

ATOMISTIC SIMULATION OF THE FORMATION OF NANOPOROUS SILICA FILMS VIA CHEMICAL VAPOR DEPOSITION

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Abstract

To date, membranes which could be used to separate gas mixtures at high temperatures (notably combustion or other process gas streams at temperatures $T > 750\text{K}$) have only been developed with limited success and it is apparent that this modest pace of growth is, in part, due to a lack of a detailed understanding of the membrane fabrication process at an atomistic level. One particular family of materials which has been shown to exhibit high permselectivities at elevated temperatures are thin films of amorphous silica glasses formed via chemical vapor deposition (CVD) techniques. In earlier work reported by this group [1-3] the possibility of generating membranes with both high kinetic selectivities for CO_2 capture and acceptable permeability has been demonstrated. However, the influence of the experimental conditions employed during the CVD fabrication process on the fundamental microscopic details of the membranes formed still needs to be clarified.

In this work, we investigate the creation of moderate density silica films via direct simulation of the CVD process at intermediate to high temperatures. To model the creation of nanoporous silica layers via CVD we apply a hybrid kinetic Monte-Carlo (KMC) method [4]. Lattice KMC [5] is used for the elementary reactions and an off-lattice method [6,7] is employed for silica network relaxation and bond switching moves. The sensitivity of the resulting layer structure to the substrate temperature, composition of the vapor, and the initial distribution of substrate seed sites is examined. The outcome of this work will assist in providing guidelines for the protocols needed to fabricate high temperature permselective membranes for the separation of CO_2 from combustion gas mixtures.

Kinetic Monte Carlo simulation of the CVD process

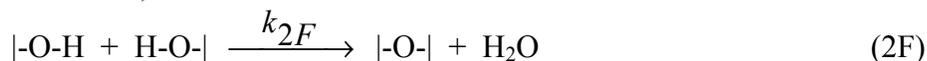
The reactions which are deemed to take place are as follows. The deposition of $\text{Si}(\text{OH})_4$ occurs as



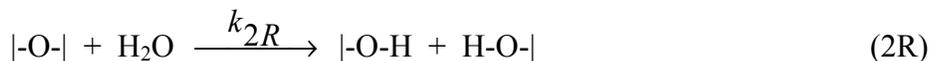
and its reverse



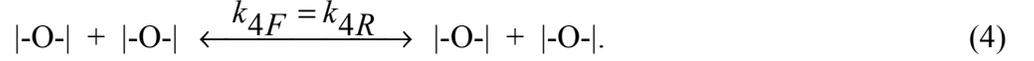
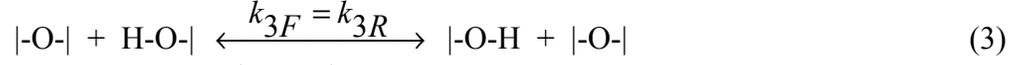
In addition the condensation (annihilation) reaction



and its reverse



take place as do the reversible switching reactions (see [6]),



These reactions allow silanol group and/or siloxane bridge mobility within the medium according to the Wooten, Winer, and Weaire formalism [8].

Hybrid KMC Algorithm

The deposition and condensation reactions (1 and 2) are treated by a lattice KMC method and the switching reactions 3 and 4 (which are believed to occur much more frequently) are treated via standard Metropolis MC). The selection of which reaction event should be sampled at any given time is determined by the frequencies of the reactions. In general for each of the above reactions we can write

$$r_{iF} = k_{iF} c_{Ai} c_{Bi} \quad \text{and} \quad r_{iR} = k_{iR} c_{Ci} c_{Di}$$

with

$$k_{iF} = A_{iF} \exp\left(-\frac{E_{A,iF}}{kT}\right)$$

In the case of the forward reaction the frequency with which we observe the reaction of one molecule of component A is

$$v_{iF} = \frac{1}{\Delta t} \Big|_F = V r_{iF}$$

Similar frequency expressions can be obtained for each of the forward and reverse reactions and in the lattice KMC algorithm one simply selects the reaction event to be considered with a probability

$$P_r = \frac{v_r}{\sum_{x=\text{reactions}} v_x}$$

To implement this a random number is selected uniformly and the event (reaction i) to be undertaken is determined by

$$\sum_{j=1}^{i-1} \frac{v_j}{\sum_{x=\text{reactions}} v_x} < \xi_1 \leq \sum_{j=1}^i \frac{v_j}{\sum_{x=\text{reactions}} v_x} \quad (5)$$

