Supported SOD membrane with steam selectivity by a two-step repeated hydrothermal synthesis

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By a two-step repeated hydrothermal synthesis, supported SOD membranes have been prepared. Compared with LTA membranes, SOD membranes are more stable and can be used in the removal of steam in catalytic membrane reactors in the presence of other species like H2, CH4 and CO2 in the feed or reten- tate. Under practice-relevant conditions, the mixture separation factors for equimolar mixtures of steam with possible reactants and products have been evaluated between 125 and 200 °C. The mixed gas separations factors for H2O/H2, H2O/CH4, and H2O/CO2 were found to decrease slightly with increasing temperatures from 125 to 200 °C and decrease from 8.1 to 4.6, from 17.9 to 14.5, and from 33.4 to 22.6, respectively. For the water separation from methanol a mixture separation factor of 200 was found.

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1. Introduction

The hydrophilic LTA membrane is the first commercialized zeo- lite membranes and it is used increasingly for the de-watering of (bio) ethanol and i-propanol by membrane-based steam perme- ation. Impressive capacities have been installed in the last few years [1]. However, the handling of LTA zeolite membrane requires careful membrane treatment in the permeation operation to avoid structural damage. Compared with LTA, the zeolite structure SOD shows a higher framework density and has, therefore, with the same Si/Al ratio of 1, a higher structural stability. The supported SOD layers show even a higher thermal stability than non-sup- ported SOD material [2]. Consequently, for water separation under harsh conditions such as from (catalytic) membrane reactors, powerful SOD type membranes have been successfully developed [3–5]. However, since the SOD structure itself is stabilized through hydrogen bonding between adsorbed water and the framework oxygen atoms, complete dehydration of SOD weakens these hydrogen bonds and may cause a partial damage of the SOD structure [6]. By intercalation of sulphur into the framework, the hydrothermal (or steam, depending on the reference) stability of SOD could be improved [7].

On the other hand, in the presence of steam, SOD membranes show remarkable stability under acidic and basic conditions [8], and SOD membranes have been successfully evaluated in membrane reactors for esterification [9] and seawater desalination [10]. SOD membranes can also be used in gas separation. As an example, by microwave-assisted hydrothermal synthesis, Xu et al. could prepare hydrogen-selective SOD zeolite membranes with a H2/n-butane selectivity >1000 [11]. Also mixed matrix membranes based on SOD with polyimide [12] or clay [13] are reported.

Because of its Si/Al = 1, SOD is hydrophilic with a pore diameter of around 2.7 Å [14], which allows the passage of small molecules like e.g. H2O (2.6 Å). Therefore, a SOD membrane is an excellent candidate to remove steam formed in chemical reactions at elevated temperatures such as in the synthesis of dimethylether (DME) and dimethylcarbonate (DMC) starting with carbon dioxide, hydrogen or methanol (MeOH) as reactants according to CO2 + H2 → DME + 3H2O and CO2 + 2MeOH ↔ DMC + H2O, respectively. Also the removal of water in MeOH synthesis starting from carbon dioxide according to CO2 + 3H2 → MeOH + H2O seems possible. Another challenging goal for the development of SOD membranes is the water extraction in the Fischer Tropsch synthesis [15]. The difficulty in the steam/water separations is the simultaneous presence of other small molecules like hydrogen (2.9 Å), carbon dioxide (3.3 Å) and methane (3.8 Å) in the gaseous reaction mixture, which are expected to remain in the feed. With other words, high H2O/H2, H2O/CH4, and H2O/CO2 selectivities are needed. Further, a high H2O/MeOH selectivity would allow the in situ removal of water in the membrane supported methanol synthesis starting with carbon dioxide as feed.

It is worth to note that the papers published so far on water permeation on SOD membranes report only pervaporation studies of liquid mixtures under 100 °C or - when using pressurized feeds - up to 165 °C [8,10,3]. It is the aim of this paper to study the separation behaviour of SOD membranes for the steam/gas mixtures
H₂O/H₂, H₂O/CH₄ and H₂O/CO₂ under practice-relevant conditions at higher temperatures between 125 and 200 °C.

2. Experimental

2.1. Materials

Chemicals were used as received: LUDOX AS-40 colloidal silica (40% SiO₂ in water, Aldrich) as Si source; aluminum foil (Fisher Scientific); sodium hydroxide (>99%, Merck); doubly distilled water. Porous α-Al₂O₃ disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as supports.

