Long-term pervaporation performance of microporous methylated silica membranes†

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The incorporation of methyl groups in microporous silica membranes was proven to enhance the service time in the dehydration of a butanol–water mixture at 95 °C from a few weeks to more than 18 months with a water flux of about 4 kg m^{-2} h^{-1} and a selectivity between 500 and 20 000.

The expected high chemical and thermal stability of inorganic membranes compared to polymer membranes has resulted in a growing research activity with the aim of replacing polymer membranes with inorganic ones. The superior separation performance, *i.e.* selectivity and flux, of silica-based membranes in the dehydration of alcohols at elevated temperatures has raised interest even further. This superior performance is required to overcome the higher unit cost price of the inorganic membrane. We estimate that a water flux of at least 3 kg m^{-2} h^{-1} for the dehydration of 5 wt% water in butanol is required. The profitable application of inorganic membranes depends also on a reliable, constant long-term behaviour. Unfortunately, information on this topic is very limited. Dehydration experiments of up to a few days indicate a fast decrease of the water flux through silica-based membranes.[1,2] The origin of this decline has not been determined as yet, but we believe that sorption processes on the inner surface play an important role. In an attempt to overcome this fast decline, we have incorporated methyl groups in the membrane. These methyl groups replace the much more reactive OH groups.[3,4] Further, de Vos[4] reports a reduced water sorption because of the hydrophobic character of the methylated silica (Me-SiO$_2$). This membrane was deemed to be more suitable for gas separation in the presence of steam. Now, we anticipate that the incorporation of methyl groups also has a stabilising effect on the water flux in pervaporation.

We applied acid-catalysed single-step[4,5] and two-step[6] hydrolysis routes to prepare sols. One pure silica sol was prepared by refluxing a mixture of TEOS, C_2H_5OH, HNO_3, and H_2O at 60 °C. One Me-SiO$_2$ sol was prepared by adding MTES towards the end of the reflux period of the pure silica sol. Me-SiO$_2$ sols with various methyl concentrations were synthesised using a two-step process. TEOS was prehydrolysed before MTES was added, and a final addition of HNO_3 and H_2O was made.

Membranes were prepared by dip-coating a mesoporous γ-alumina layer on a 1 m long tubular support, with a wall thickness of ~ 3 mm, as described elsewhere.[1,7] Subsequently, the membranes were heated in air at 250 °C (Me-SiO$_2$) or 400 °C (pure SiO$_2$) for 2 hours. Membranes could be made from the pure SiO$_2$, the 'single-step' Me-SiO$_2$, and the 'two-step' Me-SiO$_2$ sols with TEOS : MTES = 10 : 1 (10% MTES); and 10 : 3 (30% MTES). The separating layer was applied on the exterior of the tubular support.[7]

The sols were analysed using gel permeation chromatography (GPC) to assess the particle size distribution (PSD). Solid-state NMR on free-standing films prepared analogously to the membranes was used to determine the final -CH$_3$ concentration. The pore size was assessed by single gas permeation measurements (GPM) with various gases with increasing kinetic diameter, *i.e.* He, H_2, CO_2, N_2, and CH_4. Pervaporation measurements on mem-

branes, with a surface area of ~ 40 cm², at temperatures ranging from 75 °C to 165 °C were performed in a stirred vessel containing *n*-butanol (Merck P.A.) with 5 wt% ($T \leq 95$ °C) or 2.5 wt% ($T \geq 115$ °C) demineralised water. During the longevity tests the membranes were constantly kept on stream and the water content at the feed side was controlled to be 1–3 wt%. The permeate was cooled with liquid nitrogen to facilitate collection. The selectivity, α, is defined as $(Y_w/Y_b)/(X_w/X_b)$ where Y and X are the weight fractions of water (w) and butanol (b) in the permeate and feed solutions respectively. Pre-test and post-test SEM micrographs were used to study the changes of the surface as a result of the experiments, and to determine the thickness of the membranes.

