powders were prepared by drying the same sols as used for thin films in plastic Petri-dishes. Table 1 lists the different concentrations of additive used for preparing powders and thin films. For the sake of simplicity we will refer to the samples following the designations listed in Table 1.

2.3. Characterization

The viscosity of the coating sols were measured by a Brookfield DV-II+ Programmable Viscometer (Brookfield Engineering Laboratories, Middleboro, MA, USA). The instrument was calibrated using Brookfield fluid 5 (Brookfield Engineering Laboratories, Middleboro, MA, USA) as standard. The viscosity of this fluid is 4.8 MPa at 25 °C. The temperature was kept constant at 30 °C by a thermostatic water bath. The viscosity was measured using a 90 mm long cylinder with a diameter equal to 25 mm and a weight of 78.5 g. The cylinder was stirred in 25 ml of sample contained in a metallic tube. Data were recorded with increasing angular speed, ranging from 1.0 to 10.5 rad s^{-1}, followed by stepwise decreasing the speed to 1.0 rad s^{-1}.

All data on powders and films reported in this paper concern calcined samples. XRD patterns of powders were recorded using a Philips SR5056 with Cu Kα radiation. Nitrogen sorption measurements were performed at 77 K on calcined silica, using a porosimeter (Micromeretics, ASAP 2400). Pore size distributions of templated silica membranes were measured by permporometry using the type of set-up described by Cao et al. [32,33]. In the permporometer the flux of oxygen across the membrane was measured by a Varian 3300 gas chromatograph (Varian, Palo Alto, CA, USA). Scanning Electron Microscopy (SEM) images were taken on a LEO 1550 FEG. Single gas permeation measurements were carried out in a dead-end mode permeation set-up [34]. The gas flow was measured with a soap film flow meter. Hydrogen, helium, methane and oxygen permeances were measured on different samples at 200 °C, with a pressure of 4 bar on the side of the feed and atmospheric pressure on the retentate side.

Since atmospheric water can condense in the pores of the silica matrix, all membranes were dried at 200 °C in a hydrogen flow for at least 16 h before measurements were done. In a typical series of measurements, the permeation rate of different gases was determined starting from the one with the lower molecular mass, and equilibrating at least 2 h each time a new gas was introduced into the set-up.

3. Results and discussion

3.1. Sol modification

BYK-420 is a pale yellow solution and 52% of the total weight is non-volatile material. It is constituted by modified urea, which is stabilized in solution by *N*-methylpyrrolidone. Once the product has been added to the final coating solution the modified urea crystallizes in the ethanol-based solution, yielding thin fibers which result in a tridimensional network. This network confers pseudo-plastic behavior to the coating mixture. BYK-420, like other products with similar composition, is effective at 1–3% in volume, but cannot be applied to all sols. In very polar or highly non-polar systems the active component precipitates in the form of white powder.

