

INTRINSIC GAS TRANSPORT AND WATER STABILITY OF SILICA MEMBRANES FOR CO₂/CH₄ SEPARATIONS

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Paper presented at the ICIM 8 conference in Cincinnati, Ohio, USA July 18-22.

Abstract

Single component gas transport data of microporous silica membranes are presented and analyzed using a general model developed for intrinsic (micropore diffusion controlled) single-gas transport in microporous inorganic membranes.

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SUMMARY

Single component gas transport data are presented and analyzed using a general model developed for intrinsic (micropore diffusion controlled) single-gas transport in microporous inorganic membranes. It is shown that sufficiently small pores can be generated so that there is essentially no methane transport within the silica pore structure. CO₂ diffuses readily through this small pore material. Samples produced with larger pore sizes allow transport of both CO₂ and CH₄. Modeling of the transport data obtained on these samples allows the determination of adsorption strengths and diffusion coefficients of CO₂ and CH₄. Results for the water stability of these membranes is presented and a working model of the hydrolytic chemistry of silica is briefly described

1. INTRODUCTION

In this paper we present results on the synthesis, characterization and testing of silica membranes for CO₂/CH₄ separations. Single component gas transport data are presented and analyzed using a general model developed for intrinsic (micropore diffusion controlled) single-gas transport in microporous inorganic membranes. It is shown that sufficiently small pores can be generated so that there is essentially no methane transport within the silica pore structure. CO₂ diffuses readily through this small pore material. Samples produced with larger pore sizes allow transport of both CO₂ and CH₄. Modeling of the transport data obtained on these samples allows the determination of adsorption strengths and diffusion coefficients of CO₂ and CH₄. Results for the water stability of these membranes are presented and a working model of the hydrolytic chemistry of silica is briefly described.

2. EXPERIMENTAL

Silica membranes are prepared by dip-coating a sol-gel mixture onto an asymmetric alumina substrate tube, followed by air calcination at 400°C or 600°C. For membranes fabricated at ExxonMobil (EM-1, EM-2, and EM-600), substrate tubes are obtained from Kyocera Corp. (3.2 mm OD x 53 mm L) consisting of a 3-5 μ m thick OD layer of γ -alumina (4-5 nm pores) deposited on an α -alumina (100-200 nm pores) base. The sol-gel composition is the same as that described by de Vos [1], yielding a microporous silica layer of approximately 100 nm thickness. For comparison, silica membranes prepared by the same method at ECN (*ECN-1*, *ECN-2*) [2], albeit on larger diameter asymmetric substrates (14 mm OD), are also evaluated.

The membrane permeance (flux/ ΔP) is measured in a configuration having the retentate flow valved off, and the feed pressure controlled by a backpressure regulator. The dried feed (>99.9%) is supplied from a gas manifold. Permeate flow is measured at atmospheric pressure with a bubble flow meter. All membranes are heated to 350°C immediately prior to testing to remove adsorbed water and a significant portion of the chemisorbed water. 'Wet' membranes show very little pore-related (intrinsic) transport.

3. DATA ANALYSIS AND PERMEATION MODELING

In this work, we are interested in the 'intrinsic' (silica-pore related) transport properties of the silica membrane. Intrinsic permeance is obtained by correcting the measured permeance for both the support mass-transfer resistance, and bypass flow. Support corrections are made based on a series resistance model including effects of both Knudsen and Poiseuille flow through the support [3]. The bypass permeance (Q_{bypass}) includes all non-selective flow paths (large pores and defects) and is also modeled as a sum of Knudsen and Poiseuille terms. The bypass permeances of CO_2 and CH_4 are obtained under the assumption that the entire measured permeance for a large feed molecule (e.g., SF_6) is due to bypass flow. We test this assumption against expected temperature and pressure scaling, and then apply known Knudsen and Poiseuille scaling factors (molecular weight and viscosity) to derive Q_{bypass} for He, CO_2 and CH_4 . The intrinsic permeance (or flux) is then obtained by subtracting Q_{bypass} for each gas from the corresponding total measured permeance. The intrinsic permeances thus obtained are modeled by solving the appropriate diffusion equation based on chemical-potential driving force and Langmuir adsorption [4,5]. The result is

$$J = \frac{D_i q_s}{\delta} \ln \left[\frac{1 + b_i F_{\text{feed}}}{1 + b_i F_{\text{perm}}} \right] \quad (1)$$

where J is the flux for gas i , D_i is 'intrinsic' (or thermodynamically corrected) diffusion coefficient, q_s is the saturation loading (about 3 mmol/g for silica), δ is membrane thickness, b_i is the Langmuir adsorption parameter, and F is fugacity.

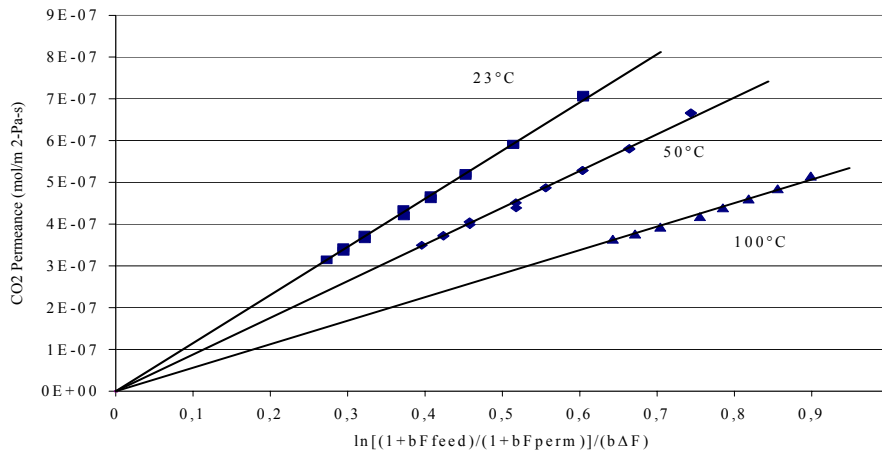


Figure 3.1 CO_2 permeance for silica membrane ECN-1 plotted in accordance with Equation (1). Langmuir adsorption coefficients (b) are obtained by fitting the CO_2 flux as a function of fugacity. The b -values for these three data sets (in units of 10^{-6} Pa^{-1}) are 3.2 at 23°C , 1.7 at 50°C and 0.54 at 100°C

