Hybrid Organic–Inorganic Microporous Membranes with High Hydrothermal Stability for the Separation of Carbon Dioxide

Hong Qi,*[a] Jing Han,[a] Nanping Xu,[a] and Henny J. M. Bouwmeester*[b]

Steam-reforming of hydrocarbons, especially methane, is one of the main routes for hydrogen production in the world.[1] However, these reactions also cause major emissions of greenhouse gases such as CO_2, which is generally believed to be responsible for global warming. The separation of H_2/CO_2 from gaseous streams with subsequent CO_2 sequestration meets demands for significant reductions of CO_2 emissions into the atmosphere. The disadvantages of common H_2/CO_2 separation technologies (such as amine scrubbing and pressure swing adsorption) include high energy costs, consumption of sorbents, and complicated processing. Consequently, there is a compelling need for the development of more viable and effective H_2/CO_2 separation technologies.[2] Inorganic membrane-based gas separation offers an environment-friendly alternative to conventional separation technologies owing to its high energy efficiency and high performance, that is, flux and selectivity, at elevated temperatures.[3,4] Such membranes generally consist of a thin separation layer (with a thickness that can range from a few tens of nanometers up to a few micrometers) superimposed onto a mechanically strong porous support. Several materials (e.g., palladium and its alloys, carbon, zeolites, and sol–gel derived ceramic membranes) have been suggested for hydrogen purification and carbon capture; among these, amorphous silica with pore sizes in the range of 2–5 Å is one of the most promising materials.[5–8] However, the modest hydrothermal stability of membranes made from pure silica severely limits their application under humid conditions. Several methods have been put forward to enhance their stability in the presence of hot steam. Imparting excellent hydrothermal stability to microporous membranes while retaining their flux and molecular sieving properties remains one of the main challenges in the field of membrane research.[4,6]

Humidity can disrupt the —Si—O—Si— bonds in silica, inducing densification of the micropourous silica network owing to the formation of mobile silica fragments. Different research groups have undertaken numerous attempts to improve the hydrothermal stability of sol–gel derived microporous silica membranes, including (1) modification of the amorphous silica matrix by doping with metal or transition-metal ions (e.g., Ni, Co, Mg, Al, Zr, Ti, Fe, Nb, and others);[4] (2) dispersion of methyl (—CH_3) functional groups into the silica matrix, so as to make its structure more hydrophobic;[9,10] and (3) use of alternatives to tetraethyl orthosilicate (TEOS) as the source for the alkoxide, such as transition-metal alkoxides or bridged bis-silyl precursors.[11–14] None of these attempts have succeeded in developing a high-enough membrane performance combined with a sufficient long-term hydrothermal stability to the degree required for application to industrially relevant gas streams and temperatures.

Herein, we report on sol–gel derived microporous hybrid inorganic–organic membranes for enhanced CO_2 separation. These are prepared by co-hydrolysis and condensation of the ethylene-bridged bis-silyl precursor 1,2-bis(triethoxysilyl)-ethane (BTESE) and niobium penta(n)butoxide, and subsequent coating of the polymeric sol on an alumina-based multilayer support. The present work was inspired by observations made in two earlier investigations. Firstly, Kanazashi et al.[11,14] recently employed ethylene-bridged silsesquioxanes for the fabrication of microporous membranes. Evaluation showed that the hybrid silica membranes exhibit a high structural stability under hydrated conditions owing to the —Si—CH_2—CH_2—Si— bridged construction of the silica network, albeit at the expense of selectivity, compared to that found for pure silica. Secondly, high H_2/CO_2 and He/CO_2 selectivities were found for microporous silica membranes upon doping with niobium oxide, as reported by Boffa et al.[15,16] A similar behavior was found for the hybrid analogue of the niobium-doped silica membranes prepared in this study. Both high acidity and water-tolerant properties are known characteristics of niobium-containing materials, which are extensively studied as heterogeneous catalysts.[17,18] Lewis and Brønsted acid sites coexist when niobium oxide is dispersed in siliceous host structures. Data from the present study indicate that niobium doping of the hybrid silica network reduces the net adsorption of CO_2. The altered density and strength of the acidic surface centers imparted by niobium doping is hypothesized to play a causal role. The niobium-doped hybrid membranes developed in this study combine high selectivity and high hydrothermal stability, and therefore hold great promise for H_2/CO_2 separation under industrial conditions.