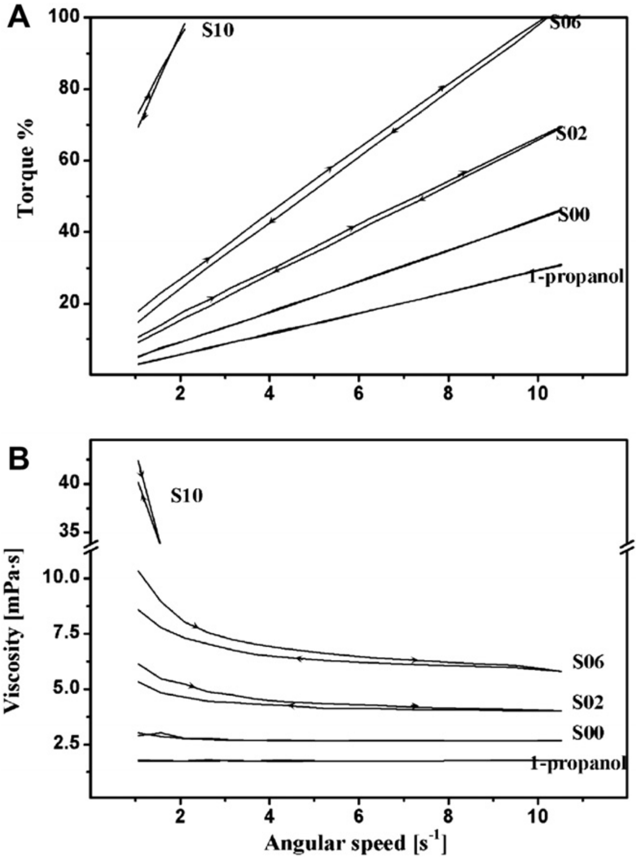

Fig. 1. Rheological properties of solvent and silica sols, before and after being modified with BYK-420. (A) Torque stress against the cylinder angular speed; (B) viscosity versus angular speed. The names of the samples are indicated on the right side of the graphs. Angular speed is expressed in rad s^{-1}.

The rheological properties of the modified sols are shown in Fig. 1. Prior to measurement, the coating solutions were prepared by stirring 50 ml of silica sol with an adequate amount of additive for 2 h. Fig. 1A shows the torque versus angular speed of different solutions. The viscosities of solvent and sols shown in Fig. 1B were calculated from these data according to the formula [35]:

$$\eta = K_1 \cdot \frac{\tau}{u}. \tag{1}$$

K_1 is a constant that depends on the geometry, weight and dimensions of the spindle stirring the fluid. As can be seen in Fig. 1B, the viscosity of both solvent and unmodified sol is independent of shear rate, which indicates that they behave as Newtonian fluids. The viscosity of 1-propanol was measured to be 1.76 mPa s, which is in agreement with the literature value of 1.72 mPa s at 30 °C [36]. The viscosity of the unmodified coating sol S00 was measured to be 2.71 mPa s.

After addition of the modifier the viscosity increased over the whole range of shear rates. The increasing viscosities at lower shear rates shown in Fig. 1B indicate the occurrence of pseudo-plasticity in the sols. After leaving the sols undisturbed for a while it was seen that the viscosity at the onset of a measurement increased to values higher than 5 MPa s for sample S02. The sol also became thixotropic after addition of BYK-420, since it was observed that the high viscosity of the coating solution is partially reduced upon prolonged stirring. This phenomenon is visible in Fig. 1A and B, where hysteretic behavior can be observed in the curves of the urea-containing sols. Higher concentrations of BYK-420 yielded sols with higher viscosities. These observations show that BYK-420 can be a suitable rheology modifier to tune the visco-elastic properties of silica sols. The appearance of S10 was turbid. Turbidity usually implies that it is not suitable for preparation of a defect-free membrane coating. A membrane was however prepared with this sol and its permporometry profile will be shown below. Concentrations of additive higher than 10 vol% on total volume resulted in unstable silica sols in which precipitation occurred rapidly.

3.2. Powder analysis

Templated silicon oxides were prepared as powder with the aim to analyse the intrinsic properties of the material and to study the effect of the rheological additive on the mesoporous structure. The XRD profile of P00 in Fig. 2 after calcination at 500 °C shows a broad peak at 2.7° 2θ, indicating the presence of long range order.

Fig. 2 also shows the XRD patterns of three powders prepared with different concentrations of BYK-420, and calcined at 500 °C. The XRD peak of P02 is broader but more intense than the one obtained from P00. The increased peak intensity can probably be explained by the

