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# Influence of the Si/Al ratio on the separation properties of SSZ-13 zeolite membranes

Nikolay Kosinov, Clement Auffret, Gerard J. Borghuis, Venkata G.P. Sripathi, Emiel J.M. Hensen*

*Schuit Institute of Catalysis, Laboratory of Inorganic Materials Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*

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ABSTRACT

SSZ-13 (CHA) zeolite membranes supported by α-alumina hollow fibers were prepared by a hydrothermal secondary growth method. The gel Si/Al ratio was varied between 5 and 100. The water adsorption depended strongly on the Si/Al ratio. Comparatively, ethanol adsorption varied less with membrane hydrophobicity. Consistent with these trends, low-silica membranes showed good performance in the pervaporative dehydration of ethanol/water mixtures. On contrary, high-silica membranes were found to be more effective for $CO_2/CH_4$ equimolar gas mixture separation. Together with increasing framework polarity, the concentration of non-zeolitic pathways (intercrystalline defects) increased with the Al content. The net effect of the influence of membrane polarity and defect density makes low-silica SSZ-13 water-selective membranes for alcohol/water pervaporation and high-silica SSZ-13 promising $CO_2$-selective membranes in gas separation ($CO_2/CH_4$).

## 1. Introduction

Microporous inorganic membranes are promising materials for many industrially and environmentally important separations [1,2]. Zeolites have attracted much attention in this field due to their exceptional thermal and chemical stability as well as their uniform system of subnanometer-sized pores [3,4]. Aside from pore size and channel dimensionality determined by the zeolite topology, chemical composition is another important parameter, influencing the overall performance of zeolite membranes. Especially, the Si/Al ratio is a variable that can be used to fine-tune the hydrophobic/hydrophilic nature of the zeolite. Introduction of a trivalent Al atom into the tetrahedral zeolite framework charges it negatively and the polarity of the zeolite increases with increasing of Al content [5]. Accordingly, low-silica hydrophilic zeolite membranes find application in the removal of water from organics, whereas high-silica zeolite membranes can be used to recover organics from water. Another aspect of zeolite framework polarity is its influence on membrane quality. It was shown for MFI membranes that increasing the Al content leads to less-intergrown membranes resulting in non-zeolitic molecular trafficking pathways with low selectivity [6]. A reasonable explanation limiting intergrowth is the negative charge of growing Al-rich zeolite surfaces [7,8]. Thus, preparation of high-quality membranes with minimum defects requires use of high or even pure-silica zeolite structures. There is, however, usually a maximum Si/Al ratio to grow particular zeolites [9]. In order to optimize synthesis of zeolite membranes while keeping the number of defects low, systematic studies dedicated to the influence of Al content on the properties of zeolite membranes are necessary.

Recently, we reported on the synthesis of high-silica SSZ-13 membranes with high permeance and selectivity in the separation of $CO_2/CH_4$, $CO_2/N_2$ and $H_2/CH_4$ mixtures [10,11]. SSZ-13 is a highly porous aluminosilicate structure with CHA topology, possessing a three-dimensional pore system of cages linked by 0.38 nm windows. The aluminosilicate SSZ-13 has the advantage of higher hydrothermal stability compared with its silicoaluminophosphate analog SAPO-34 – a material widely considered for construction of gas separation membranes [12–15]. In addition to gas separation by SAPO-34 and SSZ-13 membranes, de-watering of different organic compounds by SSZ-13 membranes has been reported. Relevant examples of both processes are reported in Tables 1 and 2.

In the present work we report the hydrothermal synthesis and performance of SSZ-13 membranes supported by α-alumina hollow fibers. The membranes were prepared by a secondary growth method with gel Si/Al ratio varying from 5 to 100. Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Ar physisorption were used for physicochemical characterization of membranes and corresponding zeolite powders. The quality of the membranes was assessed by carrying out

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* Corresponding author. Tel.: +31 40 2475178.
*E-mail address:* e.j.m.hensen@tue.nl (E.J.M. Hensen).

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**Table 1**
Literature data on pervaporation performance of SSZ-13 zeolite membranes.

| Si/Al ratio | Mixture | Flux (kg $m^{-2}$ $h^{-1}$) | Selectivity ($\alpha$) | Remarks | Ref. |
|---|---|---|---|---|---|
| 3 | $H_2O$ (9%)–Ethanol (91%) | 4.14 | 39,500 | 75 °C | [16] |
| 3 | $H_2O$ (10%)–Ethanol (90%) | 11.4 | $>60,000$ | 40 °C, highly porous support | [17] |
| 8 | $H_2O$ (50%)–*N*-methyl pyrrolidone (50%) | 36 | 1100 | 130 °C | [18] |
| 13 | $H_2O$ (10%)–Ethanol (90%) | 3.4 | 2100 | 75 °C, grown from zeolite T seeds | [19] |
| 14 | $H_2O$ (30.5%)–$HNO_3$ (69.5%) | 0.07 | 3.3 | 25 °C | [20] |

