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Cryogenic air separation at low pressure using MFI membranes

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ABSTRACT

Ultra-thin MFI membranes were for the first time evaluated for air separation at low feed pressures ranging from 100 to 1000 mbar at cryogenic temperature. The membrane separation performance at optimum temperature at all investigated feed pressures was well above the Robeson upper bound for polymeric membranes at near room temperature. The O_2/N_2 separation factor at optimum temperature increased as the feed pressure was decreased and reached 5.0 at 100 mbar feed pressure and a membrane temperature of 67 K. The corresponding membrane selectivity was 6.3, and the O_2 permeance was as high as 8.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. This permeance was about 100 times higher than that reported for promising polymeric membranes. The membrane selectivity and high O_2 permeance was most likely a result of O_2/N_2 adsorption selectivity. The increase in O_2/N_2 separation factor with decreasing pressure and temperature was probably due to increased adsorption selectivity at reduced temperature. This work has demonstrated the potential of MFI zeolite membranes for O_2/N_2 separations at cryogenic temperature.

1. Introduction

Development of more efficient methods for separation of various gas mixtures are currently of tremendous interest. Membrane gas separation technology is one such method that is already applied in industrial scale for H_2 recovery, CO_2 separation, dehydration of air and natural gas, and air separation [1]. For the latter application, polymeric membranes have been developed for separation of O_2 from air. Most of these membranes show high selectivity but low permeability, i.e., low flux [2]. Robeson has investigated the performance of different polymeric membranes and found a trade-off between the desired selectivity and permeability. The best polymeric membranes with high selectivity had relatively low permeability, and vice versa. This trade-off is known as the Robeson selectivity–permeability upper bound [3] and it was updated in 2008 [4]. It is here worth pointing out that for industrial applications, materials with as high permeability as possible, possessing sufficient selectivity, are of major interest [2]. In other words, a very selective membrane with very low permeability is not very industrially useful. Recently, Carta et al. [5] have reported microporous polymeric membranes with rather high oxygen permeability of 900–1100 Barrer and good O_2/N_2 selectivities of 4.5–6.1.

Zeolite membranes being inorganic porous membranes are known to have high permeabilities in gas separations. Due to the well-defined pore structure, zeolite membranes can also offer high selectivities. In addition, these membranes have high chemical, mechanical and thermal stability, i.e., can potentially be used at both very high and very low temperatures offering a great advantage over polymeric membranes. High temperature applications of zeolite membranes have been studied extensively. On the contrary, scientific reports on gas separation using zeolite membranes at low temperatures are rather scarce. Hong et al. [6] studied CO_2/H_2 separation using SAPO-34 membranes in the temperature range of 253–308 K. At 253 K, the reported CO_2/H_2 separation factor was as high as 110, however the CO_2 flux was only 3 kg m^{-2} h^{-1} even though the trans-membrane pressure difference was as high as 12 bar. Piera et al. [7] separated CO/air at an extremely low CO concentration of 160 ppbv using an MFI-type membrane in the temperature range of 243–303 K. The separation factor was 3.1 with an extremely low CO flux of 1.3×10^{-7} kg m^{-2} h^{-1} at 245 K. Van den Bergh et al. [8] investigated permeation and separation properties of various gases (CO_2, CH_4, N_2, and O_2) and their mixtures, using DDR membranes in the temperature range of 220–373 K. The mixture selectivities increased as temperature was decreased, especially for CO_2/CH_4, CO_2/air and N_2O/air mixtures. The CO_2/CH_4 separation factor was higher than 1000 at temperatures below 250 K. At the same time, the O_2/N_2 selectivity was low amounting to only ca. 2 and the flux was reported as "very low", i.e. lower than 7.8×10^{-2} kg m^{-2} h^{-1} in all cases. Our research group has developed ultra-thin (≈ 0.5 μm) MFI membranes on open graded alumina supports [9]. Due to the low thickness and well-defined pore structure, the membranes can display both high flux and high selectivity. These

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membranes display excellent performance for CO_2 separation from synthesis gas at high pressure and low temperature [10]. The separation factor for CO_2/H_2 was as high as 32 with a CO_2 flux of 332 kg m^{-2} h^{-1} at 275 K. We have also shown [11] that separation factors exceeding 100 can be reached below 243 K. The greater separation performance of the membranes at lower temperature was attributed to stronger adsorption of CO_2 in the zeolite pores, effectively blocking the transport of H_2. Recently, we have evaluated these membranes for air separation at cryogenic temperatures, i.e., below 123 K and the report [12] is the first on zeolite membrane separation at cryogenic temperature. The experiments were carried out in the temperature range of 77–110 K and the feed pressure was varied between 1–5 bar. Liquid nitrogen was used for cooling, which limited the lowest achievable experimental temperature to 77 K, and no vacuum system was used, which limited the lowest feed and permeate pressures to 1 bar. Helium was used as a sweep gas on the permeate side at a pressure of 1 bar. The membranes were oxygen selective, and when the feed pressure was decreased, the maximum O_2/N_2 separation factor increased whereas the optimum separation temperatures decreased. At the lowest investigated feed pressure of 1 bar and the optimum temperature of 79 K, the highest observed O_2/N_2 separation factor was 3.9, with an O_2 permeance of 6.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. We have now installed a vacuum system to enable experiments at reduced pressure, and a cryostat, which enables experiments at temperatures down to 22 K. In the present work, the membranes are evaluated for air separation at significantly lower feed pressures and membrane temperatures than in the previous work [12] using the new experimental set-up. A model for the adsorption in the zeolite pores was also developed to better understand the separation performance of the membranes.