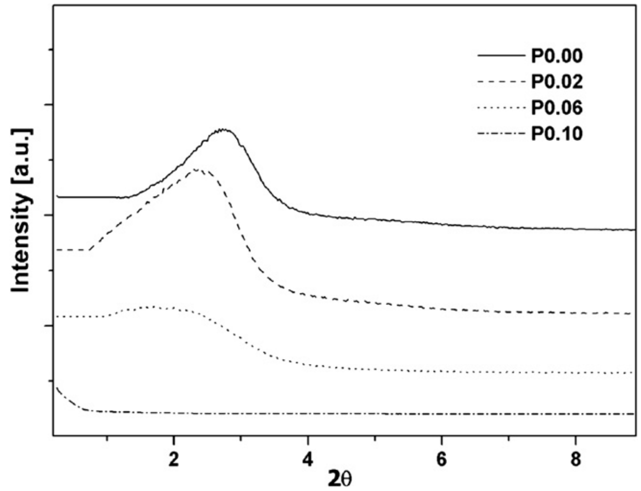

Fig. 2. XRD patterns of powders obtained with different concentrations of BYK-420 after calcination at 500 °C.

longer drying time of sol S02, which is due to the presence of the slow evaporating cosolvent *N*-methylpyrrolidone. As a result the micelles have more time to form an ordered mesostructure. In general, we found that the rheological additive had a perturbing effect on the degree of order in the templated microstructure: from P00 to P06 the peak became progressively wider and in the case of P10 it had disappeared completely. We may suppose that at least one of the components of BYK-420 is strongly interacting with the surfactant and perturbing the formation of micelles. Both solvent [37] and organic modifier [38,39] may cause the micelles either to swell or shrink, leading to larger or smaller pores in the final oxide. However, it has been noticed that the degree of long range order is higher when no perturbing agents are present [3]. Anderson et al. [40], for instance, monitored by XRD the long range order in templated silica obtained by hydrolysis of tetramethoxysilane in aqueous methanol. The long-range order of the material decreased as the methanol concentration increased, while at concentrations higher than 70 wt% a disordered arrangement of pores was observed. In Fig. 2, the shift of the reflection signal from 2.7° for P00 to about 2° for P06 suggests that BYK-420 causes an enlargement of the surfactant micelles. Indeed, similar XRD results have been obtained, for instance, by adding decane as swelling agent to a silica sol in the preparation of MCM-41 [41].

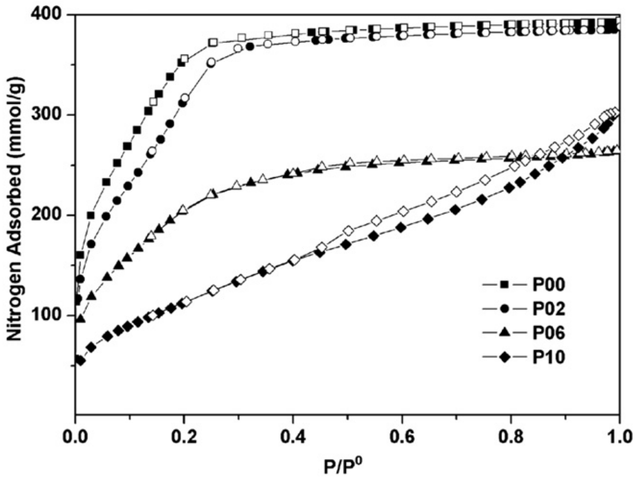

Fig. 3. Nitrogen sorption isotherms at 77 K for four samples prepared with various BYK-420 concentrations: adsorption (black bullets) and desorption (white bullets) isotherms are shown.

Table 2
BET surface area, pores fraction and average pore width as obtained from nitrogen sorption data

Sample	BET Surface area (m^2/g)	Porosity	BET average pore width (Å)
P00	1380	0.61	18
P02	1220	0.60	20
P06	790	0.40	21
P10	420	0.44	42[a]

[a] Average value of pores smaller than 650 Å. This is an average value of a broad distribution.

