

# Supporting Information

## Model for the Synthesis of Self Assembling Template-Free Porous Organosilicas

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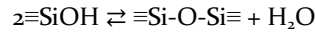
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### Development of Solvent Index

Our primary goal here is to relate the solvent index, introduced in the Results and Discussion, to the amount of solvent remaining in the gel when the molecular network reaches the rigidity transition. This amount of solvent is closely related to the eventual pore volume and surface area in the dried solid, so the solvent index becomes a useful correlating variable for these textural properties. The extent of the condensation reaction (e.g. number of bridging bonds formed) is directly related to the connectivity of the network. The connectivity of the network at the transition is found by application of the concepts of constraint counting or rigidity theory and is used to define the solvent index. The amount of solvent remaining is related to the extent of reaction through an equilibrium assumption. Hence, the solvent index is related directly to the amount of solvent remaining at the point when rigidity is reached and therefore to the surface area and porosity of the dried solid.

### Hydrolysis and Condensation

For the high  $H_2O/Si$  syntheses considered in this work, we will ignore the presence of ethanol hydrolyzed from ethoxy groups on the precursor molecules. In that case, consider generic hydrolysis and condensation reactions in the solgel system:



We assume that this reaction is at or near equilibrium at some time in the gelation and/or drying stages since significant reaction progress has already occurred and since the temperature and hence reaction rates are increased during drying. For purposes of developing a simple theory, all silanols (regardless of the other ligands on the Si) are assumed to have the same kinetic and thermodynamic properties. We can then write a single equilibrium constant

$$K = \frac{a_{H_2O} a_{SiOSi}}{a_{SiOH}^2} \quad (S1)$$

which applies everywhere. Solving for the activity of water we have:

$$a_{H_2O} = K \frac{a_{SiOH}^2}{a_{SiOSi}} \quad (S2)$$

Now assume the water in the pores is in equilibrium with low pressure vapor phase (approximately pure) water ( $a_{H_2O} = y_{H_2O} \phi_{H_2O} P_{H_2O} / P^o \sim P_{H_2O} / P^o$ ) where  $y$  is a gas-phase mole fraction,  $\phi$  is a fugacity coefficient (not to be confused with porosity as used elsewhere), and also introduce activity coefficients ( $\gamma_i$ ) and molar concentrations ( $c_i$ ) for the components in the wet gel ( $a_i = \gamma_i c_i$ ):

$$P_{H_2O} = \gamma_{H_2O} c_{H_2O} P^o = \left( K P^o \frac{\gamma_{SiOH}^2}{\gamma_{SiOSi}} \right) \left( \frac{c_{SiOH}^2}{c_{SiOSi}} \right) \quad (S3)$$

where  $P^o$  is the standard state pressure. In calculations of the extent of reaction, it is useful to track mole ratios per silicon rather than in molar concentrations so we write the above as

$$\frac{P_{H_2O}}{P^o} = \gamma_{H_2O} \frac{n_{H_2O}}{n_{Si}} \frac{M}{V} \frac{1}{MW'} = \left( K \frac{\gamma_{SiOH}^2}{\gamma_{SiOSi}} \right) \left[ \frac{(n_{SiOH}/n_{Si})^2}{(n_{SiOSi}/n_{Si})} \frac{1}{MW'} \right] \frac{M}{V} \quad (S4)$$

where  $M$  is the total mass,  $V$  is the system volume, and  $MW'$  is the mass per mole of silicon atoms of all the species which derive from the precursor molecules (the solid gel and any remaining hydrolyzed precursor molecules or fragments in solution;  $n_{Si} = M/MW'$ ). Upon rearrangement and defining the term in square brackets as  $w$ :

$$\frac{n_{H_2O}}{M} = \gamma_{H_2O}^{-1} \frac{P_{H_2O}}{P^o} \frac{V}{M} = \gamma_{H_2O}^{-1} \left( K \frac{\gamma_{SiOH}^2}{\gamma_{SiOSi}} \right) w \quad (S5)$$