**Table 2**
Literature data on gas separation performance of CHA (SSZ-13 and SAPO-34) zeolite membranes.

| Membrane | Mixture | Permeance/$10^{-7}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$ | Selectivity ($\alpha$) | Remarks | Ref. |
|---|---|---|---|---|---|
| SSZ-13/α-alumina | $CO_2/CH_4$ | 3 | 40 | Si/Al=86, 20 °C, feed pressure 600 kPa, Ar sweep gas | [10] |
| | $CO_2/N_2$ | 3 | 12 | | |
| SSZ-13/α-alumina | $H_2/CH_4$ | 2 | 22 | Si/Al=86, 20 °C, feed pressure 600 kPa | [11] |
| SSZ-13/SS | $CO_2/CH_4$ | 1.7 | 12 | Si/Al=13, 25 °C, 220 kPa | [20] |
| | $H_2/CH_4$ | 0.8 | 8 | | |
| SAPO-34/α-alumina | $CO_2/CH_4$ | 25 | 9 | Macroporous support with high porosity, 23 °C, feed pressure 100 kPa | [21] |
| SAPO-34/α-alumina | $CO_2/CH_4$ | 16 | 70 | Optimized preparation procedure, 22 °C, feed pressure 4.6 MPa, | [22] |

$SF_6$ single-gas permeation, $CO_2/CH_4$ gas separation, and water/ethanol separation by pervaporation. The hydrophilicity of the membranes was determined by water and ethanol adsorption on corresponding SSZ-13 powders

## 2. Experimental

### 2.1. Membrane preparation

Supported membranes were prepared by seeded secondary growth. First, SSZ-13 nano-crystals were prepared and deposited as a thin film on the inner surface of hollow fiber α-alumina supports (i.d. 1.8 mm, o. d. 2.9 mm, total length of 70 mm, permeation area of 1.7 $cm^2$, pores of ca. 300 nm and a porosity of 29%, supplied by Hyflux) as described in our previous publication [10]. The initial gel mixture for secondary growth had a composition of $x$SiO$_2$:2NaOH:$y$Al(OH)$_3$:2TMAdaOH:440H$_2$O, where $x+y=10.5$ and $x/y=5$; 10; 25; 50; 75; 100. Membrane samples in this work are denoted according to their mixture gel Si/Al ratios as in the following example: SM-5 refers to gel Si/Al ratio of 5. A typical mixture was prepared by mixing N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH 25%, SACHEM, Inc.) and NaOH (50%, Merck ) with demineralized water. Then Al(OH)$_3$ (Sigma-Aldrich) was added and the mixture was stirred for 0.5 h until Al(OH)$_3$ was completely dissolved. Finally, fumed silica (Cab-O-Sil M-5, Cabot) was slowly added upon vigorous stirring and the gel was aged for 6 h at room temperature. After ageing the gel was poured in 45 mL PTFE-lined autoclaves (Parr), in which the tubular supports wrapped with PTFE-tape supports were vertically placed. Hydrothermal secondary growth synthesis was performed for 6 days at 160 °C in static conditions. Pure-silica CHA crystals were prepared according to a procedure reported by Eilertsen et al. [23]. First tetraethylorthosilicate (TEOS, Merck) was mixed with aqueous solution of TMAdaOH for 12 h under continuous stirring with slow heating to 80 °C to evaporate ethanol and part of water. Then aqueous solution of HF (Alfa, 40%) was added dropwise resulting in dry gel with molar composition of 2SiO$_2$:1TMAdaOH:1HF:6H$_2$O. Then the dry gel was transferred to a PTFE-lined autoclave and heated to 155 °C for 40 h with tumbling (60 rpm).

After synthesis, the zeolite membranes and powders collected from the bottom of autoclave were thoroughly washed by demineralized water and dried at 100 °C overnight. Finally, SSZ-13 membranes were activated by calcination in pure oxygen flow at 450 °C for 80 h with heating and cooling rates of 0.2 °C/min, while SSZ-13 powders were calcined at 650 °C for 8 h in air with heating and cooling rates of 1 °C/min.

### 2.2. Characterization

The crystalline structure of the supported zeolite films was confirmed by recording XRD patterns with a Bruker D4 Endeavor diffractometer using Cu Kα-radiation. SSZ-13 films of different Si/Al ratios were prepared by the same procedure but on an α-alumina disc support for the purpose of recording XRD patterns, because the hollow fiber geometry is not amenable to accurate XRD analysis. The surface chemical composition of the membranes was analyzed by XPS using a Thermo Scientific K-alpha spectrometer equipped with a monochromatic Al Kα X-ray source. Relative atomic sensitivity factors of detected elements were used to determine the surface composition. Microscopic characterization of the membranes was performed on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 5–15 kV. Chemical composition of zeolite samples was measured by ICP-OES (Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing). Extraction was performed by dissolving the zeolite powders in HF/HNO$_3$/H$_2$O mixture. Argon adsorption-desorption measurements were carried out at −186 °C on a Micromeritics ASAP-2020 apparatus. The *t*-plot method was applied to calculate the micropore volume of the zeolite powders. Ethanol and water adsorption isotherms on zeolite powders of different Si/Al ratios were measured by gravimetry as described in detail elsewhere [24].

### 2.3. Pervaporation and permeation experiments

Separation of water–ethanol mixture by pervaporation were performed at 75 °C. The pressure on the permeate side was adjusted to ca. 0.1 kPa and the feed mixture composition was 22 mol% water–78 mol% ethanol. The feed mixture was recirculated over the membrane at a rate of 10 ml/min by means of an HPLC pump. The composition of the permeate was determined by online GC equipped with TCD. A Rt-Q-BOND column was applied to separate ethanol from water. The separation factor ($\alpha$) is defined as:

$$\alpha=\frac{X_{water}/X_{ethanol}}{Y_{water}/Y_{ethanol}}$$

where $X$ and $Y$ are molar fractions of corresponding components before and after separation, respectively. The permeate was cooled