These considerations are supported by the sorption curves in Fig. 3 and the data listed in Table 2. The increase of the concentration of rheology modifier led to the formation of a denser material, with lower specific surface area and porosity, and larger pores. Comparison of the sorption curves of P00 and P02 indicate that a small amount of additive BYK-420 does not change the total porosity of the material considerably, but it does increase the degree of mesoporosity, as illustrated by the BJH pore sizes in Table 2. At higher concentrations of BYK-420 the specific surface area decreased and the pores became larger. In the case of P10 a hysteresis loop appeared in the sorption–desorption cycle. The specific surface area was reduced from 1220 m^2 g^{-1} in P02 to 423 m^2 g^{-1} in P10, while the average pore diameter of P10 was 4.2 nm, more than double of that measured for P00. It is stressed that the average pore diameter was calculated from the BET pore volume and specific surface area. While the pore size distributions of P00, P02, and P06 were narrow, the pore size distribution of P10 was broad. Hence, although P10 has an average pore diameter of about 3.9 nm, this value is not so relevant in view of the broadness of the distribution.

3.3. SEM images

Fig. 4A and B shows SEM pictures of doubly coated and calcined M02 at different magnifications. The templated silica layer is seen to completely penetrate the support, without forming a continuous layer on top. Penetration into the support was inhomogeneous and was at least a few micrometers in depth. Upon increasing the concentration of the rheological additive to 6 vol%, a continuous flat layer was obtained as shown in Fig. 4C. The layer covered the rough support, yielding a thin film with a long range modulation of $\sim$1 μm period. In Fig. 4D a close-up of an α-alumina grain covered by the silica film is shown.

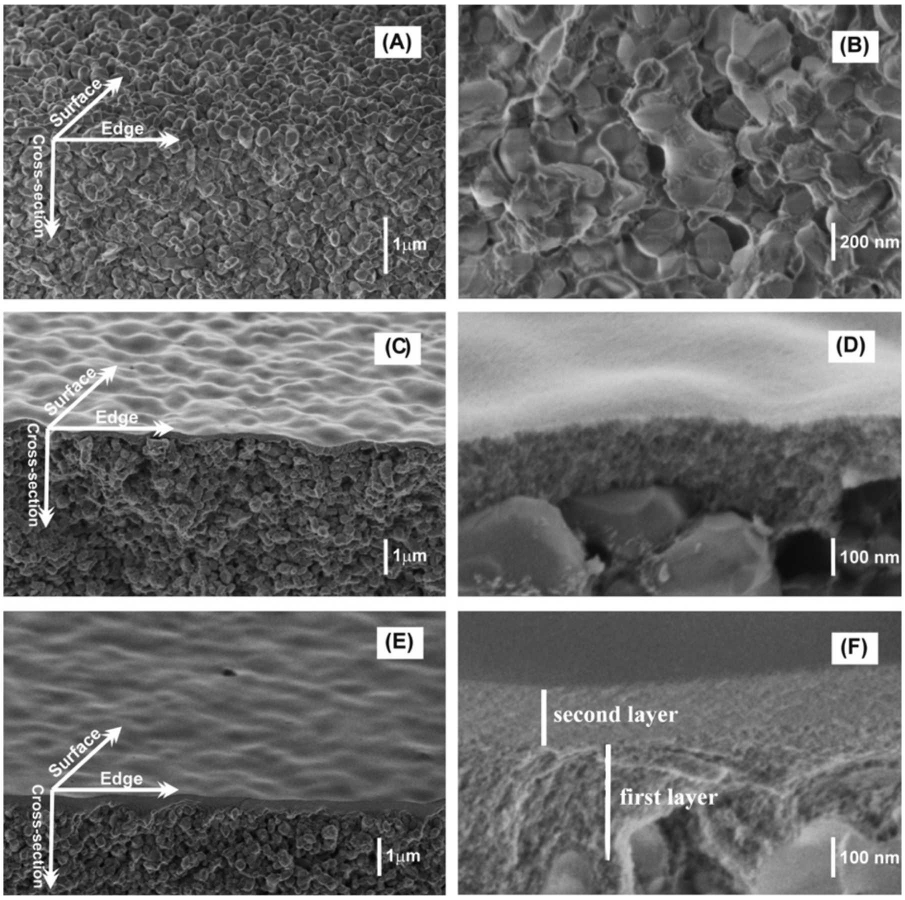

Fig. 4. SEM pictures of membranes prepared with different binder concentrations. (A) M02 twice coated: cross section and surface. (B) M02: penetration of the silica sol inside the pores of the support. (C and D) M06 after the first coating. (E and F) M06 after the second coating.

