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One-step deposition of ultrafiltration SiC membranes on macroporous SiC supports

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ABSTRACT

We fabricated nearly defect-free SiC membranes for potential ultrafiltration applications by conducting pyrolysis of allylhydrido polycarbosilane in the presence of submicron α-SiC particles. The SiC membranes were developed on commercial macroporous SiC supports by a low-temperature-process in which allylhydrido polycarbosilane acted to bond together crystalline α-SiC particles to form a porous layer. The suspensions of α-SiC powder and allylhydrido polycarbosilane in *n*-hexane or *n*-hexane/*n*-tetradecane were used for membrane fabrication by dip-coating. By using optimized *n*-hexane suspension with 5% w/w α-SiC powder and mass ratios of allylhydrido polycarbosilane to α-SiC powder of 0.6 and 0.8, we obtained nearly defect-free and uniform mesoporous membranes in a single coating procedure. No defects were found on the surface of these membranes by scanning electron microscopy. Moreover, during filtration tests, these membranes showed a water permeance of 0.05–0.06 L $(\mathrm{h\,m^2\,bar})^{-1}$ and retention higher than 93% for polyethylene glycol (PEG) with a molecular mass of 100 kDa. Retention for PEG with molecular masses of 1 kDa, 8 kDa and 35 kDa was between 25% and 71%.

1. Introduction

Nowadays, ceramic membranes are applied to a large number of ultrafiltration processes, including water purification, food and beverage processing, bioreactors, and molecular separation systems in the petrochemical and chemical industry [1–3]. Compared with polymeric membranes, ceramic membranes have higher thermal, mechanical, and chemical resistances. In particular, mesoporous γ-alumina has been frequently considered as a material for ultrafiltration membranes because defect-free films of this material can be easily deposited on macroporous supports by the sol–gel method. However, γ-alumina membranes do not demonstrate high enough chemical stability in either strongly acidic or basic environments [4]. In comparison to γ-alumina, silicon carbide (SiC) has a better chemical stability in harsh conditions, for example in corrosive and high-temperature environments [5,6]. For this reason, SiC is a convenient membrane material to withstand repeated aggressive cleaning, steam sterilization and autoclaving. As a result, SiC is well suited to food and biopharmaceutical processing [7,8]. Moreover, compared with other polymeric and oxide materials such as titania and zirconia, SiC membranes are very hydrophilic and exhibit low fouling [9,10]. However, due to the covalent nature of the Si–C bonds, high sintering temperatures and the addition of sintering aids are usually required for the production of SiC ceramics [11]. This requirement has two primary implications: (i) SiC membrane processing is costly and (ii) it is difficult to fabricate thin SiC layers in the microporous and mesoporous range by partial sintering [13]. Furthermore, the use of SiC membranes is rather limited today and it is mostly relegated to microfiltration processes. Nevertheless, alternative processing routes for the preparation of mesoporous SiC at reduced temperatures, based on the conversion of metaloorganic polymers to SiC, are now available [14,15].

The fabrication of polycarbosilane (PCS)-derived SiC membranes has been addressed concerning gas-separation applications [15–18]. Since the conversion of polymer precursors to SiC incurs a 20–30% volume film shrinkage, it is necessary to repeat the deposition and the consecutive pyrolysis steps several times in order to obtain defect-free films [12]. Moreover, direct coating of PCS cannot be performed without avoiding consistent penetration of the polymeric precursor in the pores of the macroporous support, which typically have size ≥ 100 nm [19]. On the contrary, combination of pre-formed SiC

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particles and PCS makes it possible to achieve thicker SiC coatings without cracks by a single deposition step [12]. Up until now, this approach has been used for the deposition of thick intermediate layers for gas separation membranes [17]. However, to the best of our knowledge, the fabrication of PCS-derived mesoporous SiC membranes on SiC macroporous supports for ultrafiltration applications has not been realized yet. Furthermore, only a few studies have actually emphasized the important role of the composition of the coating suspension in fabrication of defect-free mesoporous PCS-derived coatings [14,15].

In this context, we focus on the development of PCS-derived SiC mesoporous membranes supported on commercial macroporous SiC carriers for use in ultrafiltration. α-SiC particles were used to effectively cover the pores of the support, while PCS served to connect the particles and to ensure good membrane adhesion to the surface of the support. The application of a mesoporous ultrafiltration membrane on a macroporous support is not trivial, because pore size, thickness, and defect density of the coated film depend on the composition of the coating suspension, on the fabrication conditions, and also on the roughness and the surface inhomogeneity of the supports [20–22]. Therefore, in order to develop PCS-derived SiC mesoporous membranes, we consider several fabrication parameters. First, the coating mixture was optimized in order to obtain defect-free films. Second, two suspensions with composition in the range suitable for film deposition were used for the membrane fabrication. The membrane morphology was investigated by transmission electronic microscopy and nitrogen adsorption porosimetry. Supported membranes were tested by measuring their water permeance and their retention for a series of poly(ethylene glycol) molecules with different molecular masses. This technique was selected because it allows for the forecasting of the separation performances of the new membranes and comparisons with bare supports [23,24].

