



Characterization and Transport Properties of Surfactant-Templated Silica Layers for Membrane Applications

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Abstract. An intermediate surfactant-templated silica (STS) layer is applied between the supporting mesoporous γ -Al₂O₃ and the amorphous microporous silica overlayer resulting in dual-layered microporous silica membranes for gas separation applications that show improved values for both hydrogen flux and selectivity. Determination of thickness and porosity of as-deposited membrane layers by spectroscopic ellipsometry reveals that the STS layer is present as a distinctive layer of ~ 20 nm thickness, with penetration up to a depth of ~ 70 nm into the underlying γ -Al₂O₃ support layer, whose thickness and porosity are determined to be 1.3 μ m and 50%, respectively.

Keywords: microporous, surfactant templated silica, ellipsometry, gas separation, hydrogen

1. Introduction

Microporous silica membranes prepared by sol-gel processing have attracted attention for gas separation due to their good thermal and chemical stability compared to conventional polymeric membranes. Mechanical strength is provided by a macroporous support, e.g., α -Al₂O₃, while an intermediate layer of mesoporous γ -Al₂O₃ is applied to overcome the large difference in pore size between the support or supporting layers and the microporous silica top-layer. To ensure good separation and a high flux, the silica top-layer must be thin and free of defects like cracks or pinholes [1, 2]. Different strategies are applied to avoid defects, including repeated dip-coating under clean room conditions or gradual reduction of pore size of subsequently deposited layers [1]. It has been known that the application of surfactant-templated silica (STS) offers prop-

erties such as a tuneable pore size and connectivity of pores in the direction of transport [3]. Recently, Tsai et al. [4] reported that application of such a STS layer between the mesoporous γ -Al₂O₃ layer and the microporous silica overlayer shows improved membrane performance in terms of both flux and selectivity. The STS layer would prevent penetration of the silica sol into the underlying γ -Al₂O₃ layer. In the present study, dual-layer microporous silica membranes comprising an intermediate STS layer are processed and characterized by spectroscopic ellipsometry and gas permeation measurements.

2. Experimental

‘Standard’ microporous silica membranes were prepared on γ -Al₂O₃ coated on flat α -Al₂O₃ supports, as described in [1] and [2]. Membranes comprising an additional STS sublayer were prepared following the procedure as described by Tsai et al. [4].

A dip-coating solution was obtained in two steps. In the first step, tetraethyl orthosilicate (TEOS) (98%,

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Aldrich) was mixed with the appropriate amounts of EtOH (99.9%, Merck), H₂O and HCl, in a ratio TEOS:EtOH:H₂O:HCl = 1.0:3.8:1.1:5 × 10⁻⁵ (pH = 4.7), and then refluxed for 90 min at 60°C. The sol was then stored in a freezer at -30°C for one day. In the second step, additional water and HCl were added to the stock sol, followed by the addition of a 0.125 M C6-surfactant (triethylhexylammonium bromide, 99%, Aldrich). The sol was then aged for one day in the fridge. After diluting this sol with twice its volume of EtOH, the dip-coating sol was obtained. Prior to coating, the sol was filtered through a 0.45 μm filter (Nalgene). Both 'standard' as well as dual-layer silica membranes, comprising an additional STS sub-layer were subjected to spectroscopic ellipsometry and gas permeation measurements. For spectroscopic ellipsometry measurements, all consecutive coatings were deposited once. For gas permeation measurements, the γ-Al₂O₃ layer was deposited twice, while it is specifically indicated whether the SiO₂ coating was deposited one or two times.

The single gas dead-end permeance (Fig. 1) of H₂, O₂, N₂ and CH₄ was measured at 200°C. In a dead-end permeance measurement a pressure difference over the membrane is applied and the stationary flow necessary to maintain the pressure difference is determined. The spectroscopic ellipsometer used in our experiments is of a rotating polarizer type equipped with a Xe lamp and photomultiplier (Wentink, 1996). After deposition of each layer, data were acquired under vacuum after outgassing the sample overnight. During outgassing, heat was supplied by a 50 W halogen lamp, positioned 3 mm from the middle of the support-side of the sample. More details concerning the experimental procedure can be found elsewhere [5]. Dried unsupported (bulk) STS material is characterized by thermal gravimetric analysis (TGA) (Setaram, Setsys 16/18), and after calcinations at 500°C, by N₂ sorption at 77 K (Sorptomatic,

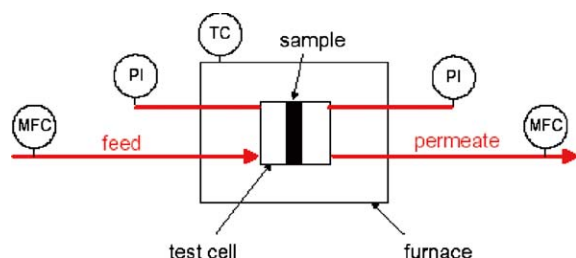


Figure 1. Schematic representation of single gas dead-end permeance set-up.

1990) employing the Horvath-Kawazoe method [6–8].

The quality of the layer deposition and its thickness were investigated by HR-SEM (LEO Gemini 1550 FEG-SEM, UK).

