Tuning the nanopore structure and separation behavior of hybrid organosilica membranes

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ABSTRACT

The exceptional hydrothermal- and solvent stability of organically linked silica makes it a promising candidate material for molecular separation membranes. Tailoring towards specific separation properties however requires precise control over the pore structure. Here we show that this can be achieved by adjusting the acid-to-Si ratio immediately before the onset of physical drying of the 1,2-*bis*(triethoxysilyl)ethane-based polymeric colloidal sols. This procedure provides uniform coating conditions and results in defect-free films. The structure development is investigated with in-situ Small-Angle X-ray Scattering, both in a solvent and during film drying. Acid-catalyzed colloidal growth in a solvent is governed by diffusion-limited cluster aggregation for all studied acid concentrations. Upon solvent evaporation, micropores (<2 nm) are formed at low acid concentrations (H^+:Si $\leqslant$ 0.1). This can be explained by compressive capillary forces exerted by the receding pore liquid. At H^+:Si = 1, reaction-limited cluster aggregation is observed during drying, followed by the formation of pores >2 nm. The compressive forces are balanced by a network strengthened by ongoing condensation reactions, and by the positive charge on the hybrid organosilica. This results in a larger pore size under more acidic conditions. The permselectivity of the supported membranes correlates with the pore structure of the unsupported materials. Thus, the adaptability of the pore structure allows a wider applicability of organosilica membranes in energy-efficient industrial molecular separations.

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1. Introduction

Rapidly increasing energy costs and climate concerns related to fossil fuel-based energy consumption call for drastic efficiency measures. Several strategies are being developed to improve the energy-efficiency of transport, heating, and industry, which each account for equal shares of the worldwide energy demand. In the chemical industry, distillation, especially cryogenic and azeotropic, is an energy intensive process and consumes billions of barrels of oil equivalent yearly. Replacing these inefficient processes by molecular separation with membranes can save up to 50% of energy of specific processes [1]. Numerous activities take place in this field focused on pervaporation of liquid mixtures [2,3] and gas separation [4,5]. A practically applicable membrane process must
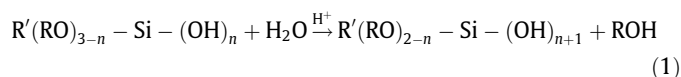
be at least as reliable as the current available technology before it can be implemented on any scale. A major technological challenge is therefore to achieve adequate structural membrane stability. In addition, membranes must be cheap, which implies a small number of simple preparation steps, and preferably be versatile, *i.e.* applicable for different processes and under different conditions.

Recently we have developed a hybrid organosilica-based material that consists of an amorphous network with both organic $Si–C_n–Si$ bridges and inorganic Si–O–Si bonds [6,7]. A one-pot sol–gel procedure allows coating of a <<1 μm-thin selective layer with high permeability on top of a mesoporous support system [8,9]. Pore sizes <1 nm find application for the molecular sieving of small molecules. Long-term chemical and hydrothermal stability has been demonstrated in liquid separation up to 190 °C, in acidic mixtures and in the presence of aggressive organic solvents [10,11]. The solvent- and hydrothermal stability are adequate for nearly all liquid separation processes. Unlike many membranes from organic polymers, permeability, selectivity, and stability are not affected by plasticization effects. With regard to versatility in

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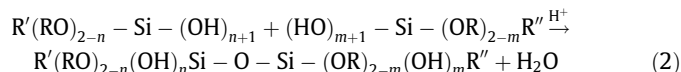
application, the efforts of several research groups are directed at modifying the selectivity, especially in gas separation [12–15]. We recently established how the size, shape, and electronic structure of the organic bridge can be adapted to tailor the separation selectivity for gas and liquid mixtures [16,17]. As a result, separation can now be based both on the relative size of the molecules and on their adsorption properties, i.e. the interaction with the pore surface. However, independent and well-controlled variation of the pore size is needed to fully exploit both size-based and affinity-based separation. Small pores are required to separate mixtures of small molecules. Larger pores permit the separation of mixtures of larger molecules, and result in improved permeability. Thus we set out to modify the wet synthesis procedure in order to accurately control the pore size, while retaining a defect-free membrane and avoid the introduction of costly preparation steps.

Here we report a general procedure that allows for adaptation of the pore characteristics, while retaining the optimal rheological coating properties required to obtain defect-free membranes. The key step is adding an acid to a colloidal sol with optimized rheological properties immediately before coating. As the synthesis procedure is straightforward and no surfactants are used, membrane fabrication remains cheap.