Dynamic light scattering was employed to probe the particle size distribution of the Nb-doped hybrid silica sols (Supporting Information, Figure S1). The particle size found was in the range 1–30 nm, with an average size of approximately 5.9 nm. Storage at −20 °C over two months entailed no apparent change of the particle size, while the sol was still clear and

[a] Dr. H. Qi, J. Han, Prof. N. Xu
     Membrane Science & Technology Research Center
     State Key Laboratory of Materials-Oriented Chemical Engineering
     Nanjing University of Technology
     Nanjing 210009, Jiangsu Province (PR China)
     Fax: (+86) 517394-2349
     E-mail: hqinjut@yahoo.com.cn

[b] Dr. H. J. M. Bouwmeester
     Membrane Technology Group, Inorganic Membranes
     Faculty of Science and Technology, MESA+ Institute for Nanotechnology
     University of Twente, P.O. Box 217, 7500 AE Enschede (The Netherlands)
     Fax: (+31) 534894611
     E-mail: h.j.m.bouwmeester@tnw.utwente.nl

     Supporting Information for this article is available on the WWW under
     http://dx.doi.org/10.1002/cssc.201000242.

WILEY
ONLINE LIBRARY

transparent. Thermogravimetric analysis of the dried sol–gel powder, referred to as the unsupported membrane material, carried out under N_2 atmosphere showed a continuous weight loss extending up to ca. 300 °C, due to the removal of sorbed solvent molecules and organic residues (Figure S2). In agreement with published data,[13, 14] including references provided by these papers, partial pyrolysis was found to occur at an onset temperature of ca. 470 °C, upon which the color changed from white–yellowish to dark black–brownish.

N_2 gas adsorption at 77 K was neither observed for BTESE nor for Nb-doped BTESE unsupported membrane materials calcined under dry nitrogen at 450 °C. The absence of N_2 adsorption in systems with a narrow microporosity (size < 0.7 nm), for example, activated carbon, is explained by kinetic restrictions at the low temperature (77 K) of the measurements.[19] To overcome this problem, CO_2 adsorption isotherms were recorded at 298 K for both hybrid membrane materials (Figure S3). The obtained results agreed with observations made by Van Castricum et al.,[13, 20] showing extensive adsorption by unsupported methylated hybrid membranes using CO_2 and C_2H_2 as adsorptives at 273 K, but not using N_2 at 77 K. The decreased adsorption capacity exhibited by Nb-doped BTESE relative to pure BTESE can be explained by the increased surface acidity of the former, decreasing the number of sites and/or affinity for adsorption of CO_2, in conjunction with some densification of the hybrid silica network upon doping with Nb. CO_2 adsorption data measured after steam-autoclaving Nb-doped BTESE at 200 °C (steam pressure ca. 1550 kPa) for 300 h and, subsequently, degassing in vacuo at 300 °C for 48 h demonstrated that the material retained its microporous characteristics, even after the severe steam treatment.