We can see that  $w$  is directly related to the state of condensation of the system ( $n_{SiOH}$ ,  $n_{SiOSi}$ ) and indirectly related to the amount of water in the gel ( $n_{H_2O}/M$ ) or to the pressure of the gas-phase water in equilibrium with the gel through the above equation. Through the kinetic definition of  $K$ ,  $w$  is also directly proportional to the ratio of the forward and reverse rates of reaction at the specified state. The first part of Equation (S5) is in the form of a water sorption isotherm

$$\left( n_{H_2O}/M = f(P_{H_2O}) \right).$$

For convenience we define an index,  $W$ , for a given precursor that is the ratio of  $w$  for that precursor at a specified state to that of a standard precursor at some other defined standard state:

$$W = \frac{w}{w_{std}} \quad (S6)$$

With this definition, we can write

$$\frac{n_{H_2O}/M}{(n_{H_2O}/M)_{std}} = \left( \frac{\gamma_{H_2O, std}}{\gamma_{H_2O}} \right) \frac{P_{H_2O}(V/M)}{P_{H_2O, std}(V/M)_{std}} = \left( \frac{\gamma_{H_2O, std}}{\gamma_{H_2O}} \right) \left[ \frac{\left( K \frac{\gamma_{SiOH}^2}{\gamma_{SiOSi}} \right)}{\left( K \frac{\gamma_{SiOH, std}^2}{\gamma_{SiOSi, std}} \right)} \right] W \quad (S7)$$

We further assume that the square-bracketed term on the right-hand-side is approximately unity when the system of interest and the standard system are at conditions not too different from one another. We then have:

$$\frac{n_{H_2O}/M}{(n_{H_2O}/M)_{std}} = \left( \frac{\gamma_{H_2O, std}}{\gamma_{H_2O}} \right) \frac{P_{H_2O}(V/M)}{P_{H_2O, std}(V/M)_{std}} = \left( \frac{\gamma_{H_2O, std}}{\gamma_{H_2O}} \right) W \quad (S8)$$

The state of the system of the precursor of interest and of the standard precursor will be defined below.

#### Rigidity Theory and the Rigidity Transition

Rigidity theory offers a method to identify the state of the gel corresponding to the critical level of strength. Consider a system of objects, each with several degrees of freedom of movement, and the constraints imposed on those movements by connections between the objects. In an average, mean-field, or generic sense, when the number of constraints reaches or exceeds the number of degrees of freedom, the collection of objects is fully constrained—it can no longer support motions of one part of the object relative to other parts. This is true unless some of the constraints are redundant or otherwise ineffective. For application to amorphous networks of organosilicates created from molecules in solution, we expect the connections to be evenly spread throughout the network so that it is not the case that some local regions will be over-constrained and others very floppy. In what follows, we follow closely the work of Gupta (11) who formulates the rigidity theory in terms of the connections between rigid polytopes rather than the more usual formulation in terms of atoms.

Consider a collection of  $M$  rigid objects, each of which might represent a silicate tetrahedron. For simplicity, we will here only consider cases where the objects are identical. Each object has characteristic numbers of translational and rotational degrees of freedom;  $n_t$  and  $n_r$ . For the usual case of three dimensional non-linear objects in 3D space,  $n_t = n_r = d = 3$ , where  $d$  is the dimensionality. For the collection of objects, there are a total of  $N_T = M(n_t + n_r)$  degrees of freedom. The col-

lection of rigid objects taken as a single entity has  $\nu_T = \nu_t + \nu_r$  degrees of freedom;  $\nu_T = 6$  in the typical 3D case.

Each object has a number of vertices  $V$  which can be merged with vertices from other objects to form a compound object or network. When vertices from two objects merge, they form a “joint”. The most relevant example is two SiOH groups (vertices) condensing to form an SiOSi corner-sharing bridge (joint). In general there can be joints that connect  $j$  objects and there are  $N_j$  of each of these types; For a bridging oxygen,  $j = 2$ , and for a terminal SiOH,  $j = 1$ . The total number of

joints in the network is 
$$N = \sum_j N_j$$
.

The average number of objects connected per joint of the entire network is 
$$C = \sum_j j C_j / N$$
. If a joint connects  $j$  objects, then it accounts for  $j$  vertices from those objects, so the sum, over all objects of all vertices in each object equals the sum, over all joints, of the number of objects connected by the joint:  $MV = CN$ .

