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Molecular Simulation of the Fabrication and Permselective Characterisation of Thin Nanoporous Silica Films

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1. Introduction

A major field of ongoing study in gas mixture separation technology involves the development of novel composite ceramic membranes suitable for use across a broad range of process conditions. A common theme in these studies is the use of mesoporous/microporous support materials (e.g. α-alumina/γ-alumina, Vycor etc) with a minimum pore size of approximately 5 nm, in some cases supplemented with a further oxide microporous layer with pore dimensions of 1-3nm, upon which is deposited a silica layer containing subnanometer pores (see for example [1-4]). This layer is the selective coating which itself is typically 30-100 nm thick. While it is generally assumed that the transport process of the gas species within the selective layer is activated in nature, there are anomalies with this simplified picture and the work presented here represents a summary of recent work undertaken to clarify some of these issues.

2. Methodology

The simulations reported in this work were conducted in three stages: (1) kinetic Monte Carlo (KMC) simulation of the formation of thin films of silica via chemical vapour deposition (CVD) onto a nonporous silica substrate; (2) KMC simulation of the formation of nanoporous silica layers on the surface of a microporous substrate; and (3) non-equilibrium molecular dynamics (NEMD) simulation of the permeation of three gases (He, N_2 and CO_2) through sample membranes formed in phase (2) of the work.

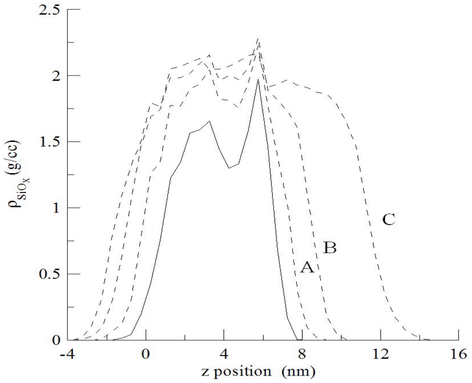

Figure 1: Evolution of silica (SiO_x) density profiles on a thin microporous membrane (solid line) with deposition from a gas phase in the range z > 8 nm.

The KMC simulations for deposition onto nonporous silica are reported in detail in [5] and include simulation of low pressure CVD (LPCVD) of $Si(OH)_4$ and $Si(OCH_2CH_3)_4$ over the temperature range 473K-873K and for precursor pressures in the range 0.00003-0.5 torr. This initial work was conducted to validate the simplified scheme of reactions (drawn from studies reported by Coltrin et al [6]) employed in the KMC computations for later use in the more time demanding simulations involving microporous substrates [7].

In the latter case KMC deposition studies have been conducted for silicic acid only and preliminary results of this work are shown in Figure 1 for $Si(OH)_4$ deposition onto a model microporous silica substrate 8 nm thick containing pores 2 nm in diameter (the dashed lines marked A, B and C represent density profiles at evolving stages during the deposition process). The substrate was formed by employing the procedure proposed by Gelb and Gubbins [8] and its density profile is indicated by the solid line in Figure 1. Note that the evolution of the deposit demonstrates that penetration of the $Si(OH)_4$ precursor deep into the substrate pores can occur even at late stage development of the layer.

The NEMD simulations were conducted on membrane samples cleaved from the body of the homogeneous region of the deposit evolving on the right hand side of the structures shown in Figure 1 and extending further out to approximately 20 nm. In the MD simulations the dynamics of the silica system were governed by the covalent network potential model of Keating [9, 10] and the gas-solid interaction potentials included both London-van der Waals terms (all gases) and Coulombic terms for the quadrupole/silica interactions in the case of N_2 and CO_2. The NEMD method employed was the external force field algorithm proposed originally by Maginn et al [11]. Using this approach steady state fluxes for each of the individual gases permeating at temperatures over the range 473-873K were monitored on twenty four independent nanomembrane configurations of varying thickness in the range 1-2 nm.

3. Results

Selected NEMD results are shown in Figure 2 for the three gases at a temperature of 873K. The solid lines shown in this figure represent a correlation of a simple model which is based on the following premises:

There are two domains within the silica films, one in which percolation occurs very rapidly and a second spatial domain wherein diffusion takes place very slowly. As shown in [12] transport within domain I is considered to take place so rapidly that, as predicted by linear response theory, a stationary concentration profile is established which decays exponentially with the thickness of the membrane.

