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Published in ChemSusChem (2009) 2, 158-160
doi: 10.1002/cssc.200800198

ECN-W--09-013 March 2009

CHEMSUSCHEM

DOI: 10.1002/cssc.200800198

Stable Hybrid Silica Nanosieve Membranes for the Dehydration of Lower Alcohols

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The key objective of the International Energy Agency (IEA) for future energy technologies[1] is to reduce CO_2 emissions by approximately 50 Gt per year by 2050. Carbon-neutral biobased fuels such as ethanol, butanol, and biodiesel are promising candidates for transportation purposes. However, effective and energy-efficient separation technologies to dehydrate the wet fuels[2] or the methanol recycle stream during biodiesel production[3] are major hurdles to a large-scale application. It is widely accepted that molecular separation membranes will play a crucial role in this transition to sustainable transportation fuels.

A hybrid distillation–pervaporation separation process is a commonly considered option for the recovery of ethanol from fermentation mixtures.[4] In this process, the crude ethanol product from the distillation is dehydrated by pervaporation using membranes based on zeolites,[5] polyvinyl alcohol,[6] various polyimides,[7] and silica[8] or methylated silica.[9] All of these options share a limited stability in the presence of acids,[10] and under hydrothermal conditions.[7,9,11,12]

We recently explored the use of organic–inorganic hybrid silica for microporous membranes. Hybrid silica precursors are versatile building blocks for porous materials.[13] We discovered that membranes based on a mixture of 1,2-bis(triethoxysilyl)-ethane (BTESE) and methyltriethoxysilane (MTES) have unprecedented lifetimes of up to 2 years in the dehydration of *n*-butanol at 150 °C.[14] Membranes prepared from only BTESE showed a further improved separation performance with separation factors (α) in the range of 1000–10000 and water fluxes of 10–20 $kg\,m^{-2}\,h^{-1}$ for this separation.[15] However, for the dehydration of ethanol and the even more challenging separation of water from methanol, membranes with narrower pore size distributions are needed. The similarities in molecular size and polarity have rendered separations on the basis of size exclusion and/or affinity challenging to date.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.200800198.

Here, we report the breakthrough performance and acid resistance of such organic–inorganic hybrid silica membranes (HybSi) in the dehydration of lower alcohols. Standard mixtures of 5 wt% water in the alcohols were used as model systems for the final dehydration step in a distillation–pervaporation process. We aimed to enhance the selectivity for water and tailor the average pore size by using bis(triethoxysilyl)methane (BTESM), which has a single -CH_2- bridging group.

Smooth and defect-free films based on BTESM were obtained by dip-coating a nanocolloidal sol on a mesoporous γ-alumina support tube.[16] The processability of the sol was optimized by engineering the colloid structure towards that of a reported BTESE membrane.[15] With this pre-condition, we compensated the preparation of a BTESM sol for the higher reactivity and network-forming properties as compared to BTESE. By tailoring towards an identical degree of condensed network bonds, the microporosity was adapted, accounting for the shorter length of the intramolecular alkyl bridge of BTESM. A scanning electron microscopy (SEM) micrograph of the cross-section clearly shows the resulting hybrid silica layer on top of the multilayered alumina substrate tube (Figure 1). The membrane layer thickness of this hybrid membrane was estimated at 400 nm.

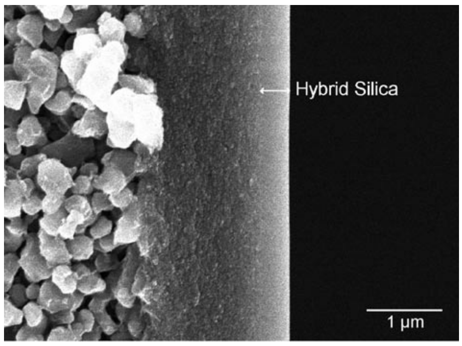

Figure 1. Cross-sectional SEM image of the BTESM membrane.

The Kelvin pore size distribution of the BTESM membrane was determined by using permporometry,[17] and compared to that of the other HybSi membranes (Figure 2). The preparation procedures of mixed BTESE/MTES[14] and pure BTESE[15] membranes are described elsewhere. The smallest average pore sizes were obtained for the membranes prepared from the BTESE/MTES mixture. However, a significant portion of the permeance of this membrane type is caused by larger micropores (1–2 nm), which are present as a tail of the pore size distribution. This tail is a standard feature of our BTESE/MTES mem-

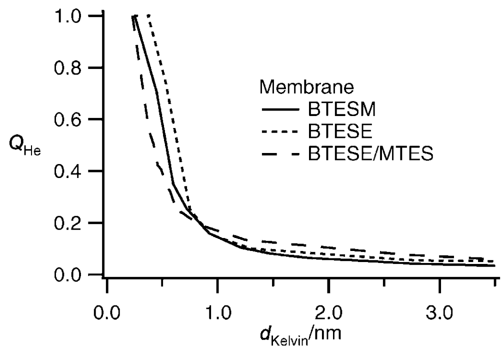

Figure 2. Kelvin pore size (*d*) distribution for BTESM, BTESE, and BTESE/MTES membranes (Q_{He} = normalized helium permeance).

branes, which strongly indicates that these pores are intrinsic to this membrane type. Importantly, the newly developed BTESM membrane has a narrower pore size distribution than both other membrane types and its average pore size is smaller than that of the BTESE membrane.

