Hybrid ceramic nanosieves: stabilizing nanopores with organic links†

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Unprecedented hydrothermal stability in functional membranes has been obtained with hybrid organic–inorganic nanoporous materials, enabling long-term application in energy-efficient molecular separation, including dehydration up to at least 150 °C.

Devising more efficient processes to reduce energy consumption is one of the prime challenges of the 21st century. A promising strategy is to apply nanostructured membranes to sieve mixtures of molecules of different sizes. Membranes can be applied in energy-efficient separation of biomass fuel and hydrogen, dehydration of condensation reactions, and breaking of azeotropic mixtures during distillation.[1,2] However, industrial usage of membranes will only become economically feasible when they can operate at elevated temperatures for several years. This is crucial considering the typical temperature of many process streams, as well as the high cost of module replacement and concomitant process discontinuation.

Several materials have been proposed as molecular sieving membranes, including polymers, zeolites and metal oxides.[2–4] A supported 30–100 nm thin film of nanoporous silica (SiO_2) is one of the most promising systems for molecular separation of gases and liquids. Amorphous silica combines high permeability for molecules < 3 Å (*e.g.*, H_2O, H_2) with very low permeability for larger ones. It has high mechanical, thermal and solvent stability and can be applied at 600 °C in dry atmospheres.[5] However, it lacks inherent microstructural stability in the presence of water at temperatures as low as 60 °C.[4,6] Prolonged exposure to water leads to hydrolysis: $\equiv$Si–O–Si$\equiv$ + $H_2O \rightarrow 2 \equiv$Si–OH, resulting in transport of silica moieties and the formation of large non-selective pores and cracks. These act as defects and impair membrane functionality.

Replacement of silica by other candidate materials has not resulted in stable membranes while retaining both selectivity and a high permeation rate. Polyvinyl alcohol is currently the most promising polymeric material, but permeances are generally lower than for ceramic membranes. In addition, as its glass transition temperature is around 85 °C, no use has been reported much above this temperature.[7] Some stability improvement of silica has been achieved by incorporation of hydrolytically stable organic groups like $-CH_3$. These were considered to 'shield' the siloxane bonds from water, but their concentration was limited to a maximum CH_x : Si molar ratio of 0.5.[8,9] The maximum operating temperature of methylated silica in dehydration applications is 95 °C.[8] At higher temperatures, degradation was reported to occur within weeks.

The strategy behind the present work was to replace as many siloxane bonds as possible by hydrolytically stable Si–C links, while raising the CH_x : Si ratio to 1. We applied a bridged bis-silyl precursor, $(EtO)_3Si–CH_2CH_2–Si(OEt)_3$ (BTESE), and the versatile and mild processing conditions of sol-gel synthesis. These precursors are also applied for periodic mesoporous organosilicas (PMOs).[10] However, PMOs have pore sizes >2 nm and therefore exhibit no molecular sieving properties. We aimed at a microporous material with pore diameters of 2–4 Å, similar to the kinetic diameter of small molecules. Our prime aim was, however, to prepare a material with a high hydrothermal stability, *i.e.*, a persisting high selectivity towards molecular separation at high temperatures in the presence of water.

To prevent the formation of unreactive cyclic carbosiloxane structures, as reported by Shea,[11] we added methyltriethoxysilane (MTES) as a co-reactant. With ^{29}Si solution NMR, we found just 30% faster condensation rates for MTES, which implies that MTES–BTESE co-condensation occurs at the expense of BTESE auto-condensation. Hence, we could lower the statistical chance of formation of inert cyclic structures. By carrying out the first reaction stage under water-lean conditions, we controlled the highly exothermic hydrolysis of the –OEt groups and thus enhanced homogeneous colloid formation. More water was added in subsequent steps to allow further development of the sol.