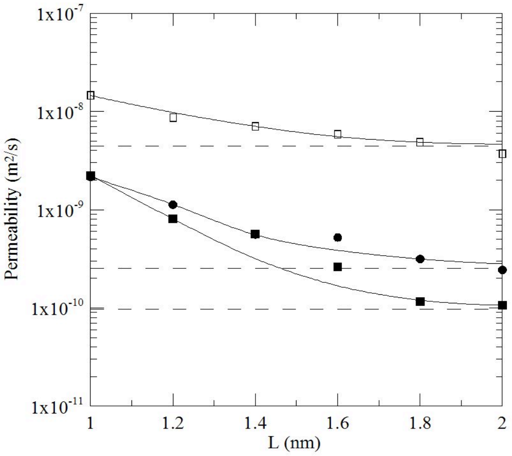

Figure 2: Permeability at 873K as a function of membrane thickness for He (□), CO_2 (●) and N_2 (■). The dashed lines are the fitted permeabilities in the limit $L \rightarrow \infty$.

The gas species within domain I undergo a slow effusive flux at the tip of the domain on the downstream side, $z = L$, and transport within domain II is simple Fickian. Combining these parallel fluxes provides

$$J = \left[D_{II} K + LK' \sqrt{\frac{kT}{2\pi m}} \exp\left(-\frac{L}{\ell} \right) \right] \frac{\Delta n_B}{L}$$

The term in square brackets is the permeability and the results shown in Figure 2, which were typical of each of the runs conducted in this work, clearly demonstrate the exponential dependence of the membrane permeability on its thickness. This exponential behaviour has been observed experimentally [1, 3]. The permeability of Nitrogen is lower than that for both Helium and CO_2 and we note that this is not due to adsorptive effects but arises due to kinetic selectivity within the membranes. The modest selectivity of 2.6 indicated here for CO_2/N_2 compared to the larger experimental values reported in [2, 4] arises due to the marginally lower membrane density of 1.95 g/cc involved in the present case in contrast with the amorphous silica glass-like densities (~ 2.1-2.2 g/cc) inferred by the data in [2, 4]

Additional results to be presented during the talk will include details of the morphological properties of the nanoporous silica materials formed during the simulated LPCVD process. These results in conjunction with equilibrium MD simulations of the gases in bulk homogeneous model silica structures are discussed in light of experimental observations.

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References

[1] D. Lee, L. Zhang, S.T. Oyama, S. Niu and R.F. Saraf, , *J. Membr .Sci.*, 231 (2004) 117.

[2] L. Cuffe, J.M.D. MacElroy, M. Tacke, M. Kozachok and D.A. Mooney, *J. Membr .Sci.*, 272 (2006) 6.

[3] S. Araki, N. Mohri, Y. Yoshimitsu and Y. Miyake, , *J. Membr .Sci.*, 290 (2007) 138.

[4] M. McCann, D. A. Mooney, D. P. Dowling, O. Antson and J. M. D. MacElroy, paper in preparation for submission to *J. Membr.Sci.*

[5] T. McDermott, T. Akter, J.M.D. MacElroy, D. A. Mooney and D. P. Dowling, submitted to *Langmuir.*

[6] M.E. Coltrin, P. Ho, H.K. Moffat and R.J. Buss, *Thin Solid Films,* 365 (2000) 251.

[7] J. Moloney, D. A. Mooney, J.M.D. MacElroy and D. P. Dowling, paper in preparation for submission to *J. Membr. Sci.*

[8] L. Gelb and K.E. Gubbins, *Langmuir*, 14 (1998) 2097.

[9] P.N. Keating, *Phys. Rev.*, 145 (1966) 637.

[10] S. von Alfthan, A. Kuronen and K. Kaski, *Phys. Rev. B*, 68 (2003) 073203.

[11] E.J. Maginn, A.T. Bell and D.N. Theodorou, *J. Phys. Chem.,* 97 (1993) 4173.

[12] J.M.D. MacElroy, *Mol. Phys.*, 100 (2002) 2369.