3. Results and Discussion

Thermogravimetric analysis of bulk STS (Fig. 2) showed a weight loss around 300°C, with a rapid burn-out of the organics as indicated by the exothermic peak at 350°C. N₂ sorption analysis of bulk STS material calcined at 500°C showed a pore size distribution around 1 nm (Fig. 3). This implies that STS itself will pose a negligible resistance to the transport of gas molecules whose size is in the range of 0.3–0.5 nm (H₂, O₂, N₂, CH₄). Material and processing parameters of the different layers used in membrane preparation are listed in the Table 1.

Figure 4 shows the single gas dead-end permeance of H₂, O₂, N₂ and CH₄, at 200°C, for silica membranes with and without a sublayer of STS, plotted as a function of the kinetic diameter of the gases. It is immediately apparent from this figure that compared with the 'standard' silica membrane, comprising two SiO₂ coatings on top of γ-Al₂O₃, deposition of a STS sublayer followed by subsequent deposition of either one or two SiO₂ overlayers significantly improves hydrogen flux, while for improved selectivity of H₂ over CH₄ still two

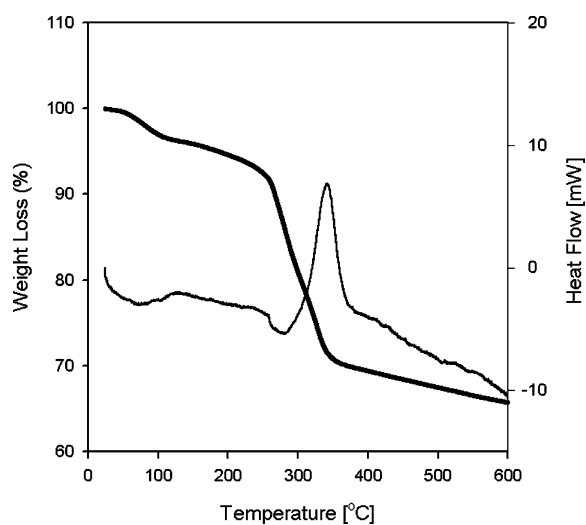


Figure 2. Heat flow (bold) and thermogravimetric weight loss for the STS material in air (1 atm) at the heating rate of 2°C/min.

Table 1. Material, processing and structural parameters of the membrane.

Layer	Material	Temperature of calcinations (°C)	Thickness	Pore size d_p (nm)	Porosity (%)
Top (membrane)	SiO ₂	400	<50 nm ^b	0.3–0.5 ^c	10–15 [5]
Sublayer	STS	500	20 + 70 nm ^a	1 ^a	10 ^a
Intermediate	γ -Al ₂ O ₃	600	1.3 μ m ^a	4 [2]	50 ^a [2]
Support	α -Al ₂ O ₃	1100	2 mm ^b	80 [2]	30 [2]

^aDiscussed in the text.

^bFrom SEM picture [1].

^cFrom N₂, CO₂, Ar sorption on unsupported (bulk) material [1].

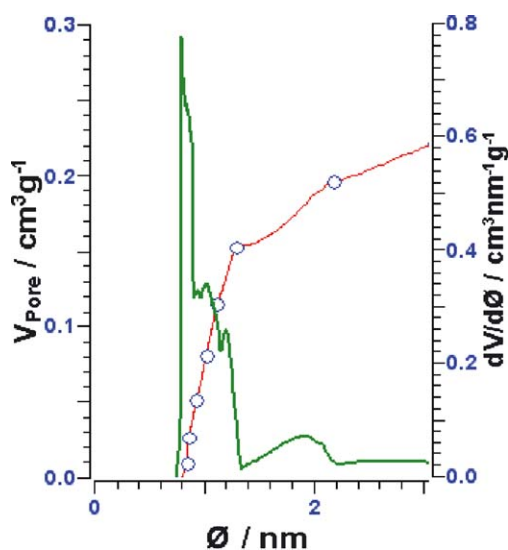


Figure 3. Pore size distribution of the STS unsupported material determined by N₂ sorption.

SiO₂ overlayers are required. An improvement in hydrogen flux due to the presence of the STS layer was also observed by Tsai et al. [3] and may be attributed to the prevention of penetration of ‘standard’ microporous silica into the γ -alumina layer.

The extent of penetration of STS into the γ -alumina layer is studied using spectroscopic ellipsometry. This technique allows evaluation of the structural properties, like layer thickness and porosity, of thin layers deposited on a supporting structure [5]. It involves measurement of change in the polarization state of an incident light beam upon reflection from a sample surface. Hence, it enables characterization of as-synthesized composite membranes in a single non-destructive way. For dielectric oxides, absorption of light is negligible and, hence, the change in the phase upon reflection Δ is only small. Therefore, only $\tan(\Psi)$, related to change in amplitude was measured as a function of wavelength λ . Graphical results are shown in Fig. 5, where the dots