The picture shows how the grains of the support are responsible for the modulation of the silica film. After the second coating a smoother layer was obtained, as shown in Fig. 4E. Thickness and morphology of the first and the second coated layer after calcination can be compared in Fig. 4F. In the figure the different layers are marked by white bars. The thickness of the first layer is inhomogeneous along the membrane surface, depending on whether it covers voids or α-alumina grains. In contrast, the second layer is about 170 nm thick over the entire surface area of the membrane. The surprising difference in morphology between the first and second coated silica layers is noted. The second coated layer looks more compact and is more regular than the first one. Indeed it is well known from the literature that the morphology of the support plays an important role in the development of morphology of templated silica films [42,43].

3.4. Permporometry

Permporometry is an effective technique for determining the pore size distribution of a mesoporous layer on a macroporous support, and to check if defects in the layer are absent. In short, two incondensable gases (nitrogen and oxygen) are injected at the two sides of the membrane. During the measurement the pores are selectively blocked by the condensation of a vapour (cyclohexane). The pore size in which capillary condensation can still occur is expressed as function of the relative cyclohexane pressure by the Kelvin equation [44]:

$$\ln P_{\mathrm{r}} = -\frac{\gamma_{\mathrm{s}} V_{\mathrm{mol}}}{RT} \frac{1}{r_{\mathrm{K}}} \cos\theta, \tag{2}$$

where θ is normally considered equal to 0. For each relative pressure all pores with radii smaller than the threshold value r_{K} are blocked by the condensed vapour. At a relative pressure of 1 all pores of the membrane are filled and gas transport trough the membrane is not possible when no macroscopically large defects and cracks are present. When the vapour pressure is reduced, pores with larger size than r_{K} are emptied and become available for gas transport. During the experiment the pressure at both sides of the membrane is kept equal to 1 bar, so that no pressure gradients are present in the system. r_{K} is the Kelvin radius of the pore, which does not correspond to the actual pore radius. To obtain the real pore radius it must to be corrected by adding the thickness of the cyclohexane monolayer, which forms on the surface of the pores before capillary condensation occurs [45]. This layer is generally called t-layer and here it is indicated as l_t. The l_t thickness can be estimated from the oxygen permeation at low cyclohexane relative pressure and is generally about 0.4 nm thick [45]. In the case of templated silica, which has pores in the region between truly microporous and mesoporous it was not possible to calculate its value. Therefore, in this paragraph we refer to the Kelvin radius of the pores only.

The results of permporometry measurements are reported in Fig. 5A. In order to calculate the pore size distribution a few assumptions were made. First of all we assumed that gas diffusion occurred in the mesoporous regime; therefore the transport across the membrane can be expressed by the Knudsen equation [46]:

$$\Phi_{\mathrm{A}} = -\frac{\varepsilon r}{\tau}\frac{2}{3}\frac{\mathrm{d}P}{\mathrm{d}z}\sqrt{\frac{8}{\pi M_{\mathrm{A}} RT}}. \tag{3}$$

This assumption is justified by the fact that in literature Knudsen flow has been reported for silica membranes that had been prepared with CTAB micelles as templates [47].