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) data of dried and calcined sol–gel powders is given in the Supporting Information. XRD showed amorphous patterns, similar to that of pure BTESE, regardless of the calcination temperature (450–550 °C, Figure S4). No evidence was found of crystallization or phase separation of Nb_2O_5. However, it can not be excluded that nanodomains of phase-separated Nb_2O_5 are present, as was suggested by a multinuclear solid-state NMR study of sol–gel derived $(Nb_2O_5)_x$-$(SiO_2)_{1-x}$ for $x = 0.3$ by Drake et al.[21] For lower contents ($x = 0.03$ and 0.075) the [17]O magic-angle spinning (MAS) NMR spectra unequivocally showed the presence of niobium as NbO_4, forming part of the silica network. The presence of absorption bands characteristic of sp^3 C–H stretching vibrations in the FTIR spectra, at 2870–2980 cm^{-1}, is regarded as evidence for the preservation of the ethylene bridge after calcination of Nb-doped BTESE under N_2 at 450 °C for 3 h (Figure S5).[13]

Nb-doped BTESE membranes were prepared by dip-coating of the Nb-doped hybrid sol onto a mesoporous γ-alumina support. Inspection of the membranes after calcination at 400–550 °C in nitrogen by using optical microscopy indicated the formation of a continuous, crack-free, and smooth surface. Scanning electron microscopy (SEM) analysis showed that the Nb-doped hybrid membrane had a thickness of approximately 150 nm (Figure S6). Single gas permeances at 200 °C for BTESE and Nb-doped BTESE membranes, calcined at 450 °C, are com-

pared with data from prior studies on microporous silica and hybrid silica membranes in Figure 1. The permeance of BTESE to He and H_2, that is, the gases having the smallest kinetic di-
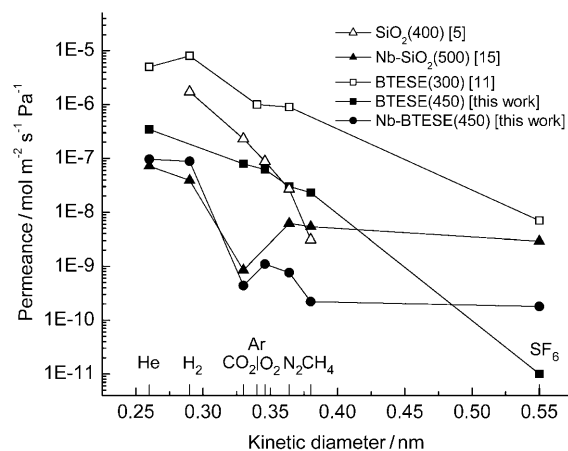

Figure 1. Single-gas permeances at 200 °C for pure and Nb-doped BTESE membranes (both calcined at 450 °C) as a function of the kinetic diameter of the permeating gas molecule. Also shown are data for pure, metal doped silica and hybrid membranes from the cited references. Membrane calcination temperatures (in °C) are given in parentheses.

ameters in this study, was about half an order of magnitude lower than that reported for microporous silica,[5, 8] and about one order of magnitude lower than that reported for BTESE membranes.[11, 14] The latter might possibly be explained by the different deposition characteristics (e.g., sol viscosity, particle size, and others), affecting thickness and integrity of the separation layer, and the lower calcination temperature of 300 °C used in the study by Kanazashi et al.[11, 14] The effective pore diameter of BTESE, calcined at 450 °C, appears to be less than the kinetic diameter of SF_6 (5.5 Å), given the fact that its permeance for SF_6 was found to be below the detection limit (ca. 10^{-11} mol m^{-2} s^{-1} Pa^{-1}). The ratio of single-gas permeances, referred to as the ideal selectivity, was calculated to be more than 3×10^4 for He/SF_6, which is much higher than the corresponding Knudsen value (6.0). The He/CO_2, He/N_2, and He/CH_4 selectivities (4.4, 11.5, and 14.9, respectively), although lower than those found for state-of-the-art silica membranes,[5, 8] are all higher than their corresponding Knudsen values (3.3, 2.6, and 2.0, respectively). As suggested above, some densification may occur upon doping BTESE with Nb, which in part explains the observed decrease in gas permeance. Compared with pure BTESE, the Nb-doped BTESE membrane showed an almost one order of magnitude lower He permeance, and an almost two orders of magnitude lower permeance towards CO_2, O_2, N_2, and CH_4. In conformity with data reported for microporous Nb-doped silica membranes by Boffa et al.,[15] a very low permeance was observed for CO_2 in view of its moderate kinetic diameter. The ideal H_2/CO_2 and He/CO_2 selectivities, at 200 °C, were calculated to be 200 and 220, respectively. The nonvanishing SF_6 permeance suggests the presence of a small fraction of supermicropores. Further optimization of the preparation procedure might prevent the occurrence of such pores.