To determine the stochastically distributed increments in time at which the sequence of events takes place it has been shown that the time increment to be added to the 'clock' after each event has been addressed is simply [10]:

$$\tau_{incr} = -\frac{\ln(\xi_2)}{\sum_{x=\text{reactions}} \nu_x} \quad (6)$$

We can express the reaction frequencies in the reference form, $\nu_r^* = \frac{kT}{k_{1F}} \nu_r$, which gives for the forward deposition reaction (1F):

$$\nu_{1F}^* = V k T c_{OH} c_{Si(OH)_4} = \langle K_s \rangle N_{OH} p_{Si(OH)_4} \quad (7)$$

Similar expressions can be written for the other reactions. Note that we have used the Henry's law partitioning relationship between the bulk gas and the nanopores of the evolving layer

$$c_{Si(OH)_4} = \langle K_s \rangle c_{Si(OH)_4}^B = \langle K_s \rangle \frac{P_{Si(OH)_4}}{kT}$$

The local equilibrium partition coefficients are readily calculated in situ during layer development using a simple MC insertion technique in conjunction with the expression

$$\langle K_i \rangle = \frac{1}{\Delta V} \int_{\Delta V} \left\langle \exp\left(-\frac{u_{si}(\mathbf{r})}{kT}\right) \right\rangle_{\Omega} d\mathbf{r} \quad (8)$$

where ΔV is a volume element within the medium and the angular brackets represent averaging over the orientation of the reactant whose centre of mass is located at \mathbf{r} .

To incorporate the position dependence of the selection probabilities it is noted that there are individual reaction events in each volume element \mathbf{r} (where we divide the simulation box into small cubes of side length approximately 0.5 nm). Each of the above reactions strictly apply to each volume element so that the denominator of each probability expression must now be an integral over all space and the individual numerators are each functions of \mathbf{r} . In a volume element ΔV of the medium each of the reactions may take place with modified frequencies to reflect the position dependence of the parameters (k_r in each case is assumed to be independent of \mathbf{r}) which allows us to write a position dependent version of equation 7 as

$$\nu_{1F}^*(\mathbf{r}) = \Delta V k T c_{OH}(\mathbf{r}) c_{Si(OH)_4}(\mathbf{r}) = \langle K_s(\mathbf{r}) \rangle N_{OH}(\mathbf{r}) p_{Si(OH)_4} \quad (7b)$$

Note that in the above expressions an OH species has been selected as the 'target' component in the reaction by explicitly introducing its total number $N_{OH}(\mathbf{r})$. It is also important to note that $N_{OH}(\mathbf{r})$ should read as 'the number of sites OH located within ΔV at \mathbf{r} with which reaction is feasible'. Again similar equations are written for the other reactions.

At each step in the KMC algorithm we sum (integrate) all of these frequencies over all volume elements to obtain the denominator of the selection probability. The reaction event to be selected is obtained by noting the running sum (summing over reaction types in each bin first then summing over bins) and similarly to equation 5 a random number is selected and the event (reaction i in bin k) to be undertaken is determined by

$$\sum_{j=1}^{i-1} \sum_{r=1}^{k-1} \frac{v_{r,j}^*}{\sum_{i=1}^{N_{BIN}} \sum_{r=1}^{N_{RXN}} v_{r,i}^*} < \xi_1 \leq \sum_{j=1}^i \sum_{r=1}^k \frac{v_{r,j}^*}{\sum_{i=1}^{N_{BIN}} \sum_{r=1}^{N_{RXN}} v_{r,i}^*} \quad (5b)$$

Equation 6 is similarly modified so that the time increment becomes

$$\frac{k_{1F}}{kT} \tau_{incr} = \tau_{incr}^* = \frac{-\ln(\xi_2)}{\sum_{i=1}^{N_{BIN}} \sum_{r=1}^{N_{RXN}} v_{r,i}^*} \quad (6b)$$

In the switching reactions each reaction event is chosen with equal probability but now the conditional probability is given by the Boltzmann factor for the transition

$$p_{i \rightarrow f} = \exp\left(-\frac{(U(f) - U(i))}{kT}\right) \quad (9)$$

This requires the full evaluation of the system energies prior to and after the reaction event. At typical CVD process conditions the switching reactions occur far more frequently than the deposition, condensation and (if water vapour is present at a reasonable pressure) hydration reactions.

Cluster Analysis

As mentioned above, the reagent concentrations are calculated via the Henry's law partitioning relationship in small volume elements within the layer. However not all volume elements with a favorable Henry's law coefficient are available for reaction to occur, as the reagents access to these regions may be blocked by higher density regions above them. It is necessary to identify the volume elements in the layer which are favorable for a reagent molecule *and* which are accessible through a connected path to the vapor phase above the layer.

