Tailor-Made Nanostructured Ion Selective MCM-48 Membranes

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ABSTRACT

Mesoporous templated MCM-48 silica was prepared using a C_{16} surfactant as template. The MCM-48 powders and thin films were characterized by different techniques. Two types of porous supports were used, namely macroporous α-alumina and silicon microsieves. The supported MCM-48 layers were applied as liquid permeable membranes in pressure-driven nanofiltration and electric field-mediated ion transport experiments.

INTRODUCTION

A disadvantage of conventional mesoporous inorganic membranes such as γ-alumina is their wide pore size distribution and the high tortuosity of the separating layer, which affects the intrinsic separation selectivity and permeability negatively. These disadvantages may be solved by employing template-directed synthesis methods for the formation of the mesoporous layer. A well-known example of a templated inorganic material is mesostructured silica. Templated silica can be synthesized using arrays of self-assembled surfactant molecules as structure directing templates, around which the inorganic precursor species are polymerized [1]. Depending upon surfactant concentration and processing conditions, the final pore structure of silica will exhibit hexagonal, cubic (MCM-48) or lamellar symmetry [1,2]. In view of their high porosity and well-ordered pore geometries with narrow pore size distributions and low tortuosity, thin films of templated mesoporous materials are potential candidates for membrane applications. Although thin film formation on dense substrates has received considerable attention lately [3,4], only few works on film formation on porous supports have been reported to date [5]. MCM-48 has an interconnected 3D channel system [6], so that a low tortuosity in all directions is expected. This feature should lead to a high liquid permeability of the layer. The small pore sizes and narrow pore size distributions allow complete double layer overlap inside the membrane pores, which can give rise to high selectivity in ion-separation processes. Two types of applications will be demonstrated here. The first is nanofiltration (NF), where ion size and charge, as well as membrane surface charge and double layer thickness determine the level of separation [7]. Here the electrical double layer overlap inside the membrane pores will prevent charged solute transport through the membrane under application of an external mechanical pressure field. The second type of application involves the use of an externally tuneable electrical field over the membrane, so that active control over the transport of specific ionic species can be achieved. This development may lead to new intelligent interconnects between fluid channels in micro-chemical systems (MiCS) and micro-total analysis systems (μTAS) [8]. The transport of cationic species through MCM-48 membranes mediated by a variable external electric field can be regarded as a model system for some of these applications [9,10]. Control over the transport rate of species is obtained by the electric field [10,11], while anion or cation selectivity is achieved

by the complete overlap of a negatively or positively charged diffuse double-layer inside the pores, depending on the total ionic strength [10] and pH.

In this study it is demonstrated how mesoporous MCM-48 silica layers on different porous supports can be used in these two types of membrane processes.

EXPERIMENTAL DETAILS

Preparation of supported surfactant templated mesoporous silica membranes

The α-alumina supports (2 mm thick, 39 mm diameter, pore size ~100 nm, porosity ~30%) were made by colloidal filtration of well-dispersed 0.4 μm α-alumina particles [12]. Silicon microsieves® (1 μm thick, 0.5 cm diameter with circular-shaped perforations of 0.5 μm diameter, overall porosity ~30%) were supplied by Aquamarijn (The Netherlands).