The limiting value for the permeance at low pressure is $Q_0 = J_0/\Delta F = Dbq_s/\delta$. By fitting equation (1) to the intrinsic CO_2 flux, the values of b and D are obtained, as shown in Figure 1. The adsorption parameters derived from the Figure 1 data are in good agreement with bulk measurements [1,4]. Diffusion coefficients are consistent with those found for zeolite membranes with similar pore sizes to that of silica (about 0.35 nm).

4. RESULTS AND DISCUSSION

The above model has been employed to characterize changes in the membrane transport properties resulting from variation in the calcination temperature and exposure to water vapor. The final results obtained from the above data analysis are summarized in Table 1. Fugacity corrections are not applied because of their small impact at 100°C and relatively low pressures.

Table 4.1 *Summary of gas testing results obtained at 100°C on silica membranes prepared with variable calcination temperature (T_{calc}) and with and without deliberate water exposure*

Membrane	T_{calc} [°C]	Gas	Q_0 10^{-8} mol/m ² -s-Pa	D 10^{-8} cm ² /s	b 10^{-6} Pa ⁻¹
EM-1	400	CO ₂	610	190	0.59 ^a
EM-2	400	CO ₂	680	210	0.59 ^a
EM-2-H2O	400	CO ₂	480	120	0.75
EM-600	600	CO ₂	86	18	0.86
ECN-1	400	CO ₂	71	15	0.86
ECN-2	400	CO ₂	56	17	0.62
EM-1	400	CH ₄	47	54	0.16
EM-2	400	CH ₄	38	42	0.17
EM-2-H2O	400	CH ₄	14	24	0.10
EM-600	600	CH ₄	<1	<1	NA
ECN-1	400	CH ₄	<0.2	<0.2	NA
ECN-2	400	CH ₄	NA	NA	NA
EM-1	400	He	440	8000	0.01 ^b
EM-2	400	He	490	8900	0.01
EM-2-H2O	400	He	380	6900	0.01
EM-600	600	He	190	3500	0.01
ECN-1	400	He	180	3400	0.01
ECN-2	400	He	260	4800	0.01

^a Due to large support correction, b -values for EM-1 and EM-2 are fixed at this typical value.

^b Helium b -value is a rough estimate.

Though EM and ECN membranes are prepared by the same basic procedure and are roughly the same thickness (about 100 nm), the EM membranes show significantly higher intrinsic permeances for He, CO₂ and CH₄. Q_{bypass} values for SF₆ are 0.3, 0.2, 0.4, 1.9, 0.5, and 1.2 (in units of 10^{-8} mol/m²-s-Pa) for the six membranes displayed in Table 1. Therefore, CH₄ is clearly permeating the pore structure in the EM membranes. These results strongly suggest a larger controlling pore size for the EM membranes. The observation of intrinsic CH₄ permeance allows calculation of a Langmuir adsorption parameter (b) and a diffusion coefficient (D) for CH₄ in the microporous silica membrane. Adsorption results for CH₄ are in reasonable agreement with bulk measurements. [1]

Higher calcination temperatures are known to produce higher CO₂/CH₄ selectivities for silica membranes [1]. Increasing the calcination temperature from 400°C to 600°C (Table 1) results in decreases in the intrinsic permeance (Q_0) for CO₂, CH₄, and He of 87%, >98%, and 60%, respectively. These permeance losses are accompanied by significant decreases in the calculated diffusion coefficients, consistent with a smaller average pore size. The CH₄ data also indicate that the higher calcination temperature transforms a largely intrinsic permeance at 400°C (EM-1 or EM -2) to mostly bypass permeance at 600°C (EM-600). It can be seen that the ECN membranes (calcined at 400°C) have transport properties, for all three gases, similar to that of the EM membrane calcined at 600°C.

Table 1 includes transport data obtained on the EM-2 membrane calcined at 400°C, after it had been exposed to water vapor at 20°C for 2 hr, then dried at 350°C. This treatment results in modest decreases in Q_0 and D for all three gases. The ideal CO₂/CH₄ selectivity (based on Q_0) increases by a factor of two with water exposure, reflecting a more effective molecular sieving separation in the smaller pores. Finally, the Langmuir b -value increases slightly for CO₂, but decreases slightly for CH₄. These results are consistent with surface hydrolysis of the silica in the presence of water to generate a more hydrophilic, hydroxyl-rich surface that adsorbs CO₂ more strongly, and CH₄ more weakly. The instability of silica membranes in the presence of water at high activity leads to shelf-life aging effects and limits the utility of these materials for gas separations. The reduced intrinsic permeance of the ECN membranes is consistent with differing exposure to ambient moisture. The EM membranes were tested shortly after preparation, while the ECN membranes were stored under ambient conditions for significant periods of time prior to testing.

In summary, we have demonstrated the successful extraction of adsorption and diffusion coefficients from permeance measurements. The transport-controlling pore size in silica can be varied by calcination temperature or water exposure. Exposure to water at high activities, even at low temperature, results in irreversible changes in the silica membrane pore structure.

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