Figure 1 shows a two dimensional representation of the system. Each square represents one of the small volume elements (a cube of side 0.5 nm). Black regions are unfavorable locations for the reagent, where the Henry's law constant (evaluated within the local volume element using equation 8) is below a critical value. White and yellow regions are favorable positions for the reagent. However, only the yellow regions are accessible from the top via a connected path. Favourable regions are connected if the squares share a common edge (the cubes in the box share a common face). The cluster of accessible volume elements (cluster 1 in figure 1) is determined using the Hoshen-Kopelman algorithm [9]. Note that the layer grows in the Z direction and periodic boundary conditions are applied laterally.

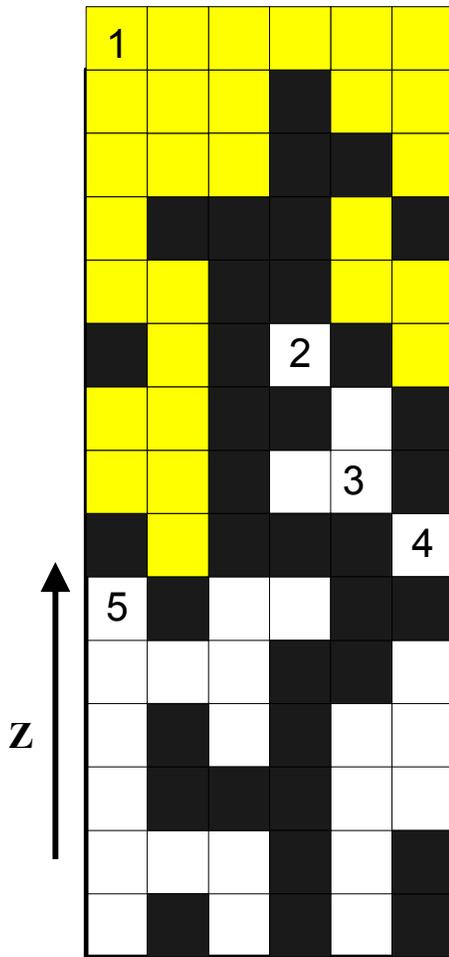


Figure 1: Two dimensional representation of the cluster algorithm

Preliminary results

The simulations began with a flat square surface of side 3.0 nm which was seeded with a number of OH groups placed randomly. Each cycle of the algorithm involved a KMC reaction event followed by many relaxation steps involving switching reactions and MC moves. The simulations were carried out at temperatures of 580 K and 1160 K and initial seed densities of 0.56 OH/nm² and 5 OH/nm² with a vapor phase compositions of $p_{\text{H}_2\text{O}}/p_{\text{Si(OH)}_4} = 0.001$. The simulations were carried out for 1000 cycles and for each set of process conditions the results were averaged over five independent runs.

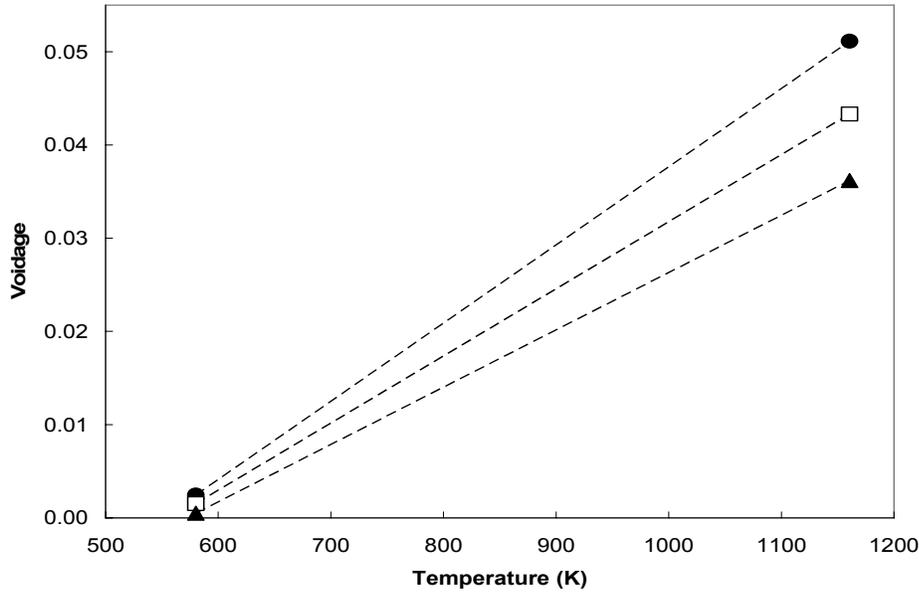


Figure 2: Voidage of the layer versus temperature. The initial seed density was 0.56 OH/nm^2 and $p_{\text{H}_2\text{O}}/p_{\text{Si(OH)}_4} = 0.001$ (● O₂, □ N₂, ▲ CO₂).