Surfactant-templated silica sols were synthesized using the cationic surfactant cetyl-trimethyl-ammonium bromide (CTAB, Aldrich) and tetraethoxy-orthosilicate (TEOS, Aldrich) derived sols as described elsewhere [13]. Spin-coating and dip-coating techniques were used to deposit thin silica films on silicon wafers (004 type) and α-alumina supports, respectively. After coating the layers were dried at room temperature and subsequently heated to 400°C in air for 2 h to calcine the silica film (thickness ~200 nm) and remove any residual organics.
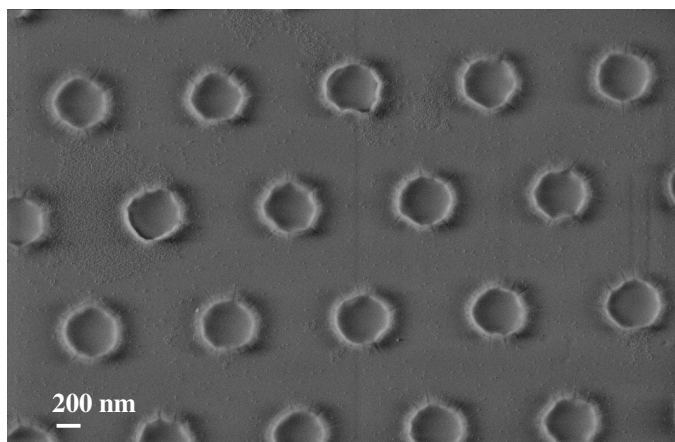

Figure 1. SEM photo of a MCM 48 coated silicon microsieve

The MCM-48 films were checked under SEM for the absence of defects, see figure 1. X-ray diffraction (XRD) patterns of supported silica layers were recorded using a Philips SR5056 with Cu Kα radiation. BET measurements (Micromiretics) were performed at 77 K on dried and calcined silica powders with N_2 as the condensable gas.

Nanofiltration experiments

The steady state water fluxes through a α-alumina supported MCM-48 membrane, a α-alumina support and a conventional α-alumina supported γ-alumina membrane were measured. NF measurements were performed with the water-soluble amino acid phenylalanine (Aldrich) as

a model solute at a concentration of 0.6 mM. Retention studies were carried out in a dead end NF cell [14]. The volume of the cell is 1 dm^3 and the operating pressure was kept in the range of 1-7 bar. The stirring speed in the cell was kept constant at 200 rpm. The retention of a membrane is expressed by the retention coefficient which is defined by $R_{obs} = 1 - C_p/C_b$, with C_p the solute concentration in the permeate solution and C_b the solute concentration in the feed solution. The concentration of the amino acid was measured with UV-vis spectrometry at 213 nm (Pharmacia Biotech, Ultraspec 3000 UV/ Visible Spectrophotometer).

Field mediated transport experiments

The experimental set-up is shown in figure 2. The membrane (surface area 0.038 cm^2) was placed between the two halves of a U-shaped tube. The pH was regulated with NaOH or HNO_3 solutions. The Cu^{2+} ion concentration was analysed by atomic absorption spectroscopy. A dc potential difference ΔV was imposed [10] between Pt electrodes using a potentiostat. ΔV is defined as $\Delta V = V_B - V_A$, with V_A and V_B the electrode potentials at the A and B side, respectively. The ion fluxes were calculated from the concentration changes with time after reaching steady state conditions. Prior to the experiment the membranes were left for 12 h in the buffer solution to ensure complete wetting.
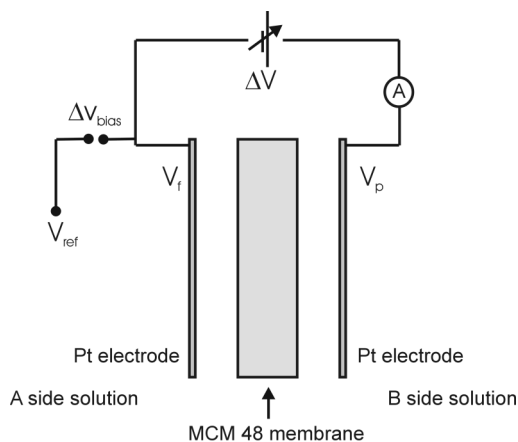

Figure 2. Schematic diagram of the experimental set-up.

