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Sol–gel derived silica membranes with tailored microporous structures

A. Ayral, C. Balzer, T. Dabadie, C. Guizard *, A. Julbe

Laboratoire des Matériaux et Procédés Membranaires —CNRS UMR 9987, Ecole Nationale Supérieure de Chimie, 8, rue de l'Ecole Normale —34053 Montpellier Cedex 1, France

Abstract

The template effect of amphiphilic systems on the porous structure of silica gel layers has been studied. Membranes with a tailor-made microporosity and pore diameters of between 1 and 2 nm were obtained from these gels. Two different preparation methods have been used and their influence on the sol-to-gel transition of silicon alkoxide sols has been investigated. The first method entails the incorporation of non-ionic surfactants which modify the porous structure of gels. In this case, specific surface area, pore size and porous volume can be varied in the final material as a function of chain length and concentration of the surfactant. In the second method, self-assembled systems made of cationic surfactants develop during the gelation process and lead to an ordered gel structure. After elimination of the organic mesophase by heating, the membrane material exhibits an ordered microporosity with pore size directly related to the size of the surfactant molecules.

1. Introduction

Dense and porous inorganic membranes have been extensively investigated for application in membrane reactors. Commonly used materials for dense membranes have included metals or metal alloys (palladium and palladium alloys, platinum, silver, nickel ...) and more recently dense ceramics (stabilized zirconia, perovskite-type oxides ...). Certain gases e.g. hydrogen or oxygen are selectively transported through these membranes via a diffusion mechanism. Their high selectivity make them good candidates for membrane reactors, although their rather low permeabilities and stability problems are disadvantages mainly in the cases of the metal membranes. In contrast micro and mesoporous ceramic membranes can exhibit rather high permeabilities, selectivities and stabilities. These properties require a very sharp control of the porous structure (pore sizes and pore size distribution) and a small membrane thickness without defects and pinholes.

Until recently mesoporous ceramic membranes have been obtained by the sol–gel process and successfully applied to liquid filtration [1]. Other recent works have been devoted to the preparation of microporous membranes [2–5]. Their characteristics do however not exactly fit the requirements for membrane reactors and most of the applications reported for porous ceramic membranes failed or exhibited a poor efficiency, mainly because of the texture or/and the porous structure. New developments in the field of ceramic membranes are anticipated from the application of recent advances in the sol–gel process [6,7]. One of them concerns the use of the

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* Corresponding author.

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polymeric route with reactive media containing molecular precursors and amphiphilic systems. These systems include the use of surfactant molecules and liquid crystals as template agents in order to obtain sol–gel derived inorganic membranes with a tailored porous structure. In the present work, this concept is illustrated with the preparation of silica membranes exhibiting a microporous structure with pore diameters in the 1 to 2 nm range. This pore size range has recently been recognized as very important to achieve a high conversion rate and high selectivity in membrane-mediated chemical reactions.

2. Experimental

2.1. Preparation of silica gel layers containing non-ionic surfactants and related membranes

Sols were prepared from TEOS (commercial tetraethylorthosilicate, Aldrich). Hydrolysis of the alkoxide, diluted in ethanol, was performed in acidic (HCl) medium by refluxing at 80°C for one hour. The hydrolysis ratio was fixed at 4 using ultrapure water (18 MΩ). The resulting molar composition of a standard sol is TEOS (1)/ethanol (4.5)/water (4)/HCl (0.02). Non-ionic surfactants (Triton from Rhom and Haas) were introduced into the refluxed sols, cooled at room temperature. The general formula for the Triton surfactants is $(CH_3)_3C(CH_2)C(CH_3)_2$–C_6H_4–$(OCH_2$–$CH_2)_X$–OH with X the length of the polyoxyethylenic chain. Surfactants with $X = 1, 3$, 9–10, 30 were tested in sol preparation.

Unsupported gel layers were prepared by casting sols on aluminum foils. After drying in air at room temperature, the pieces of transparent film were removed from the support and fired at 450°C for 2 hours in alumina crucibles. The corresponding membranes were obtained by slip-casting TEOS polymeric sols on asymmetric α-alumina tubular supports (SCT-US Filter) which were previously coated with a mesoporous silica membrane using a method already published [8]. The microporous membranes were fired at 450°C for 2 hours under flowing air.

2.2. Preparation of silica gel layers containing self assembled amphiphilic systems and the related membranes

In this case TMOS (tetramethoxy orthosilicate, Aldrich) was used as molecular precursor for the formation of gel layers in the presence of cationic surfactants. Alkyltrimethylammonium bromides with alkyl chain length C_x varying from $x = 8$ to 14 carbons were directly introduced into the sol with water and TMOS, giving the following standard weight percent composition: surfactant (21%)/TMOS (12%)/water (67%). This composition corresponds with adequate conditions for the formation of an ordered mesophase during sol-to-gel transition. The amount of ultrapure water used in the process is equivalent to a hydrolysis ratio of 47.5 for TMOS. Various sols were prepared with surfactants exhibiting x values of 8, 10, 12 and 14. The gelation time was estimated macroscopically to be about 3 hours for the various sols. Gelation time for the equivalent isotropic sol (without surfactant) was estimated at about 24 hours. Unsupported and supported membranes have been prepared in the same way as described in Section 2.1. The only difference was in the intermediate mesoporous layer which was made of γ-alumina instead of silica.