Transport through microporous membranes conforms to an activated diffusion mechanism.[6] The apparent activation energy (E_a) is the algebraic sum of the isosteric heat of sorption and the activation energy of diffusion. Activation energies calculated from data of single gas permeance measurements in the range 60–200 °C under dry conditions indicate that transport of CO_2 ($E_a = -6 \pm 2$ kJ mol^{-1}) through the Nb-BTESE membrane is adsorption-dominated, while that of He ($E_a = 24 \pm 1$ kJ mol^{-1}) is found to be diffusion-dominated.

Much to our surprise, the He/CO_2 selectivity of the Nb-doped BTESE membrane at 200 °C was even found to increase during steam exposure, from an initial value of 220 to a value of ca. 3700 after 300 h of in situ exposure to 100 kPa steam. The corresponding data are displayed in Figure 2. As seen in
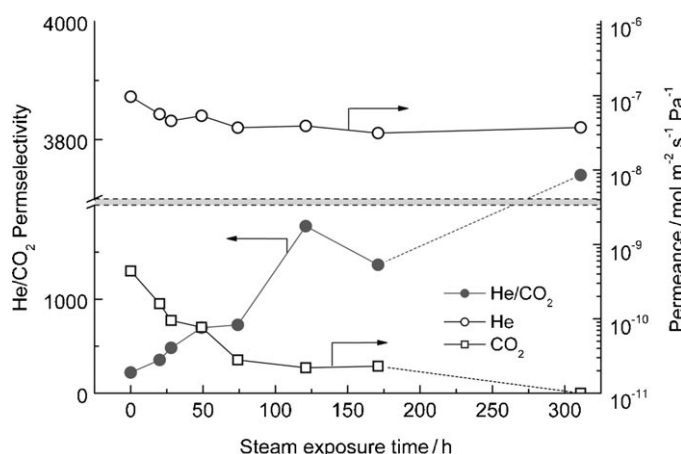

Figure 2. Hydrothermal stability test of the Nb-doped BTESE membrane. Shown are the He and CO_2 gas permeances at 200 °C and the calculated single gas He/CO_2 selectivity as a function of the time of exposure to steam (100 kPa).

this figure, the He permeance remained fairly constant at a value of ca. 4×10^{-8} mol m^{-2} s^{-1} Pa^{-1} over the entire duration of the steam exposure test. A small decline in the He permeance was observed during the first 24 h. Meanwhile, the CO_2 permeance remained low, decreasing with steam exposure time to reach ultimately a value below the detection limit (ca. 1×10^{-11} mol m^{-2} s^{-1} Pa^{-1}). Most of the surface hydroxyl groups were removed from the structure during the calcination at 450 °C under dry nitrogen. The pore surface will gradually acquire its Brønsted acidic strength again during the exposure to steam by partial hydrolysis of Si—O—Nb and Nb—O—Nb bondings. The creation of strongly acidic surface hydroxyls is believed to reduce the net sorption of CO_2 molecules and, hence, induce a decrease of the CO_2 permeance with steam exposure time.