Figures 2 and 3 show that the voidage of the deposited layers was low and it tended to increase with temperature and initial OH seed density. Further runs are being carried out to study the effect of vapor composition (varying the ratio $p_{\text{H}_2\text{O}}/p_{\text{Si(OH)}_4}$) and also to examine the behavior of the layers when subjected to hydrothermal treatment and these will be reported in the presentation. Figure 4 shows that the layer grew linearly with time and experimental work being carried out in this group will allow the KMC time on the abscissa of figure 4 to be related to real time.

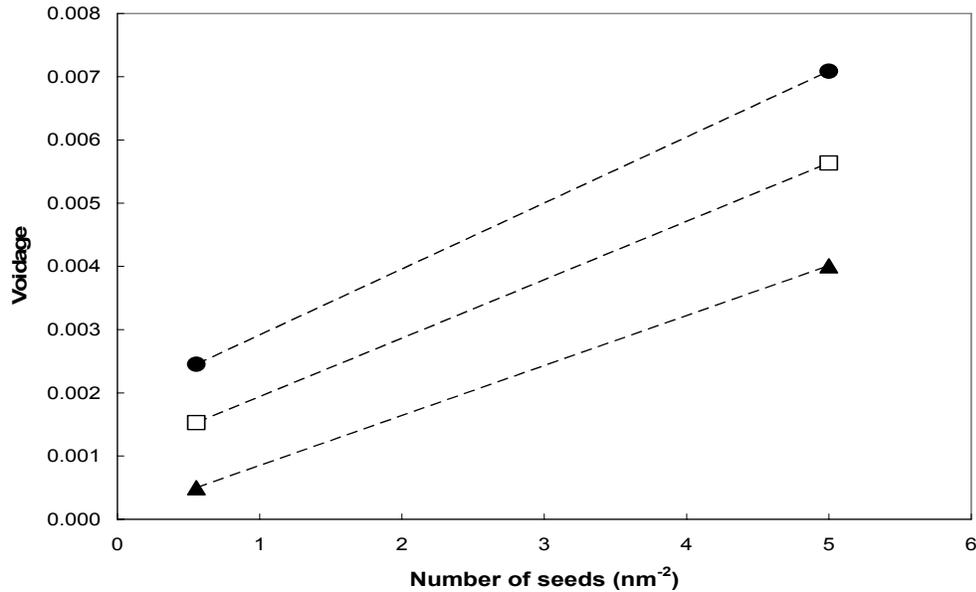


Figure 3: Voidage of the layer versus the initial seed density. The temperature was 580 K and $p_{\text{H}_2\text{O}}/p_{\text{Si(OH)}_4} = 0.001$ (● O₂, □ N₂, ▲ CO₂).

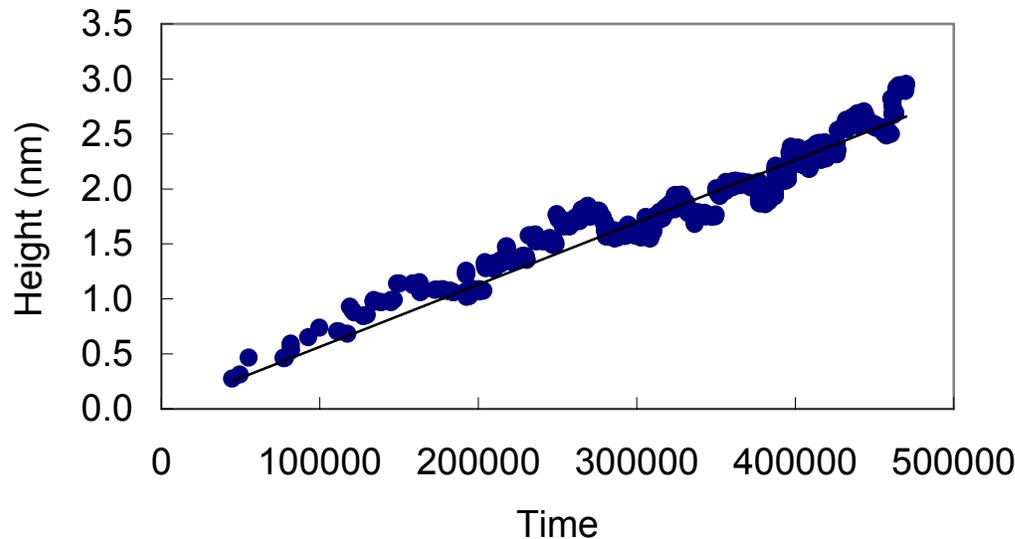


Figure 4: The growth curve for the layer grown from a seed density 0.56 OH/nm^2 at 580 K , with $p_{\text{H}_2\text{O}}/p_{\text{Si(OH)}_4} = 0.001$

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