2.2. Preparation of zeolite SOD membranes by repeated synthesis

A clear precursor solution with the molar ratio 50Na₂O: 1Al₂O₃:5SiO₂:100H₂O, was prepared according to the procedure reported elsewhere [3]. Typically, 11.11 g sodium hydroxides were dissolved in 25 g deionized water at room temperature, then 0.15 g aluminum foil was added to obtain the aluminate solution. The silicate solution was prepared by mixing 2.08 g LUDOX AS-40 colloidal silica and 23.75 g deionized water at 60 °C under vigorous stirring. The prepared aluminum solution was added into the silicate solution and stirred overnight at room temperature to produce a clear solution. α-Al₂O₃ support was then horizontally placed face down in a Teflon-lined stainless steel autoclave which was filled with synthesis solution. After hydrothermal synthesis over 24 h at 120 °C, the solution was decanted off and the membrane was washed with deionized water and dried in air at 110 °C overnight. To prepare a more compact SOD membrane, the dried membrane was subject to repeated hydrothermal synthesis under identical conditions. Finally, the dried membrane was further characterized and evaluated in gas permeation measurement. Following this recipe, 8 SOD membranes have prepared and all preparations were successful and showed similar separation behaviors (Table 2).

2.3. Characterization of zeolite SOD membranes

The morphology and thickness of the zeolite SOD membranes were characterized by scanning electron microscopy (SEM), which was carried out on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 μA. The chemical composition of the SOD-layer was characterized by energy-dispersive X-ray spectroscopy (EDXS) using the same SEM microscope at 20 kV and 20 μA. The phase purity and crystallinity of the zeolite SOD membrane layers were confirmed by X-ray diffraction (XRD). XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA.

Fig. 1. SEM top views (a) (b) and EDXS mapping of top view (c) (orange: SOD islands, green: Al₂O₃ support) of the α-alumina support after hydrothermal SOD synthesis prepared by secondary growth method with SOD seeds deposited by dip-coating, no dense SOD layer has been formed, the uncovered alumina support can be seen.

Fig. 2. SEM top view of zeolite SOD membrane by one-step hydrothermal synthesis (a), SEM top view (b) and cross-section (c) of zeolite SOD membrane by two-step repeated hydrothermal synthesis.
2.4. Evaluation of single gas permeation and mixed gas separation

Zeolite SOD membranes supported on \( \alpha-\text{Al}_2\text{O}_3 \) disks were evaluated by single gas permeation and mixed gas separation. For permeation experiments, the supported zeolite SOD membranes were sealed in a permeation module with silicone O-rings. In the feed side, deionized water was heated to 200 °C and vaporized before the measurements. Then the water vapor was led to the permeation cell in a heated pipe, and the permeate gases was kept heated until they were injected into gas chromatograph. The
volumetric flow rates of the single gases \( \text{H}_2 \text{O} \), \( \text{H}_2 \), \( \text{CO}_2 \), and \( \text{CH}_4 \) as well as of the equimolar binary mixtures of \( \text{H}_2 \text{O} \) with \( \text{H}_2 \), \( \text{CO}_2 \) and \( \text{CH}_4 \) were measured using the Wicke–Kallenbach technique, as shown in detail elsewhere [16]. The sweep gas \( \text{N}_2 \) was fed on the permeate side to guarantee enough driving force for permeation. To avoid the condensation of water, the measurements were carried out at 125\( ^\circ \)C, 150\( ^\circ \)C, 175\( ^\circ \)C and 200\( ^\circ \)C, respectively. Atmospheric pressure was kept on both sides of the membranes. Fluxes of both feed and sweep gases were controlled by mass flow controllers (MFCs) for gases, while the flux of feed water was controlled by a MFC for water. A calibrated gas chromatograph (HP6890) was used to determine the gas concentrations. The separation factor \( \alpha_{i,j} \) of a binary mixture permeation is defined as the quotient of the molar ratios of the components \((i,j)\) in the permeate, divided by the quotient of the molar ratio of the components \((i,j)\) in the retentate, as shown in Eq. (1).

\[
\alpha_{i,j} = \frac{y_{i,Perm}}{y_{i,Ret}} \cdot \frac{y_{j,Perm}}{y_{j,Ret}}
\]  

Table 1
Comparison of the mixed gas selectivities \( \alpha_{\text{real}} \) determined for equimolar mixtures acc. to Eq. (1) and the ideal gas selectivities \( \alpha_{\text{ideal}} \) determined as the ratio of the single component permeances.