In conclusion, we have developed a hybrid organic–inorganic microporous membrane with high hydrothermal stability for the separation of H_2 and He from CO_2-containing gas streams. The membranes offer great potential for integration in pre-combustion CO_2 capture technologies. The low CO_2 permeance exhibited by the membranes is attributed to an increased acidity of the pore surface, as a result of modification of the hybrid silica network with niobium oxide. Prolonged exposure of the Nb-doped hybrid membrane to steam at 200 °C leads to a further decline of the CO_2 permeance, with an increased He/CO_2 selectivity, measured in this study as high as ca. 3700, while the He permeance and overall integrity of the membrane are retained. The microstructure and acidity of the Nb-doped microporous hybrid silica network may be tailored by adjusting various synthesis and processing parameters. Optimization of these is expected to further improve the performance of the membranes.

Experimental Section

Sol synthesis: 5 mL of 1,2-*bis*(triethoxysilyl)ethane, ($C_2H_5O)_3$Si—CH_2—CH_2—Si($C_2H_5O)_3$ (BTESE) was used as-received (purity 97%, ABCR) and dissolved in 5 mL absolute ethanol (dried, Secco Solv., max. 0.02% H_2O, Merck). This solution was immediately placed into an ice bath to prevent premature hydrolysis. A total amount of 1.08 mL aqueous HNO_3 was added in two portions under continuous stirring. Half of it was added at the beginning, the other half after refluxing at 60 °C for 90 min. Addition took place after placing the obtained sol in an ice bath. Subsequently, 3.75 mL niobium penta(*n*)butoxide (NPB, purity 99%, ABCR) dissolved in 13 mL absolute ethanol (dried, Secco Solv., max. 0.02% H_2O, Merck) was added drop-wise (Si/Nb = 3:1), and the refluxing was maintained for an additional 90 min. The sol was cooled to room temperature and diluted 6 times with ethanol for dip-coating.

Powder and membrane preparation: Unsupported membranes (powder) were obtained by drying sols in a Petri dish overnight. If not used as such, they were calcined for 3 h in dry nitrogen at 400–550 °C using heating and cooling rates of 0.5 °C min^{-1}. Supported membranes were prepared by a single dip-coating of the sol onto home-made multilayered mesoporous γ-alumina supports under class-1000 clean room conditions. Dip-coating was performed at a velocity of 12 mm s^{-1} by using a MEMDIP 5 coating unit (Pervatech B. V., The Netherlands). The membranes were calcined for 3 h in dry nitrogen at 450 °C, with heating and cooling rates of 0.5 °C min^{-1}.

Characterization: Effective particle sizes in the polymeric sols were measured by dynamic light scattering (DLS) using a Zetatrac analyser (Microtrac Inc.). Thermal evolution of the unsupported membrane materials was measured using a combined thermogravimetry and differential thermal analysis (TG/DTA) apparatus (STA-449-F3, Netzsch). Measurements were conducted in nitrogen atmosphere (30 mL min^{-1}) with a heating rate of 10 °C min^{-1}. Gas adsorption measurements were conducted at 77 K (N_2) and 298 K (CO_2) on Belsorp-mini (Bel Japan, Inc.) and ASAP 2020 (Micromeritics) instruments, respectively. Prior to measurements, samples were degassed under vacuum at 300 °C for 48 h. FTIR spectroscopy was performed both on dried and calcined unsupported films at room temperature in the wavenumber region 4000–500 cm^{-1} on a Tensor 27 FT-IR spectrometer (Bruker Optics), using a transmission cell and KBr as reference. X-Ray diffraction (XRD) data of unsupported membrane materials were recorded by a Bruker D8, Advance diffractometer, using a target of Cu Kα operated at 40 kV and 40 mA. Field-emission scanning electron microscopy (FE-SEM) images were obtained by using a LEO Gemini VP 1550 (Zeiss) instrument.