RESULTS AND DISCUSSION

Characterization of the templated silica membrane

Figure 3 shows a small angle XRD pattern of 200 nm thick uncalcined and calcined silica films after deposition on a dense silicon wafer. The x-ray pattern matches the pattern of an ordered mesoporous MCM-48 phase with unit cell $a\sim9.2$ nm. The marked sharp peaks are probably from crystalline CTAB and they disappear upon calcination. The sample retains its mesostructure after calcination but with smaller d-spacing (figure 3, $a\sim6.3$ nm). We did not observe diffraction at low angles in the films that had been deposited on porous α-alumina supports. This is probably due to the roughness and texture of the alumina support, which

promotes local nucleation and growth of ordered domains with different orientations at length scales that are too small to be detectable by XRD. Permporometry experiments [12] with cyclohexane on the alumina-supported MCM-48 membrane indicated that the calcined silica films are porous, defect-free and have a Kelvin radius <1.7 nm. This is in agreement with nitrogen sorption data on unsupported MCM-48 powder, from which an average pore diameter of 2.8-3.4 nm was calculated.
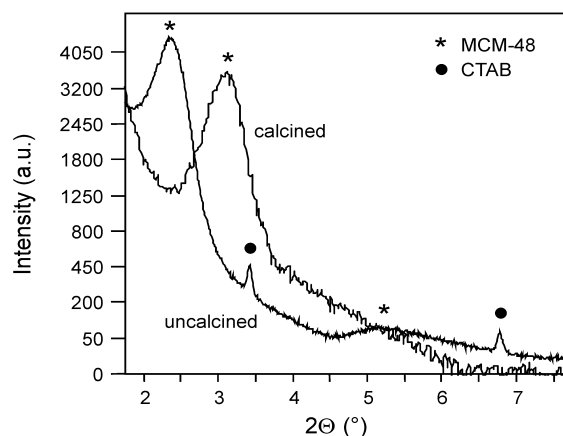

Figure 3. XRD diagrams of uncalcined air-dried and calcined silica layer on silicon (004) wafer.

Nanofiltration experiments

The steady state water flux through the supported mesoporous silica membrane is shown in figure 4. The water flux increased with increasing pressure. The permeability of water through supported MCM-48 was lower than that of the macroporous α-alumina support, but larger than the conventional supported γ-alumina membrane. Since the γ-alumina layer is ~1 μm thick, has a pore size of 4-6.5 nm and a total porosity of ~50%, the higher permeability of the MCM-48 membrane can be explained by its lower tortuosity, smaller layer thickness (~65-70 nm) and higher porosity (~60%).

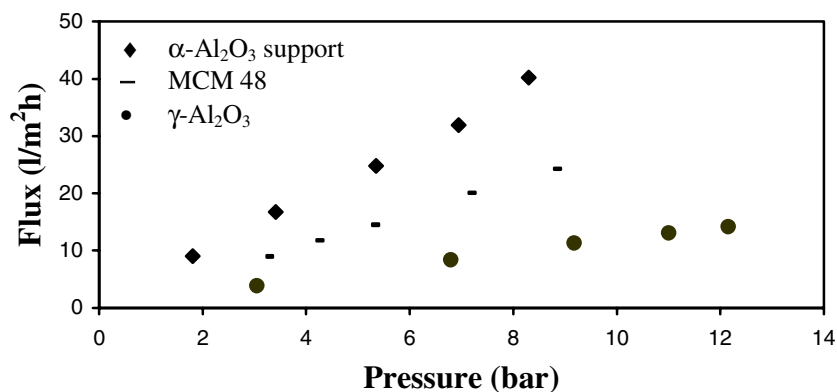**Figure 4**. Comparison of water fluxes through α-alumina supported MCM-48 and supported γ-alumina.