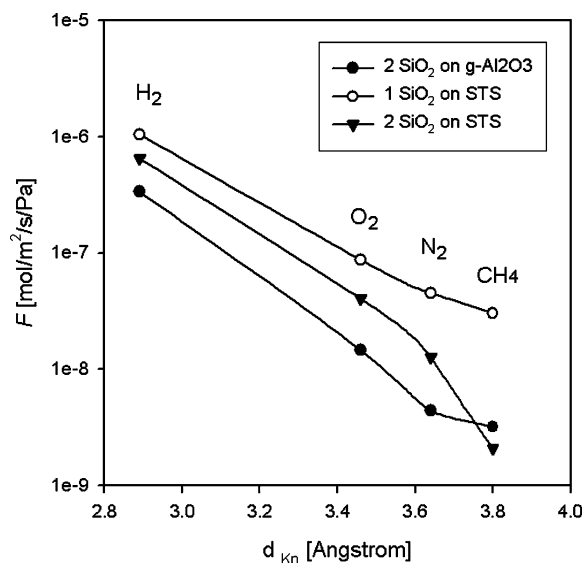


Figure 4. Gas permeation results of the membrane measured on 200°C.

correspond to experimental data and lines correspond to the best fit spectra. Fitting was done using an optical model with the optical properties and thickness of each layer as parameters [5]. Parameters obtained from fitting are listed in Table 1.

The closed dots in Fig. 4 correspond to an α/γ -alumina sample. The thin film produces an interference pattern, leading to oscillatory behaviour of $\tan(\Psi)$ versus λ . As can be seen, the presence of the STS sublayer induces significant modulation in the peak amplitudes as well as in the width of the peaks. Best fits were obtained when the penetration depth of STS into the γ -Al₂O₃ support was taken into account as a separate interface layer, with weighed properties of the constituting materials. The quality of the layer deposition as well as thickness of γ -Al₂O₃ and STS layers determined by spectroscopic ellipsometry, corresponds well with HR-SEM measurements of these layers (not shown).

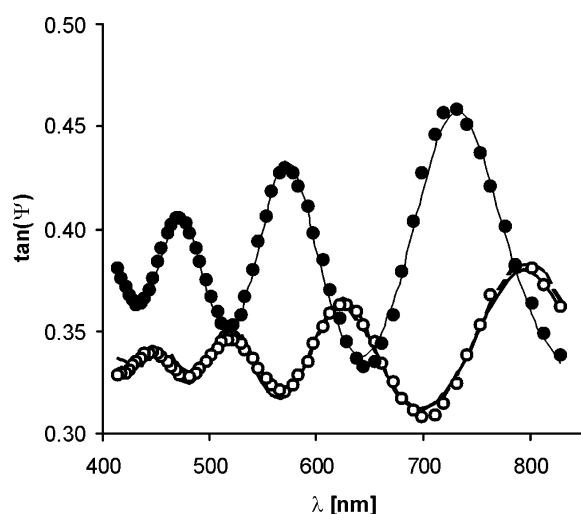


Figure 5. Wavelength dependence of $\tan(\Psi)$ for the γ -alumina layer on top of α -alumina layer (black symbols), and for the additional STS layer on top of γ -alumina (open symbols). Symbols represent the measured data; lines represent fit of the optical model.

Utilizing an effective medium approach, the porosity of each layer can be determined from its optical properties. Since the pore dimensions of the α -alumina support are comparable to 1/4th of the wavelength of visible light, an effective medium approach fails. Using the relation of Bruggeman [5], while assuming that the optical properties of dense γ - Al_2O_3 are identical to those of sapphire, the porosity of the γ - Al_2O_3 support layer is estimated to be $\sim 50\%$ and corresponds well with the literature data for the unsupported material [1]. The porosity does not vary significantly with λ as expected. Assuming that the optical properties of dense STS are identical to those of quartz, the porosity of the STS layer is calculated to be $\sim 10\%$. Although this porosity again does not vary significantly with λ , the value is probably an underestimate (the porosity of amorphous silica is already 15–20%). Most likely, the assumption of similar optical properties for dense STS and quartz is not valid. When it is assumed that there is no STS/ γ - Al_2O_3 interface, but only a STS top-layer, a thickness of approximately 50 nm is obtained. However, the porosity calculated from the optical properties in that case would be strongly dependent on the wavelength, which is physically not plausible.

4. Conclusions

Microporous silica membranes were prepared, comprising an intermediate surfactant-templated silica (STS) between the mesoporous γ - Al_2O_3 support layer and the amorphous microporous silica overlayer. Compared with a standard membrane for gas separation applications, i.e., without a STS sublayer, single gas dead-end permeation measurements (H_2 , O_2 , N_2 and CH_4) indicate a significant increase in the values for the hydrogen flux as well as selectivity. Investigations of as-deposited membrane layers by spectroscopic ellipsometry reveal that the STS layer is present as a distinctive thin layer (22 nm), with additional intrusion (73 nm) into the underlying γ - Al_2O_3 (thickness 1.33 μm). While the porosity of γ - Al_2O_3 complies with the previous findings (51%), in case of siliceous layers (top silica and STS sublayer) the current results indicate a porosity of the STS layer of $\sim 10\%$. This value is probably an underestimate due to the invalid assumption of similar optical properties for dense STS and quartz.

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