2. Experimental

2.1. Membrane fabrication

Commercially available α-SiC powder (NF25, ESK, Germany) with an average particle size $d_{50}=0.4$ μm and allylhydridopolycarbosilane (SMP-10, Starfire, USA, herafter termed AHPCS) with molecular mass of 5000–12000 Da according to the supplier's information were used for the fabrication of nanoporous SiC thin films. Suspensions of AHPCS with the α-SiC powder were prepared in 100 mL glass bottles using *n*-hexane (Sigma Aldrich) or a mixture of 70% *n*-hexane and 30% *n*-tetradecane (Sigma Aldrich) as solvents. The concentration of α-SiC powder in the solvent varied from 3–7% w/w and the mass ratio of AHPCS and α-SiC powder (hereafter termed as AHPCS/α-SiC ratio) varied from 0.2–2. After treatment in an ultrasonic bath for 2 h, the suspensions were used for coating the macroporous flat SiC disks (diameter 2.5 cm, thickness 0.5 cm) supplied by Liqtech International A/S (Ballerup, Denmark).

The supports were examined for defects by a scanning electron microscope (SEM, Evo60, Carl Zeiss, Oberkochen, Germany) prior to coating. The criterion for the selection of the supports for subsequent coating was no defects (particles, cracks, and pinholes) larger than 100 μm on the surface. The supports were first cleaned in acetone and then heat-treated at 450 °C for 2 h in air. Polymer-derived SiC membranes were obtained by using a simple homemade apparatus for dipping in and withdrawing disks from the coating suspension at a constant rate. The disks were dipped and withdrawn at an angular speed of 1.3 rad s^{-1}. After coating, the samples were heat-treated in argon at the flow rate of 100 L h^{-1}, in a tube furnace (RHTH 120 600/18, Nabertherm, Lilienthal, Germany) at 200 °C for 1 h, 400 °C for 1 h, and then 750 °C for 2 h. The heating and cooling rates were 2 °C min^{-1} and 3 °C min^{-1}, respectively. As reported by other authors, such a low heating rate makes it possible to obtain good cross-linking of amorphous SiC materials and minimizes defect formation [17,25]. In all cases a single coating was applied to the supports.

2.2. Membrane characterization

The presence of defects on the membrane surface and the membrane thickness values were investigated by analyzing the membrane surfaces and cross sections by SEM. The membrane structure and porosity were investigated on unsupported samples, which were prepared by the same heat-treatment procedure as the supported membranes. Transmission electron microscopy (TEM) images were obtained with a JEOL 3010-UHR instrument (acceleration potential: 300 kV). Samples for TEM investigation were prepared on a holey-carbon-coated copper grid by dry deposition. Specific surface area (according to Brunauer–Emmett–Teller theory, BET) and porosity were determined on about 0.2 g of unsupported sample by N_2 adsorption at the liquid-nitrogen boiling point in a gas-volumetric apparatus (ASAP2020, Micromeritics). In order to avoid undesired interferences from gaseous products from the membrane samples during the gas-volumetric determinations, the samples were outgassed in vacuum (residual pressure 10^{-5} bar) at 373 K for 8 h prior to analysis. Pore volume and pore size distribution were calculated by using the Density Functional Theory (DFT) method [26] applied to the entire adsorption branch of the isotherm.

2.3. Filtration tests

Filtration tests were performed on a dead-end stainless steel filtration apparatus at a static pressure of 10 bar. The filtration apparatus was designed for housing the flat SiC disks. The permeate flux was measured gravimetrically. Different feed solutions were filtered: pure deionized water (18.2 MΩ cm), an aqueous solution of polyethylene glycol (PEG, Sigma Aldrich) of three different molecular masses (M_n), namely 1 kDa, 8 kDa, and 35 kDa, and a solution of PEG (Sigma Aldrich) of molecular mass 100 kDa. The concentration was 1 g L^{-1} for all the PEGs. The determination of the PEG concentration in the membrane feed and permeate was performed as described in details elsewhere [21] by using a size exclusion chromatography (SEC) column PolySep GFC-P interfaced with an evaporative light scattering detector. This SEC column allowed us to obtain a good peak separation for PEG masses of 1 kDa, 8 kDa, and 35 kDa, but not for 100 kDa. For this reason, the latter compound was filtered separately from the others.

3. Results and discussion

3.1. Membrane supports and coating materials

Considerable evidence suggests that the surface properties of the support (roughness, wettability, inhomogeneity, and defect density) influence the uniformity and the integrity of the coated membrane [27,28]. Recent works [21,29] and our preliminary tests revealed that inherent defects of commercial macroporous SiC supports challenge the development of a defect-free top layer. For this reason, high priority was given to the selection of suitable disk substrates (Fig. 1a) for membrane coatings in order to mitigate the influence of surface irregularities on the quality of the final ultrafiltration membrane. Fig. 1b shows a representative SEM micrograph of surface structure of macroporous SiC disk supports used in this study. The disks have an asymmetric structure consisting of several layers with a gradual decrease in particle size from the bulk support to the top layer (Fig. 1c), which has a