<table>
<thead>
<tr>
<th></th>
<th>125( ^\circ )C</th>
<th>150( ^\circ )C</th>
<th>175( ^\circ )C</th>
<th>200( ^\circ )C</th>
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<tr>
<td>( \alpha_{\text{real}} )</td>
<td>( \alpha_{\text{ideal}} )</td>
<td>( \alpha_{\text{real}} )</td>
<td>( \alpha_{\text{ideal}} )</td>
<td>( \alpha_{\text{real}} )</td>
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<tr>
<td>( \text{H}_2 \text{O}/\text{H}_2 )</td>
<td>8.1</td>
<td>4.8</td>
<td>6.7</td>
<td>3.2</td>
</tr>
<tr>
<td>( \text{H}_2 \text{O}/\text{CH}_4 )</td>
<td>17.9</td>
<td>12.1</td>
<td>16.4</td>
<td>9.7</td>
</tr>
<tr>
<td>( \text{H}_2 \text{O}/\text{CO}_2 )</td>
<td>31.4</td>
<td>26.1</td>
<td>28.4</td>
<td>24</td>
</tr>
</tbody>
</table>

Fig. 6. Mixture separation factors for \( \text{H}_2 \text{O} \) over other gases from equimolar mixtures (left) and the 48 h stability measurement for the single gas permeances on the SOD membrane (right) at 175\( ^\circ \)C and 1 bar.

Fig. 7. Mixture separation factors for \( \text{H}_2 \text{O} \) over other gases from equimolar mixtures (left) and the 48 h stability measurement for the single gas permeances on the SOD membrane (right) at 200\( ^\circ \)C and 1 bar.

Fig. 8. Mixture separation factors for \( \text{H}_2 \text{O} \) over other gases through a zeolite SOD membrane prepared by two-step repeated hydrothermal synthesis as a function of temperature.
3. Results

In situ growth and secondary growth methods are the most common techniques for the preparation of zeolite membranes. Due to the separation of nucleation (at high supersaturation) and crystal growth (at low supersaturation), the seeded growth method suppresses non-desired secondary nucleation and growth, and allows therefore more control of the microstructure of zeolite membranes. In view of this, we first tried to prepare SOD membranes by secondary growth. Initially, SOD seeds have been prepared and successfully deposited on the α-alumina supports by dip-coating. Then the SOD membrane was prepared in the same synthesis solution as described in 2.2 over 24 h at 120 °C. However, the SEM shows that after secondary growth, the SOD seed crystallites are not intergrown to a dense SOD layer (Fig. 1). Accordingly, the permeation of steam/gas mixtures shows that the SOD membrane has no H2O/H2, H2O/CH4, or H2/CO2 selectivity at all.

Therefore, we decided to develop an “in situ” seeding method for the direct growth of the SOD layer on the substrate [17]. In this method, the bare α-alumina support is immersed in a SOD precursor solution and then subjected to hydrothermal growth at 120 °C. After the first hydrothermal SOD synthesis, SEM indicates that no compact SOD seed layer had formed and on some spots the support surface can be seen (Fig. 2a). Although SOD crystallites could not fully cover the entire substrate surface after the first hydrothermal synthesis, after repeated synthesis the surface of the alumina support has been completely covered by a tightly packed SOD layer (Fig. 2b), and no visible intercrystalline defects can be detected.

The cross-section image (Fig. 2c) shows a well-intergrown SOD membrane layer with a thickness of about 8 μm. One could assume from the top views, that the SOD layers prepared by single-step (Fig. 2a) and repeated hydrothermal synthesis (Fig. 2b) are rather heterogeneous due to the different size and shape of the crystallites, and contain different crystalline phases. However, the XRD results confirmed that in both the SOD layers prepared by single-step and repeated hydrothermal synthesis, no foreign crystalline phase is present (Fig. 3). After the repeated hydrothermal synthesis, the membrane shows stronger SOD peaks relative to the alumina support because of the increased SOD layer thickness (XRD minima support because of the increased SOD layer thickness (XRD).

Figs. 4–7 shows the mixture separation factors for the three equimolar mixtures H2O/H2, H2O/CH4, and H2O/CO2 as well as the single gas permeances for a 48 h permeation time at 125 °C, 150 °C, 175 °C and 200 °C, respectively. It can be seen that the permeances of H2, CH4 and CO2 kept unchanged for 48 h, indicating the stability of the SOD membrane at high temperatures (above 125 °C) even for steam as undiluted feed. In complete accordance with this stable permeation behavior, no structural degradation of the SOD structure could be observed by XRD and electron microscopy (not shown here). The scattering of the steam permeances (Figs. 4–7) is a measuring effect due to the repeated condensation/evaporation of water vapor in the equipment at low temperatures which settles with increasing permeation temperature. Table 1 shows that, surprisingly, all mixture separation factors $\chi^{\text{real}}$ are higher than the ideal selectivities $\chi^{\text{ideal}}$ calculated from the single gas permeances. This experimental finding can be explained by the extreme hydrophilicity of the SOD structure. In the case of the mixed gas permeation, the water becomes strongly adsorbed in the SOD framework in the whole temperature window between 125 and 200 °C. This strongly adsorbed water effectively suppresses the adsorption and diffusion of the second component.