2.3. Characterization of membrane materials

Pore size distributions in amorphous silica were determined from N_2 adsorption experiments at 77 K, using a Micromeritics ASAP 2000 apparatus. Isotherm interpretations were performed both with the modelless pore (MP) method, applying to pores of any shape and the Horvath–Kawazoe method applying to slit-shaped pores. The formation of mesophases in the sols and the structural evolution of related gel layers and fired membrane materials were followed using a low angle X-ray diffraction device which allowed the determination of Bragg spacings up to 90 Å. The morphological aspect of the fired unsupported and supported membranes was observed by field emission scanning electron microscopy (Hitashi S 4500).

3. Results and discussion

A number of parameters have been demonstrated to have a major effect on the evolution of porosity in silica gels and subsequently on the resulting silica materials [9]. Dense, micro-or mesoporous silica materials can be obtained according to the experimental conditions under which hydrolysis and condensation reactions of silicon alkoxides are carried out. In our group special attention has been paid to the utilization of amphiphilic systems as reactive media to control the kinetics of the sol–gel transition of transition metal alkoxides [10]. More recent work has been devoted to the role of these amphiphilic systems in the preparation of ceramic membranes exhibiting a tailored microporosity [7]. In particular surfactant molecules and related self assembled systems have been used as template agents during sol–gel processing of silica membranes. The effect of both non-ionic and cationic surfactants in silica gel formation has been investigated. The template effect of a non-ionic surfactant series has been found. Further investigation using cationic surfactants has shown that an ordered microporosity can be obtained from self-assembled surfactant molecular systems acting as templates in silica gel formation.

3.1. Effect of Triton X surfactants on TEOS derived sols, gels and related membrane materials

The effect of non-ionic surfactants, alkylaryl polyether alcohols Triton ($X = 1, 30$) of different molecular weights added to tetraethoxysilane sols was investigated. On the basis of sol and gel characterizations (gelation time, ^{29}Si-NMR, QELS, SAXS) the effect of surfactant chain length (X) and Triton/TEOS ratio have been explored [11]. Surfactants are susceptible to interaction with silica oligomers derived from TEOS by van der Waals forces or by interaction with OH groups. Due to these interactions, we can assume the formation of an organic shell between the clusters made of surfactant molecules. The resulting steric hindrance limits further condensation of clusters during sol aging. A reduced number of Si–O–Si bonds between the clusters explains the formation of more stable sols and gels with weak intercluster connections.

A remarkable result is the influence of the size and the concentration of surfactant molecules on the structure of the membranes. During heat treatment of the gel layer, the elimination of the organic shell around the particles produces a homogeneous microporous membrane consisting of distinct nanometric silica particles. Nitrogen adsorption experiments performed on these materials revealed that nitrogen molecules (kinetic diameter = 3.96 Å) do not penetrate the structure of the material prepared without adding Triton molecules. When surfactants were used, type I

Table 1
Influence of the size and concentration of Triton X surfactants on the porous structure of unsupported silica membranes

X	SAA/TEOS	S_{BET} (m^2/g)	Porous volume (cm^3/g)		Porosity (%)	RH distribution (Å)	
			Total	Microporous		Range	Mean
1	0.55	400	0.217	0.210	32.2	3–7	3.9
3	0.16	250	0.121	0.105	20.9	3–6	3.2
3	0.35	470	0.197	0.190	30.1	3–6	3.4
3	0.55	500	0.249	0.239	35.5	3–6	3.7
10	0.55	728	0.510	0.480	52.7	5–9	6.3
30	0.55	800	0.541	0.514	54.2	4–10	6.0

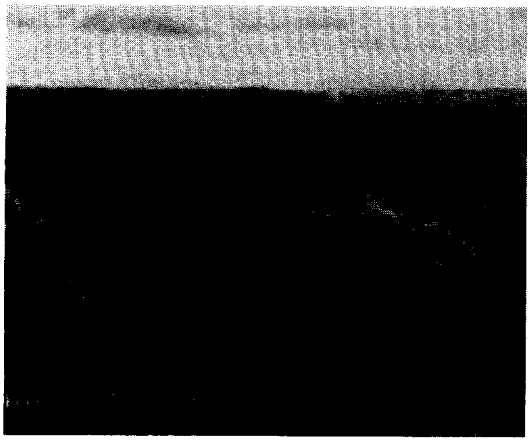

Fig. 1. FESEM images of a microporous silica membrane ($X=3$, SAA/TEOS = 0.55) deposited on a mesoporous silica intermediate layer.

isotherms were obtained and which are characteristic of microporous materials. Results obtained with the Triton series are given in Table 1.