The PSD of the pure silica and 'single-step' Me-SiO$_2$ sols are similar and polydisperse with a maximum at M_w of ~ 4 kg mol^{-1}. The 'two-step' Me-SiO$_2$ sols have a much narrower PSD and the particles are smaller ($M_w \approx$ 1 kg mol^{-1}). A higher methyl content in the 'two-step' sol results in smaller species. The NMR data on free-standing films proved that the -CH$_3$ groups were not removed from the membrane during the heat treatment. The GPM indicates that the micropores in all Me-SiO$_2$ membranes are larger than those in the SiO$_2$ membranes, but remain smaller than 1 nm. The pore structure is clearly not only dependent on the particle size but also on other factors like the condensation rate between neighbouring particles during the formation of the membrane layer. This is consistent with the observations by de Vos.[4] SEM micrographs of the cross section of the tube showed that the thickness of the 'single-step' membrane is ~ 150 nm and that of the 'two-step' membranes is ~ 60 nm.

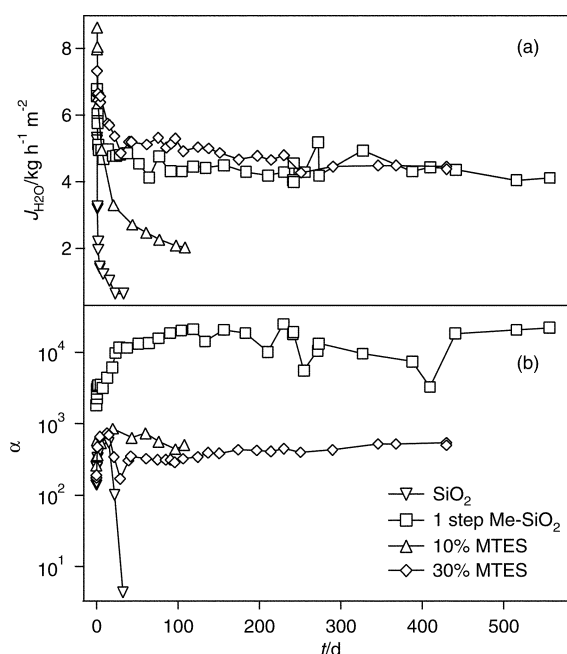The long-term pervaporation measurements at 95 °C are presented in Fig. 1. The data are representative for the various

Fig. 1 The water fluxes, J_{H_2O} (a), and the selectivities, α (b), as a function of time for the various membranes at 95 °C, with a feed composition of 5% water in *n*-butanol, as determined in pervaporation measurements.

† Electronic Supplementary Information (ESI) available: details of the sol synthesis; GPC and NMR measurements; and additional SEM micrographs. See http://www.rsc.org/suppdata/cc/b4/b401496k/

membrane systems under investigation. We see that the water flux for the SiO_2 membrane reduces to very low values within a week. We believe that this effect can be attributed to pore blocking by water molecules that are bound to the internal pore surface through interactions that are stronger than those of physisorption, *e.g.* hydrogen bridges or chemisorption. On increasing the -CH_3 content, we see that the flux decrease reduces. For high -CH_3 concentrations, the water flux reduction is very limited indeed. This is consistent with our proposed mechanism of pore blocking. The -CH_3 groups render the surface more hydrophobic and a water molecule is less likely to be adsorbed on the inner surface. In addition, the larger pore sizes of the 'Me-SiO_2' membrane may prevent total blocking by water. The 'SiO_2' membrane shows failure within weeks, as can be seen from the very low selectivity after 32 days. The '10% MTES' membrane shows a more-or-less constant selectivity, but the water flux reduces to 2 kg m^{-2} h^{-1} after 100 days. However, the two membranes with the highest -CH_3 concentration used in this study showed no sign of serious degradation during the first 15 and 18 months of operation, with butanol fluxes of ~ 10 and ~ 200 g m^{-2} h^{-1} respectively. We think that this difference in butanol flux is mainly due to a difference in thickness between the two membranes, with the thinner membrane, '30% MTES', having the higher butanol flux. Other possible explanations, such as differences in morphology of the membrane because of the variations in PSD of the sol and -CH_3 group distribution, are not as important. The decrease in water flux of the 'single-step' Me-SiO_2 membrane is limited to ~ 7% per year after the first week of operation.

The origin of the increased stability at 95 °C is not totally clear. It is unlikely that the incorporation of -CH_3 groups results in a substantial stabilisation of the siloxane bond itself. The methyl group is not sufficiently electronegative to achieve this. Instead, effects because of the reduction of reactive -OH groups and some kind of shielding through the bulky -CH_3 are probably more important.