Dynamic light scattering was used to monitor and optimise the sol size distribution. As the growth rate depends on the total amount of water added, we were able to tune the mean colloid size close to the mean diameter of the support layer. Colloids with average sizes much smaller than the average pore diameter of the support layer (*i.e.*, $\ll 5$ nm) were drained into this layer. We thus optimised the sol preparation

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Table 1 Internal surface areas A of unsupported thermally consolidated sol-gel silicas. Hybrid silica ($CH_x : Si = 1$) exhibits smaller pores than methylated ($CH_x : Si = 0.5$) and inorganic silica ($CH_x : Si = 0$), as based on selective molecular adsorption

Vapour	Molecular diameter/nm[14]	A_{Hybrid}/ $m^2\ g^{-1}$	$A_{Methylated}$/ $m^2\ g^{-1}$ [13]	$A_{Inorganic}$/ $m^2\ g^{-1}$ [13]
C_2H_2	0.24	1340	222	261
CO_2	0.28	344	155	360
N_2	0.30	0	403	33

procedure to obtain a mean colloid diameter close to that of the support layer. Large colloids ($\gg 10$ nm) gave thick films, resulting in cracks and low membrane separation selectivity. We also tuned the colloidal sol to a fractal dimension (*i.e.*, connectivity of the sol particles) of 1.1. This value was chosen well below the maximum of 1.5, which is a strict requirement for obtaining a solid network with a percolative structure and pores <2 nm.[12] We applied small angle X-ray scattering for the selection of a sol with the targeted fractal dimension.

Fourier transform infrared spectroscopy confirmed the persistence of organic moieties in unsupported films after consolidation (300 °C in N_2). TGA-MS revealed decomposition of organic groups in argon only above 470 °C. Even in an oxidative atmosphere, the material was found to be thermally stable up to 315 °C. This indicates that no cleavage of the Si–C bonds had occurred at the applied conditions.

The unsupported hybrid films exhibited a narrow pore size distribution with very small pores. We found extensive adsorption of CO_2 and C_2H_2, but none of N_2 (Table 1). When we consider the diameters of these molecular probes, it follows that the average diameter of nanopores is close to 0.24 nm, and that all pores are below 0.3 nm in width. The pores are smaller than in inorganic and methylated silica films,[13] which is advantageous for the separation of small molecules. This can be explained by the shorter Si–C and C–C bond lengths and their associated angles in the hybrid material with respect to those of Si–O. At the same time, the high thermal stability of the hybrid material presents a great advantage over organic polymers that can clearly be related to the inorganic part of the network, *i.e.* the Si–O–Si bonds.

By dip-coating under class 1000 clean room conditions, we deposited a thin hybrid silica film from the sol on a mesoporous alumina membrane support system.[15,16] Inspection with optical microscopy indicated a continuous and completely smooth crack-free surface after thermal treatment. SEM analysis showed that the layer had a constant thickness of about 100 nm (Fig. 1).

As great interest exists in energy-efficient dehydration of solvents, we chose pervaporation of a 95 wt% *n*-butanol–5 wt% water mixture at 150 °C as a model separation. This was earlier applied for testing inorganic and methylated silica membranes.[8] Pervaporation has a much higher energy efficiency than commonly applied distillation.[1] We found a high initial water flux of about 10 kg m^{-2} h^{-1}, which, after a stabilization period typical for inorganic membranes, settled at only 4% per month flux change (Fig. 2). The half-time of the flux is about 500 days. The water content in the permeate remained at 98 wt%, even after 1.5 years of continuous testing. This corresponds to a selectivity of 930, which is sufficiently high for practical application. In comparison, inorganic silica and methylated silica deteriorated within weeks at 95 °C and 115 °C, respectively (Fig. 3).[8] The ability to function without substantial performance decline at such a high temperature can therefore be anticipated to have major implications for large-scale industrial use.