The mean hydraulic pore radius *RH* (estimated by the MP method) varied between 3.2 and 7.0 Å. This parameter is slightly affected by the surfactant/precursor ratio (SAA/TEOS) but tends to increase with the surfactant chain length X. Furthermore, the pore size distribution becomes wider when X increases. From these results it can be said that the surfactant acts as a template agent by increasing pore size when increasing surfactant molecule size, but does not allow control of pore size distribution in the material. Polyether chains of too great a length ($X=30$) for the surfactant have to be avoided because they lead to a large pore size distribution. Another effect of surfactant addition is an increase in porous volume and specific surface area with an increasing X and SAA/TEOS ratio. The effect is optimum for X ranging from 3 to 10 and SAA/TEOS = 0.55, with values for the porosity between 35% and 50% and for the specific surface area of ca. 500 m^2/g. Crack-free membranes, 200–500 nm thick, have been prepared from this kind of sol, Fig. 1.

3.2. *Liquid crystal template effect on silica membranes synthesized using quaternary ammonium surfactants*

A more efficient way to obtain monodispersity of the pore size distribution and control of the pore size is to develop materials with an ordered microporous structure. Concerning the polymeric gels, the use of an ordered medium acting as a template for the growing inorganic network can be considered [12]. Moreover this gelation medium must be easily eliminated without collapse of the solid part of the gel. This route is currently being explored using lyotropic liquid crystals as a gelation medium. The template effect of lamellar systems made of non-ionic surfactants on sol–gel derived silica materials has been already investigated [13]. We describe here the first results concerning the use of hexagonal phases as gelation medium for silica microporous gels. These phases consist of hexagonal packing of micellar cylinders surrounded by an aqueous phase.

The chemical composition of the sols described in the experimental section corresponds to an isotropic region in the water–surfactant binary diagrams. This is consistent with what we observed experimentally: the sols are initially very fluid and easily deposited as crack-free coatings. The ordered mesostructures develop during the gelation process. The process of silica polymerization and lyotropic hexagonal phase formation take place simultaneously. The formation of the liquid crystal phase seems to be induced by the formation of silicate oligomers near the cationic surfactant head groups. Thus it can be assumed that a templating effect is produced by the micellar cylinders on the silicate polymers which are growing in the aqueous phase.

The template effect of the hexagonal phase on the structural and textural properties of the materials has been demonstrated after a first thermal treatment up to 450°C in a nitrogen atmosphere. A second thermal treatment at the same temperature in air, to remove residual organics, does not produce any significant structural and textural change. A first remarkable result concerning the thermally treated materials is that a diffraction peak can be observed on their diffractograms. Thus, an ordered, porous texture seems to be preserved after the removal of the surfactant. Characteristics of the porous structure, obtained from

Table 2
Porous structure characteristics of unsupported silica materials exhibiting an ordered microporosity, obtained from nitrogen sorption measurements

Sample (C_x)	Surface BET (m^2/g)	Porous volume (cm^3/g)	Porosity (%)	Microporosity (%)
C_8	1260	0.67	60	81
C_{10}	1040	0.60	57	88
C_{12}	1100	0.74	62	86
C_{14}	1090	0.78	63	71

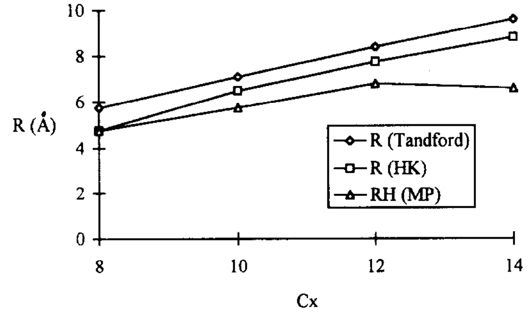

Fig. 2. FESEM image of a microporous silica membrane ($X=3$, SAA = 0.55) deposited on a mesoporous silica intermediate layer.

nitrogen sorption measurements are reported in Table 2.

Whatever surfactant is used the specific surface area is very large (> 1000 m^2/g). The pore volume is also large and essentially microporous, leading to a porosity of about 60%. The micropore size distribution is generally narrow but not totally monodispersed. The average micropore sizes were measured using a nitrogen adsorption method and according to two different models: MP and Horvath–Kawazoe, Fig. 2. The average pore radius clearly appears to be proportional to the number x of carbons of the alkyl chain. The pore radius can also be estimated from calculation on the template unit (micellar cylinder), using Tanford's equation [14]. Assuming a full interpenetration of surfactant molecules in micellar cylinders, it should approximate to half the chain length. In Fig. 2, we can see that there is a very good agreement between measured and calculated values.

4. Conclusion

The concept of template agents, using amphiphilic systems, for the preparation of tailor-made microporous ceramic membranes has been successfully applied to silica membranes prepared by the sol–gel method. The surfactant molecules can simply modify the sol-to-gel transition with a template effect or can participate in the formation of gels through a self organization process leading to an organized gel structure. In this latter case, the utilization of template agents in sol–gel derived membranes offers an alternate way to create zeolite-like membranes, in order to obtain membrane materials with an ordered porosity. In fact, current investigations on these two methods proceed in a complementary way. The sol–gel approach yields micropores larger than 1 nm while the method involving zeolites leads to ultramicropores of less than 1 nm.

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