2. Experimental

2.1. Membrane preparation

MFI membranes were prepared on graded porous α-alumina discs (Fraunhofer IKTS, Germany), using a previously reported method [9]. The support had a diameter of 25 mm and was comprised of a 30 μm thick top layer with a pore size of 100 nm and a 3 mm thick base layer with a pore size of 3 μm. The alumina disc was masked and then seeded with a monolayer of MFI crystals of 50 nm in size as described previously [13]. After that, a hydrothermal treatment was carried out, where the seeded support was immersed in a synthesis solution with a molar composition of $3TPAOH{:}25SiO_2{:}1450H_2O{:}100C_2H_5OH$ and kept in the solution at 361 K for 72 h. Thereafter, the membrane was rinsed in a 0.1 NH_3 solution overnight and calcined at 773 K for 6 h at a heating rate of 0.2 K min^{-1} and a cooling rate of 0.3 K min^{-1}.

2.2. Membrane characterization

Adsorption-branch *n*-hexane/helium permporometry [14] was used to characterize the amount of flow-through defects in the membranes. This technique has recently been demonstrated to be an effective and reliable way to evaluate micropore defects down to 0.7 nm [15,16] and mesopore defects [14] in MFI membranes. The procedure for the permporometry characterization is described in our previous work [15].

The morphology of the membranes was characterized by SEM using an FEI Magellan 400 field emission XHR-SEM without any coating of the samples.

2.3. Gas separation measurements

The membrane was mounted in a stainless steel cell and sealed with graphite gaskets (Eriks, the Netherlands). A type T thermocouple inserted inside the cell was used to monitor the temperature. Prior to the gas separation, the membrane was dried in a helium flow at 573 K for 6 h at a heating rate of 1 K min^{-1}.

The separation experiments were carried out using the experimental set-up illustrated in Fig. 1. A flow of 500 ml min^{-1} (purity > 99.999%, AGA) of synthetic air, consisting of 79.2% N_2 and 20.8% O_2, was fed to the membrane at feed pressures of 100 mbar, 400 mbar, 660 mbar and 1000 mbar (at a feed pressure of 100 mbar, the feed flow rate was reduced to 100 ml min^{-1} due to the limited capacity of the vacuum pump). A pressure of 10 mbar, 40 mbar, 66 mbar, or 100 mbar, was applied on the permeate side of the membrane, in order to keep the ratio of feed pressure to permeate pressure at 10. Since the pressure ratio may affect the separation performance, the pressure ratio was kept constant in all experiments. The gas flow rate was controlled by mass flow controllers (Bronkhorst, F-201CV). Vacuum pumps (Pfeiffer Vacuum, MVP 020 and MVP 040) installed after the pressure regulators in the retentate and permeate lines reduced the pressures on both sides of the membrane. The pressures were controlled by dosing valves (Pfeiffer Vacuum, EVN 116). The membrane cell was kept in a custom-built cryostat (ICEoxford UK, DRYICE25K) and the separation temperature could be set at any value ranging from 22 K to 573 K with a deviation of less than 0.05 K. The permeate flow was measured with a mass flow meter (Bronkhorst, F-201CV). The permeate composition was analyzed by a mass spectrometer (GAM 400, InProcess Instruments) every 5 s. A pressure transmitter (Pfeiffer Vacuum, CMR 362) was used to measure the permeate pressure. A column packed with 5A zeolite pellets was dried before the experiment and was used (at room temperature) to adsorb any traces of moisture in the feed gas.

The permeance Π_i (mol m^{-2} s^{-1} Pa^{-1}) was defined as

$$\Pi_i = F_i/(A_{film}\Delta P_i), \tag{1}$$

where F_i is the molar flow rate of component i through the membrane, A_{film} is the membrane area, and ΔP_i is the partial pressure difference of component i.

The separation factor was determined as follows:

$$\beta_{i/j} = (y_i/y_j)/(x_i/x_j), \tag{2}$$

where y_i and x_i are the molar fractions of species i in the permeate and feed streams, respectively.

The membrane selectivity (also referred to as the permeance-based selectivity) was calculated as

$$\alpha_{i/j} = \Pi_i/\Pi_j, \tag{3}$$

where Π_i and Π_j are the permeances of species i and j, respectively.

O_2 and N_2 single gas permeation experiments were also carried out. A stream of 500 ml min^{-1} of O_2 (> 99.999%, AGA) or N_2 (> 99.999%, AGA) was fed to the membrane at 1000 mbar while the permeate side was kept at 100 mbar.

3. Modelling

In order to gain some insight into the experimental observations, the adsorption of N_2 and O_2 was modelled. Heats of adsorption and Langmuir adsorption parameters for N_2 and O_2 in high silica MFI [17] are given in Table 1. It may be expected that the membrane would be N_2 adsorption selective because of the larger heat of adsorption and Langmuir adsorption parameters than those for O_2. However, for mixture adsorption where the