Fig. 8 and Table 1 show the mixture separation factors for H2O over other gases through a zeolite SOD membrane as a function of temperature. It was found that the mixed gas separations factors for the three systems under study H2O/H2, H2O/CH4, and H2O/CO2 decreased slightly with increasing temperature (from 8.1 to 4.6, from 17.9 to 14.5, and from 33.4 to 22.6), respectively. Permeation of a species through the membrane is a result of the interplay of adsorption and diffusion. The “membrane selectivity” can be estimated as product of “diffusion selectivity” multiplied by “adsorption selectivity”. In the whole temperature window between 125 and 200 °C, the hydrophilic SOD preferentially absorbs water thus restraining the diffusion of the rarely adsorbed H2, CH4, and CO2. As temperature increases, slightly less H2O becomes adsorbed and, thus, the other components H2, CH4, and CO2 can diffuse in the resulting free volume, leading to a reduction of the selectivity of H2O/H2, H2O/CH4, and H2O/CO2. The SOD membrane switches with increasing temperature from “adsorption control” in the direction of “diffusion control”. This temperature-dependent interplay of adsorption and diffusion has been developed for describing permeation through organic polymer membranes [18], but it has been successfully applied to permeation through MFI pore membrane with hydrogen as the weakly and i-butane as the strongly adsorbed component [19]. In the adsorption-controlled state at low temperature, the MFI membrane is butane-selective, with increasing temperature the MFI membrane becomes hydrogen-selective. Fig. 9 presents the increase of the single component permeances with increasing temperature. Obviously, the decreased adsorption with increasing temperature has been over compensated by the increased diffusivity of the guest species. However, from the only slight increase of the water single component permeance with increasing temperature (Fig. 9) it can
be concluded that reduced water adsorption and increased diffusion in SOD almost compensate. This increase of the permeance with increasing temperature has been also observed in pervaporation studies up to 165 °C with pressurized liquid water as feed [3,10].

As a proof of the good reproducibility of the two-step repeated hydrothermal synthesis method, Table 2 shows the gas permeation performances of 8 different zeolite SOD membranes prepared following identical synthesis protocols. The mixed gas selectivities and water permeances at 150 °C do not scatter more than ±10%, which proofs both the good reproducibility of the SOD membrane preparation as well as of the SOD membrane testing.

Table 3 shows the mixture separation performance for H2O over MeOH through a zeolite SOD membrane at different temperatures (from 125 °C to 200 °C), which indicates that the removal of water from methanol is also successful in the whole temperature window due to molecular sieving (pore size SOD ≈ 2.7 Å, water 2.6 Å, MeOH 3.8 Å). This finding recommends SOD membrane for in situ water removal in methanol synthesis acc. to CO2 + 3H2 → MeOH + H2O.

4. Conclusions

After a two-step repeated hydrothermal crystallization, a well intergrown SOD membrane layer with a thickness of about 8 μm could be obtained on the α-alumina support. The SOD membrane displayed water selectivity in steam permeation of equimolar mixtures of H2O/H2, H2O/CH4, and H2O/CO2 under practice-relevant conditions. The mixed gas separation factors of H2O/H2, H2O/CH4, and H2O/CO2 were found to decrease slightly with increasing temperature. These selectivity data of steam removal in the presence of hydrogen, methane, and carbon dioxide are promising for the use of SOD membranes in (catalytic) membrane reactors. However, the selectivity has to be improved further. It was found that the mixed gas separation factors for the three systems under study H2O/H2, H2O/CH4, and H2O/CO2 decreased slightly from 125 to 200 °C (from 8.1 to 4.6, from 17.9 to 14.5, and from 33.4 to 22.6), respectively. Water is also separated from methanol with mixture separation factors near 200. However, the water permeance of 0.43 kg/m²·h·bar at 200 °C is relative low due to the 8 μm thickness of the SOD membrane.

Acknowledgements

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References

[1] Industrial applications of LTA membranes between 2009 and 2012: (a) Mitsui-Sulzer Chemtech at 130 °C: Singapore, 27 t IPA/day, 100 m² membrane area; Finland, 216 t EtOH/day, 800 m²; Ukraine, 150 t EtOH/day, 400 m²; (b) Fraunhofer IKTS-GFT Membrane Systems at 140 °C: Lithuania, 80 t EtOH/day, 400 m²; (c) Dalian Univ. of Techn.-Yancheng Inst. of Techn. at 140 °C: 150 t IPA/day, 200 m²; (d) Nanjing Jingsu Nine-Heaven Hi-Tec Co.: 7.5 t IPA/day, 35 m², 6 t IPA/day, 52 m², 9 t MeOH/day, 84 m², 9 t IPA/day, 56 m²; (e) Dalian DIC of CAS-Xinha Chemical Co. Ltd. At 140 °C: 140 t IPA/day, 350 m²; Dalian DIC of CAS-Sopo China at 120 °C: 80 t EtOH/day, 350 m².