Single gas permeation measurements were conducted in a dead-end mode set-up. The membranes were sealed in a stainless steel module using fluoroelastomer O-rings with the separation layer ex-

posed to the feed side. The pressure differential across the membrane was 0.3 MPa, while the permeate side was vent to the atmosphere. Prior to measurements, the membranes were dried overnight at 200 °C. The gas permeances were measured in the temperature range 60–200 °C in a sequence, starting with the smallest kinetic diameter, from He (0.255 nm), CO_2 (0.33 nm), O_2 (0.346 nm), N_2 (0.365 nm), CH_4 (0.382 nm), to SF_6 (0.55 nm). The hydrothermal stability of the membranes was tested by single gas permeance measurements, at 200 °C, before and after in situ exposure to steam at atmospheric pressure (100 kPa) over a total period of more than 300 h. Further stability tests were carried out by subjecting unsupported membrane materials to saturated steam at 200 °C for 300 h in an autoclave. CO_2 gas adsorption measurements were conducted before and after these tests.

Acknowledgements

[1] R. Bredesen, T. A. Peters, *Membranes for Energy Conversion, Vol.2*, Wiley-VCH, Weinheim **2008**.

[2] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer, *IPCC special Report on Carbon Dioxide Capture and Storage*, Cambridge University Press, New York **2005**.

[3] G. Q. Lu, J. C. D. da Costa, M. Duke, S. Giessler, R. Socolow, R. H. Williams, T. Kreutz, *J. Colloid Interface Sci.* **2007**, *314*, 589.

[4] N. W. Ockwig, T. M. Nenoff, *Chem. Rev.* **2007**, *107*, 4078.

[5] R. M. de Vos, H. Verweij, *Science* **1998**, *279*, 1710.

[6] A. Ayral, A. Julbe, V. Rouessac, S. Roualdes, J. Durand, in *Membrane Science and Technology, Vol.13* (Eds.: R. Mallada, M. Menéndez), Elsevier, Amsterdam **2008**.

[7] H. Verweij, Y. S. Lin, J. H. Dong, *MRS Bull.* **2006**, *31*, 756.

[8] R. M. de Vos, H. Verweij, *J. Membr. Sci.* **1998**, *143*, 37.

[9] Q. Wei, F. Wang, Z.-R. Nie, C.-L. Song, Y.-L. Wang, Q.-Y. Li, *J. Phys. Chem. B* **2008**, *112*, 9354.

[10] R. M. de Vos, W. Maier, H. Verweij, *J. Membr. Sci.* **1999**, *158*, 277.

[11] M. Kanezashi, K. Yada, T. Yoshioka, T. Tsuru, *J. Am. Chem. Soc.* **2009**, *131*, 414.

[12] G. I. Spijksma, C. Huiskes, N. E. Benes, H. Kruidhof, D. H. A. Blank, V. G. Kessler, H. J. M. Bouwmeester, *Adv. Mater.* **2006**, *18*, 2165.

[13] H. L. Castricum, A. Sah, R. Kreiter, D. H. A. Blank, J. F. Vente, J. E. ten Elshof, *Chem. Commun.* **2008**, 1103.

[14] M. Kanezashi, K. Yada, T. Yoshioka, T. Tsuru, *J. Membr. Sci.* **2010**, *348*, 310.

[15] V. Boffa, J. ten Elshof, A. V. Petukhov, D. H. A. Blank, *ChemSusChem* **2008**, *1*, 437.

[16] V. Boffa, D. H. A. Blank, J. E. ten Elshof, *J. Membr. Sci.* **2008**, *319*, 256.

[17] T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641.

[18] M. Ziolek, *Catal. Today* **2003**, *78*, 47.

[19] R. V. R. A. Rios, J. Silvertre-Albero, A. Sepulveda-Escribano, M. Molina-Sabio, F. Rodriguez-Reinoso, *J. Phys. Chem. C* **2007**, *111*, 3803.

[20] H. L. Castricum, A. Sah, R. Kreiter, D. H. A. Blank, J. F. Vente, J. E. ten Elshof, *J. Mater. Chem.* **2008**, *18*, 2150.

[21] K. O. Drake, D. Carta, L. Skipper, F. E. Sowrey, R. J. Newport, M. E. Smith, *Solid State Nucl. Magn. Reson.* **2005**, *27*, 28.