Defect-free membranes from alkoxysilanes can only be prepared under acid-catalyzed conditions, i.e. below the isoelectric point (IEP). At the IEP, which is at pH $\sim$ 2.2 for SiO$_2$ [18], the net surface charge (with charged species consisting of $Si - OH_2^+$ and $Si–O^-$) equals zero. The generalized reactions involved are hydrolysis:

$$R'(RO)_{3-n} - Si - (OH)_n + H_2O \xrightarrow{H^+} R'(RO)_{2-n} - Si - (OH)_{n+1} + ROH \tag{1}$$

and condensation:

$$R'(RO)_{2-n} - Si - (OH)_{n+1} + (HO)_{m+1} - Si - (OR)_{2-m}R'' \xrightarrow{H^+}$$
$$R'(RO)_{2-n}(OH)_nSi - O - Si - (OR)_{2-m}(OH)_mR'' + H_2O \tag{2}$$

where in n, m = 0, 1, or 2, R is an alkyl group, and R′ and R″ can be various organic groups. The rate of condensation (in which network bonds are formed) is at a minimum around the IEP [19]. Below the IEP, open polymeric structures are formed with a low degree of branching, which, unless a special procedure is followed, give a microporous structure after drying. While the smallest pore size and pore volume result around pH $\sim$ 2, larger values are found at higher acid concentrations [18–20]. The first systematic investigations of pore formation under acidic conditions involved gelled SiO$_2$ materials with substantial sodium contents [20–24]. The formation of larger pores under more acidic conditions was explained by 'increased aggregation and coalescence of particles as a result of condensation' [23], in which the acid acted as a 'dehydration agent' [22]. More recent studies, related to the preparation of silica membranes from tetraalkoxysilanes, explained the larger pore volumes and -sizes by the packing of the larger and more branched colloids in the sol state [25–30]. At higher acid concentration, larger colloids and higher fractal dimensions D_f were found in SAXS experiments. However, the rheology of such sols was not always found suitable for the preparation of defect-free membranes. Iler also stated that the acid concentration mainly affects the size to which the particles grow before gelation [18]. In short, all these studies relate pore structure to the degree of condensation, expressed in terms of size and branching degree of the colloidal particles, in which more acid gives a higher degree of condensation in the same period. However, the data also suggest a correlation with acid concentration that is independent of the colloid size and structure [27].

By adjusting the acid concentration at the last moment (within a minute before coating), we aimed to establish to what extent the pore structure formation is related to the colloid size, i.e. to the degree of condensation at the onset of drying, and to the acid concentration itself. This procedure assured uniform coating conditions as sols with optimized colloid size distributions were used. Structural effects related to the amount of deposited material were thus avoided. Structure development during the drying process was followed in situ with Small-angle X-ray scattering by means of a specially designed device. To the best of our knowledge, this is the first time that the formation of porous organosilica is studied with any in-situ technique. The structures of unsupported materials were investigated with sorption techniques using various molecular probes. Membrane performances were determined in gas permeation and liquid pervaporation tests. Finally, with long-term applications in mind, hydrothermal, acid, and base stability were assessed using quantitative dissolution tests.

While this study focuses on ethane-bridged materials, which were subjected to extensive membrane tests, the process allows for pore size tailoring of a broad range of silica and hybrid silica membranes. The development of precursors with organic functionalities [31–33] has led to a wide and topical interest in bridged organosilica materials. Controlled variation of the porosity also allows for further fine-tuning of their applicability as low-k dielectrics [34,35], drug-release carriers, sensors, and catalyst supports [36–38].

2. Experimental

2.1. Material preparation

1,2-Bis(triethoxysilyl)ethane (BTESE) was obtained from ABCR. Ultrapure Milli-Q water (18.2 MΩ cm) and HNO$_3$ (65 wt% in water, Aldrich) were added to dry ethanol, and BTESE was subsequently added to this mixture under vigorous stirring. The mixture was then immediately placed in a water bath at 333 K in a closed glass container. The initial concentration of 1,2-bis(triethoxysilyl)ethane was 0.9 mol/l, the hydrolysis ratio (H$_2$O:ethoxy) was 1 and the acid-to-silicon ratio (H$^+$:Si) was 0.01. The hydrolysis ratio of 1 ensured that hydrolysis was not compositionally limited. After 3 h heating under continuous stirring, the mixture was diluted with an equal amount of ethanol, and split into three portions. The first was used as is, and different amounts of 65 wt% HNO$_3$ were added to the other two portions. The resulting H$^+$:Si ratios were 0.01 (sol **1**), 0.1 (sol **2**), and 1 (sol **3**). Adding the nitric acid also resulted in a slight increase of the hydrolysis ratio and dilution of the sol. Note that the dilution step with ethanol was not applied in the study of growth and drying processes with in-situ SAXS.

Unsupported xerogel films were obtained by drying the sols in a Petri dish. Supported mesoporous γ-Al$_2$O$_3$ membranes were prepared by a dip-coating procedure of a boehmite sol on a 30 cm long tubular α-Al$_2$O$_3$ support system (i.d./o.d. = 8/14 mm) [39,40]. The freshly prepared organosilica sols were coated onto this γ-Al$_2$O$_3$ layer. Coating procedures were carried out under class 1000 cleanroom conditions to minimize defect formation due to dust particles. All layers were applied on the outside of the tubes. The unsupported and supported films were consolidated by a thermal treatment at 523 K for 2 h in a nitrogen flow (99.999% pure), applying heating and cooling rates of 0.5 K/min. The resulting materials are designated as 'powders' and 'membranes', respectively.

2.2. Characterization of colloidal sols and unsupported films

Colloid sizes in the freshly prepared sols were determined by dynamic light scattering (DLS). The sols were diluted with three volume parts of ethanol and the colloid size distribution was