The geometry of the pores also plays a role. Assuming that all pores are cylindrical and parallel, we can express the density function with the following equation:

$$n(r_{\mathrm{K}}) = -\frac{3}{4}\frac{\tau l A_{\mathrm{tot}}}{r_{\mathrm{K}}^3}\sqrt{\frac{RTM}{2\pi}}\left(\frac{\Delta F_{\mathrm{acc}}}{\Delta r}\right). \tag{4}$$

Eq. (4) was used to calculate the pore size distribution of M06 in the different stages of its preparation, as shown in Fig. 5B. The distributions were derived assuming a cylindrical pore shape and normalized to unity. The support has pores with Kelvin radii larger than 40 nm. After the first deposition of S06 two different kinds of pores were detected (see Fig. 5B): a distribution of pores with main radius equal to 1.3 nm, which is a typical value for CTAB-templated silicas [26], and larger pores, which may be macropores of the support that are only partially occluded by the deposited layer. After the second coating the average pore Kelvin radius was about 1 nm and no defects were detected. As we already mentioned in Section 2, we were not able to prepare a defect-free membrane based on just one dip-coated layer. For this reason a second coating was applied on all samples presented here.

As shown in Fig. 5A, M02 and M06 showed similar permporometry profiles, but M02 was more permeable to oxygen. Despite the fact that no layer was observed with SEM (see Fig. 4A), in M02 the deposited templated silica film appeared to form a selective barrier with pores smaller than 5 nm. Therefore, we may conclude that the membrane is defect-free. In Fig. 5C the pore size distributions of the powder and the membrane obtained from S02 are compared. In the case of the powder the distribution was calculated by nitrogen desorption at 77 K using the BJH

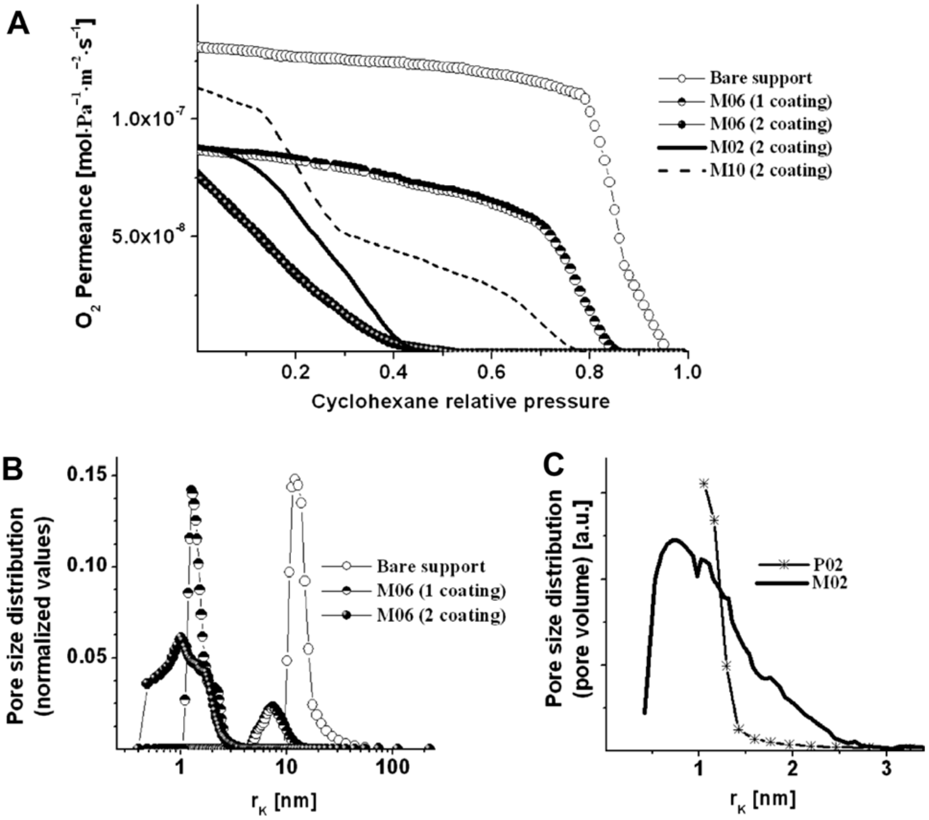

Fig. 5. Permporometry analysis of support and membranes: (A) oxygen permeance as function of the cyclohexane relative pressure; (B) evolution of the pore size distribution of M06 in the different stages of the membrane preparation, calculated according to the Eq. (4); (C) comparison between the pore size distributions of powder (N_2 desorption, BJH method) and supported film (permporometry, desorption mode) obtained from the sol S02.