In figure 5 the retention of phenylalanine through MCM-48 is shown. The phenylalanine retention is 20-25%. The pH of the solution was 4.3, which is below the isoelectric point of phenylalanine of 5.48. At this pH the silica surface is negatively charged, but since the solute molecules are positively charged an attractive interaction occurs between the membrane pore surface and the solute molecules. This may explain the relatively low retention of phenylalanine.
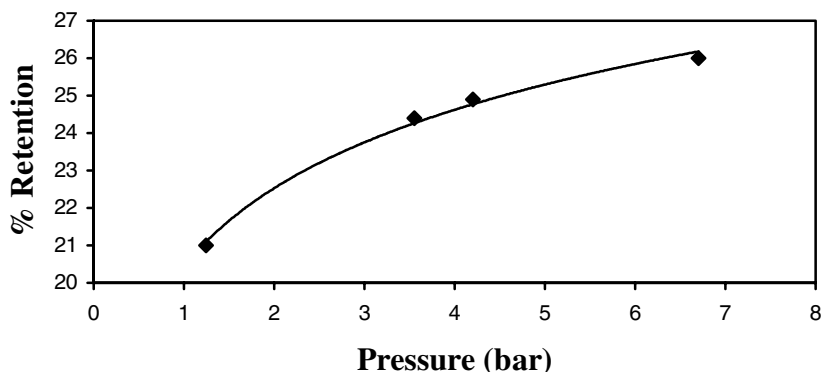
Figure 5. Retention behaviour of phenylalanine in water through MCM-48.

Field mediated transport experiments

Figure 6 shows the flux of Cu^{2+} ions versus potential difference (ΔV). The flux of Cu^{2+} increased with increasing ΔV. As shown in figure 6 a Cu^{2+} flux was present at all ΔV and the flux was directed from the negative to the positive electrode. When $\Delta V = 0$, a flux of Cu^{2+} ions ($1.67 \cdot 10^{-4}$ mol m^{-2} s^{-1}) was observed. The mode of transport at $\Delta V = 0$ is normal Fick diffusion. When $\Delta V > 0$ the flux of Cu^{2+} ions increased, while the flux of Cu^{2+} ions decreased when $\Delta V < 0$. This implies that the transport rate of cations can be controlled over a wide range by external variation of ΔV.
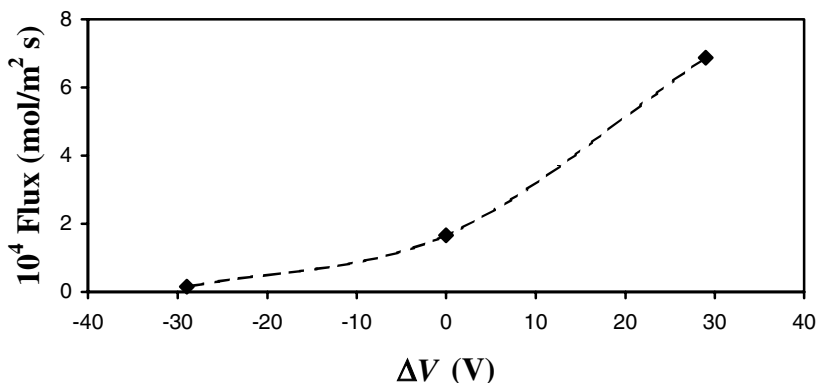
Figure 6. Cationic flux versus ΔV at low ionic strength. Permeating ion: $[CuCl_2] = 2.3$ mM (A-side), $[KF] = 0.25$ mM and $[KCl] = 1.5$ mM (B-side); pH 5.5. Drawn line serves as guide to the eye.

CONCLUSIONS

Defect-free MCM-48 layers were deposited on macroporous α-alumina supports and silicon microsieves. The alumina-supported MCM-48 membranes showed higher water permeability than conventional γ-alumina supported membranes. MCM-48 can be applied as NF membrane, as was illustrated by the retention of phenylalanine in water. The application of MCM-48 membranes as ion-selective membrane in electric-field driven ion transport was also demonstrated. It was shown that the cation flux through the microsieve-supported MCM-48 membrane could be controlled by manipulation of the dc potential difference over the membrane.

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