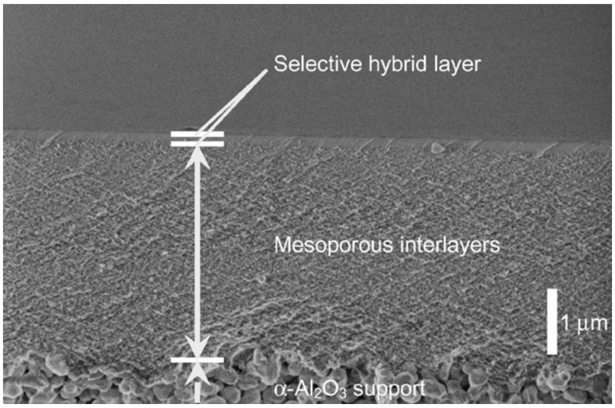

Fig. 1 Cross-sectional SE micrograph of a hybrid composite membrane, showing the supporting layers and the selective hybrid silica top layer (thickness ~0.1 µm).

The enhanced durability of the hybrid silica membrane compared to pure and methylated silica is clearly related to the incorporation of organic linking groups. By the application of BTESE, large stable monomers are introduced with extensive (six-fold) bonding to the surrounding material. This greatly limits their mobility and suppresses defect formation. Even more crucial is that drying and shrinkage invariably result in highly strained bonds in sol-gel silica. This can give rise to macroscopic cracking and increases the sensitivity of the network to hydrolysis.[17] The flexibility of the bridging alkyl groups in the hybrid material now permits stress relaxation and thus limits hydrolysis. The mechanical properties of BTESE-based materials were also recently reported to exhibit greatly increased fracture-resistance compared to pure silica,[18] so the intrinsic materials properties with respect to crack propagation have also improved. An additional advantage

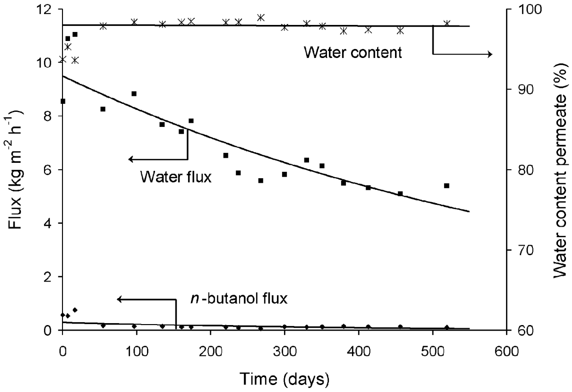

Fig. 2 Separation performance of a hybrid silica membrane towards dehydration of *n*-butanol (5 wt% water) by pervaporation at 150 °C. The membrane undergoes a very slow flux decline over more than 1.5 years and is still highly selective at the time of submission.

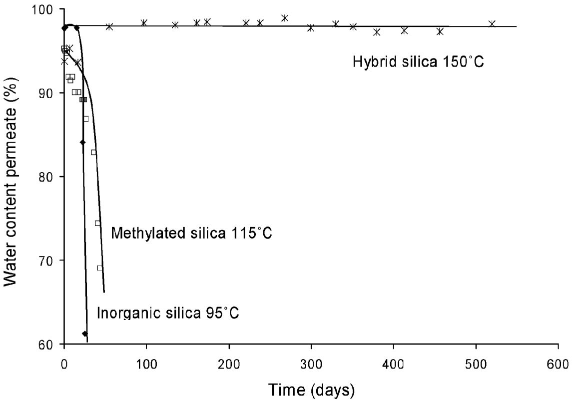

Fig. 3 Water content in permeate for a hybrid membrane at 150 °C in 5% water–*n*-butanol (this paper) compared to methylated and inorganic silica.[7] The latter materials were reported to be unstable and to lose selectivity within weeks at and above the indicated temperatures.

of using BTESE is thus that crack (defect)-free membranes can be prepared with much greater ease.

In summary, we have designed a new nanoporous hybrid material with high hydrothermal stability. It combines high selectivity and permeability when applied in a molecular separation membrane. By incorporating organic Si–C_xH_y–Si links into an inorganic network, we have complemented the high thermal and solvent stability of Si–O–Si bonds with a high hydrothermal stability. We expect that this finding will have a considerable impact on separation technology as it can effect practical application with greatly reduced energy consumption.

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