method. Although pores with radius smaller than 2 nm cannot be assessed with this method, the assumptions on which the calculation is based are similar to those that have been used above for the determination of a distribution from the permporometry measurement, namely (1) pores in the mesoporous regime, (2) validity of the modified Kelvin equation and (3) cylindrical pore shape. Hence direct comparison of the two curves, which are derived from materials obtained from the same sol, is allowed. The average pore diameter of supported silica M02 was calculated from the distribution in Fig. 5C and was found to be 1.8 nm. This value is comparable with the one obtained for P02, which was 2.0 nm. Despite the fact that the main pore width is almost the same for the two samples, the pore size distribution of the supported film seems to be broader than that one of the powder, and it also has a consistent number of larger pores. This difference can be attributed to the lower shrinkage of the supported material during calcination as a result of being clamped to a rigid support. Furthermore, the drying rate of thin films is much faster because of the higher surface/volume ratio and the effect of solvent drainage by the porous support. The rate of drying can affect the structure of the sol since longer drying times provides more time for the sol to condense into a more regular mesostructure.

At a cyclohexane pressure equal to zero, M10 was more permeable to oxygen than M02 (Fig. 5A). Nevertheless oxygen permeated through the membrane already at a relative pressure of about 0.75, which corresponds to pores with a Kelvin radius of about 8 nm. This observation is in agreement with what was measured by nitrogen sorption on P10, a measurement in which pores larger than in the other samples were observed. S10 yielded more permeable membranes, but these are less selective in processes in which particles/molecules with sizes below 10 nm are involved.

3.5. Gas permeation

As a general rule the flow of a gas permeating through macroporous media can be described in terms of viscous flow. Knudsen diffusion is typical for transport of gases in mesopores, and for micropores the transport rate is generally described in terms of activated transport [46]. We suppose that Knudsen transport is dominant in our material; indeed the sorption data in Table 2 show that the prepared materials are mesoporous.

From Eq. (3) it follows that the ideal permselectivity for a binary mixture consisting of gases A and B (where $M_B > M_A$) that are permeating through a mesoporous membrane is:

$$\alpha_{A/B} = \frac{\Phi_A}{\Phi_B} = \sqrt{\frac{M_B}{M_A}}. \tag{5}$$

In the system under consideration here, a mesoporous thin film is supported by a macroporous α-alumina support. Permselectivities below the Knudsen limit (Eq. (5)) indicates a defective mesoporous layer, i.e., a membrane with a significant contribution of non-selective viscous flow on the overall rate of molecular transport. Therefore, gas permeation measurements not only give a direct indication of the performance of a membrane in terms of flux and selectivity, but may also provide a proof of either the presence or absence of macroscopic defects in the silica layer. As reported in Fig. 6, Knudsen-type selectivity was observed for M02 and M06. This means that all support macropores are filled or covered with a templated silica layer, and the layer does not have measurable defects.