The test results of the three different membrane types are summarized in Table 1. The water fluxes (J_{H2O}) depend mainly on the test conditions and less on the membrane material, therefore, the measured range of water fluxes is given. They increased with decreasing polarity of the alcohol from which water was extracted by pervaporation. This is a well-known effect and is related to the driving force that increases owing to the higher water activity in longer alcohols.[18] The water permeance (Q_{H2O}) decreased with an increase of the alcohol size. This behavior can be explained by stronger hindered adsorption and hindered diffusion in case of the longer alcohols in combination with a somewhat stronger polarization effect at higher fluxes.[18]

Table 1. Separation performance of the three types of hybrid membrane for the dehydration of alcohol/water (95:5 wt%) mixtures.[a]

Mixture	T [°C]	J_{H2O}	Q_{H2O}	H_2O in permeate [wt%] BTESE/MTES	BTESE	BTESM
*n*BuOH	95	2.0–3.6	4.3–8.0	95.8	99.6	99.8
*n*PrOH	85	1.5–2.8	7.2–13	83.5	99.5	99.5
EtOH	70	0.8–1.5	11–20	42.0	89.2	92.2
MeOH	55	0.3–0.6	14–34	4.6	18.6	55.1

[a] Performance measurements made on two individual membranes for each type; water content numbers averaged over three measurement points.

The water content in the permeate, and thus the selectivity, increases on going from the BTESE/MTES mixed precursor membrane to the BTESE and the BTESM membranes. This is best noticeable for the shortest two alcohols, methanol and ethanol. For ethanol, the water content in the permeate reaches a level of 92 wt% ($\alpha = 219$), while for methanol 55 wt% water was achieved in a single step ($\alpha = 23$). Clearly, the smaller average pore diameter of the BTESM membrane is beneficial for these separations. This performance compares well with zeolite[5] and ceramic-supported polyimide[7] membranes, which however have a limited lifetime. The key feature of the hybrid silica membranes is found in the hydrothermal and acid stability.[14,15]

The acid resistance is of great importance, as fermentation mixtures contain significant amounts of carboxylic acids, which can significantly shorten the membrane life. The stability of BTESE-based membranes in the presence of the inorganic acid HNO_3 was demonstrated previously.[15] In the present study, long-term measurements were performed using three individual BTESM membranes in EtOH/H_2O (95:5 wt%) containing 0, 0.15, and 1.5 wt% acetic acid (Figure 3). The latter values correspond to 0.02 and 0.2 mol L^{-1}, respectively. Clearly, the presence of acetic acid does not have a significant influence on the long-term performance. The observed differences between the individual membranes are caused by small variations in our current preparation procedure. The initial flux decline is comparable to the observations made for other microporous membranes in dewatering applications.[9,10,14,15] This effect is most pronounced in the first 10–30 days of operation. Compared to state-of-the-art zeolite A membranes, the BTESM hybrids have a much higher acid stability.[5b,11] In addition, the preparation and scale-up of these sol-gel-based membranes is straightforward.

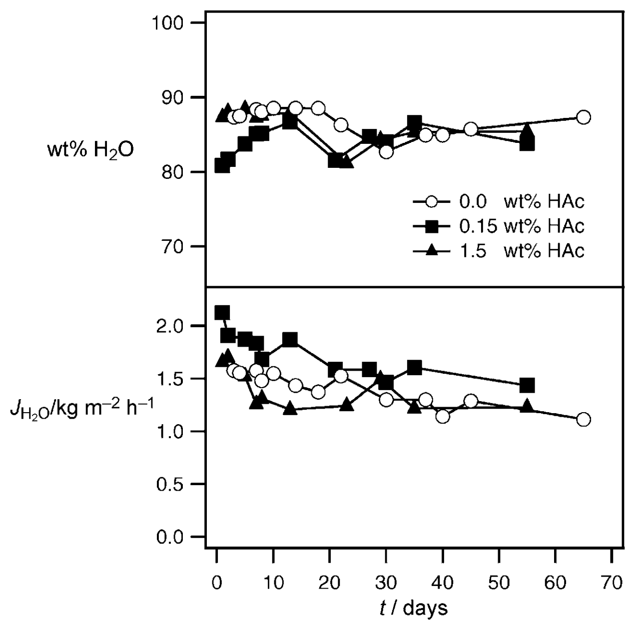

Figure 3. Dehydration performance of BTESM-based membranes for EtOH/H_2O mixtures containing acetic acid at 70 °C. The water content permeate (wt% H_2O) and water flux (J_{H2O}) are shown.

In conclusion, we have demonstrated the broad applicability of HybSi nanosieve membranes in the separation of binary (bio)alcohol/water mixtures. The novel microporous BTESM membranes, containing the shortest possible organic bridge, have a narrower pore size distribution than BTESE membranes. We believe that this is caused by the formation of smaller ring structures in the silica network, leading to a smaller average pore size. The stability in the presence of acetic acid opens the way for processes in which membranes dewater the crude product of a distillation column, which potentially contains significant amounts of carboxylic acids. Therefore, these hybrid membranes provide an essential step in the sustainable production of biofuels. Current tests are focused on the dehydration of lower alcohols at elevated temperatures. This will increase the flux, allowing for a decrease of the required membrane surface area in the final application.

Keywords: biofuels · membranes · microporous materials · organic–inorganic hybrid composites

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Received: October 10, 2008
Revised: November 12, 2008
Published online on January 15, 2009