Dehydration experiments were also performed at 115, 135 and 165 °C. The various membrane systems failed after 4 to 40 days. The scatter in the service time is of the order of 7 days and prevents the observation of a relation between service time and membrane
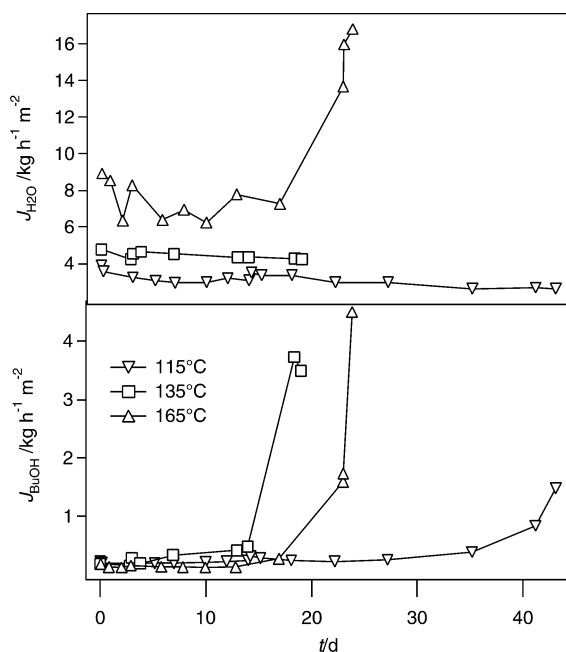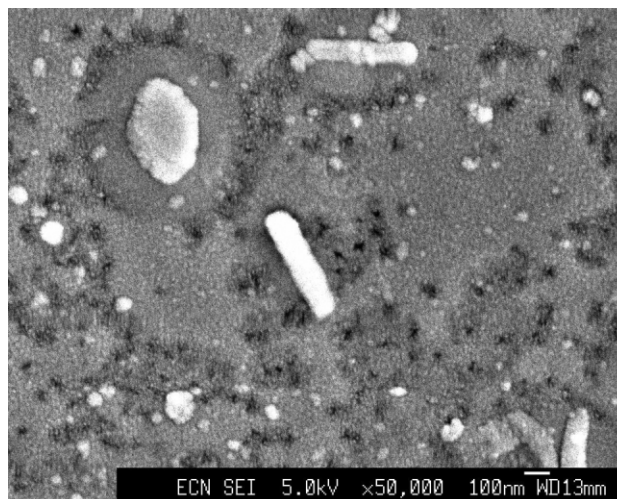

Fig. 3 SEM micrograph of a '30% Me-SiO_2' membrane after testing in pervaporation at 135 °C for 7 days.

type, temperature or any other property that might be of influence. In Fig. 2, we present some representative data of our 'single-step' Me-SiO_2 membrane. In all cases we observe a strong increase in the butanol flux, indicating that the pore size increases over time. The water flux is fairly constant at 115 °C and 135 °C indicating that the structure remains microporous. At 165 °C we observe that both fluxes increase rapidly after ~ 20 days. We believe that this is due to the formation of mesopores or pinholes in the separating layer. Further evidence for this can be found in the post-test SEM micrographs. The example in Fig. 3 is illustrative in this respect. We observe white particles, rectangular and egg-shaped, that we believe to be dense silica, and black spots that we think are pin holes in the membrane. Pre-test SEM micrographs are all featureless on the same length scale, however a limited number of imperfections of about 1 μm are present. The change in surface structure of the membrane is likely to be due to hydrothermal reorganisation, with mass transport over up to 100 nm, and it is likely that this is the origin of the processes leading to the failure observed in our pervaporation experiments at temperatures above 95 °C.

In conclusion, the incorporation of -CH_3 groups in silica membranes is a successful route to obtain satisfactory separating performances at temperatures up to 95 °C, under the current measurement conditions, for more than 18 months. The service time at higher temperatures is severely limited due to reorganisation of the separating layer. As a consequence, we conclude that the application window of state-of-the-art silica-based membranes for use in dehydration processes is limited to 95 °C.

Notes and references

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Fig. 2 The water, J_{H2O} (a), and the butanol, J_{BuOH} (b), fluxes of a 'single-step' Me-SiO_2 membrane, at various temperatures, with a feed composition of 2.5% water in *n*-butanol as determined in pervaporation.