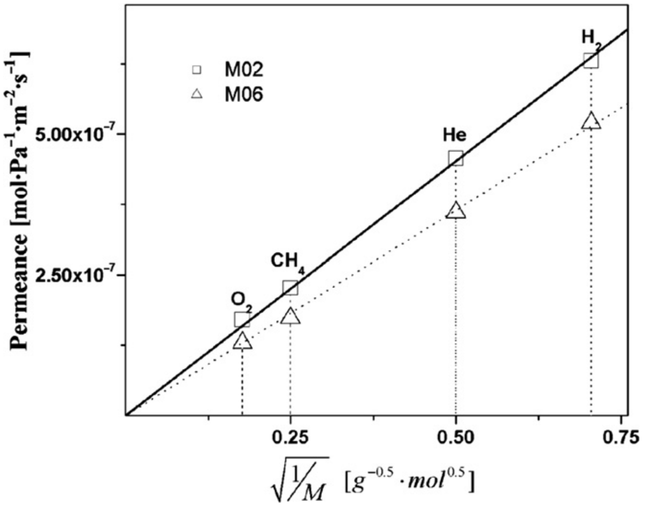

Fig. 6. Single gas permeance of templated silica membranes M02 and M06 as function of the molecular mass of the probe molecules. The Knudsen behavior of M02 and M06 is stressed respectively by a continuous line and a dotted line.

A “defect free” templated silica membrane can be defined as a film with the selectivity of a mesoporous layer. This definition is often used in membrane technology in cases in which membrane selectivity is more important than the intrinsic structural quality of the separating layer. Gas permeation and permporometry, which are methods based on the measurement of membrane performance, have been used as a proof for the absence of defects in the top-layer. This is certainly true for mesoporous layers obtained by deposition of colloidal sols, where penetration is negligible and membrane performance is determined by the quality of the top layer. On the other hand, in the case of membranes obtained by polymeric sols the penetrated material also plays a role. The most representative case is membrane M02: although Knudsen separation was observed for this membrane and its pore size distribution was in the mesoporous range, Fig. 4A clearly demonstrates that a top layer that is as such recognizable is completely absent. Hence, gas permeation measurements are not an exhaustive proof of the existence of a continuous porous film obtained from a polymeric sol. The high resistance to gas transport of M06 suggests a comparable degree of penetration of silica into the α-alumina support. In the case of M06 some degree of penetration is visible in Fig. 4C. BYK-420 is an effective additive in order to obtain silica membrane on a macroporous α-alumina. Nevertheless it is not possible with this method to avoid penetration in the support completely. In Fig. 4C silica on the α-alumina grains is still visible in a region deeper than 1 μm.

The permeance values reported in Fig. 6. are higher than those obtained by Nishiyama et al. [26] with membranes that had been prepared by hydrothermal treatment on commercial alumina plates (NGK Insulators, Ltd.). The hydrogen permanence of those membranes was about 2.7×10^{-7} mol Pa^{-1} m^{-2} s^{-1} at 295 K, while that of the asymmetric supports was 1.1×10^{-4} mol Pa^{-1} m^{-2} s^{-1} at a temperature of 295 K and an overpressure of 2.7 bar. These commercial substrates had on the top a pore size of about 0.1 μm, which is similar to that of the home-made supports utilized by us. The supports that we used were prepared by colloidal filtration from a suspension of alumina powder in water. Commercial supports are usually asymmetric systems with smaller pores located on the side where the coating is deposited, and pores of a few microns width on the opposite side. Commercial supports have gas resistances smaller than 10^5 Pa m^2 s mol^{-1} (expressed as the reciprocal of permeance), but often a high number of defects is present on their surface. The symmetric supports prepared by us have a ten times larger resistance. On the other hand their surface is very well defined. The roughness depends only on the alumina grains, which have dimensions of a few hundred nanometers. Defects like scratches or holes are not detectable by optical analysis. For this reason we chose them as support for lab testing and preliminary studies. The next step of this research is to test this procedure on commercial tubular supports, which will eventually yield membranes with enhanced permeances.

4. Conclusions

Templated silica membranes were successfully prepared by direct coating of a thixotropic polymeric sol onto a macroporous support. BYK-420 was able to confer a thixotropic behavior to the sol at relatively low concentrations. As result the penetration of the sol into the support during the coating procedure was strongly inhibited. Doubly coated membranes showed no indications of defects and pores larger than 5 nm were not detected, while the main pore width was about 1.8 nm. Membranes with such pore size distribution can be applied as molecular sieves in many industrially relevant processes. For instance they can be use in order to separate homogenous catalysts [48] or drugs [49,50] from their reaction mixtures.

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