When vertices from  $j$  objects are merged to form a joint,  $d(j-1)$  translational constraints are imposed on the motion of the system. The total number of such constraints due to the joints with  $j > 1$  is:  $n_t N(C-1)$ . We also suppose that for each joint connecting  $j$  objects, there are  $n_\theta$  other constraints imposed (e.g. bond bending constraints). The total of these is:

$$N_\theta = \sum_j n_\theta N_j = n_\theta N$$

In order to find the net structural (internal) degrees of freedom of the system, we subtract from the total degrees of freedom, the number of constraints and the degrees of freedom of the entire network of objects.

$$\begin{aligned} F &= N_T - N_c - v_T \\ &= M(n_t + n_r) - n_t N(C-1) - n_\theta N - v_T \\ &= N \left[ C \left( \frac{n_t + n_r}{V} - n_t \right) + n_t - n_\theta - \frac{v_T}{N} \right] \end{aligned} \tag{S9}$$

where we have used  $MV = CN$ . Eliminating the number of joints in favor of the number of objects gives an equivalent expression in terms of the number of objects,

$$F = M \left[ n_t + n_r - n_t V + (n_t - n_\theta) \frac{V}{C} - \frac{v_T}{M} \right] \tag{S10}$$

For large systems ( $N, M \rightarrow \infty$ ), the final terms within the brackets vanish.

We seek the state of connectivity of a large system such that the structural degrees of freedom vanish. The system is then incipiently rigid. Setting  $F/M = 0$  or  $F/N = 0$ , we find:

$$C^* = \frac{(n_t - n_\theta)V}{n_t V - (n_t + n_r)} \quad (\text{S11})$$

For a large 3D system of tetrahedra with vertexes at the corners,  $n_t = n_r = 3$  and  $V = 4$  so that:

$$C^* = \frac{(3 - n_\theta)4}{3 \cdot 4 - 6} = 2 - \frac{2}{3}n_\theta \quad (\text{S12})$$

If there are no angular constraints around the joints ( $n_\theta = 0$ ), then  $C^* = 2$ . As shown by Gupta (11), this is equivalent to the result of Phillips (19) which was used to justify why  $\text{SiO}_2$  so easily forms a glass from the melt; when fully connected (each O atom connects 2  $\text{SiO}_4$  tetrahedra;  $C = 2$ ), the system lies on the rigidity transition. This formulation is appropriate at high temperatures near the melting transition for silica at which the  $\text{SiOSi}$  bond angle is effectively unconstrained.

We now form a hardness index (12) which represents the average connectivity of the joints in excess of that required for the rigidity transition;  $h = C - C^*$ . When  $h < 0$ , the material is expected to be floppy and when  $h > 0$ , the material is expected to be rigid. For materials with real bond constraints rather than idealized infinitely stiff constraints, when  $h > 0$ , a finite modulus (and other mechanical properties) should be expected and it should increase as the hardness index increases (12). If we restrict our application to systems with joints that have either connectivity 1 (terminal joints such as –

OH or  $-\text{CH}_3$ ) or connectivity 2 (bridging O or bridging  $-\text{CH}_2-$ ), then  $C = \sum x_j C_j$  where the fraction of joints with connectivity  $j$  is  $x_j$ . The average number of angle constraints is similarly  $n_\theta = \sum x_j n_{\theta j}$ . With these definitions, the hardness index becomes:

$$h = C - C^* = \sum x_j \left( C_j - 2 + \frac{2}{3}n_{\theta j} \right) \equiv \sum x_j \lambda_j \quad (\text{S13})$$

The hardness index is seen to be in the form of a linear group-contribution method where the group parameter for a joint

with connectivity  $j$  is  $\lambda_j = C_j - 2 + \frac{2}{3}n_{\theta j}$ .

Bridging joints in the systems considered in this work consist of oxygen atoms, methylene groups, or the para-benzene group. For both oxygen and the organic bridging groups, we use the usual formula  $(2C-3)$  (11) for the number of bond bending constraints, yielding  $n_\theta = 1$ . Siloxy ether chains are known to be more flexible than those associated with the other bridging groups (20) and a temperature-dependent, bridging group specific,  $n_\theta$  should provide a more accurate description (21, 22), but we ignore that possibility in this work as have most previous studies. For purposes of counting constraints, we count the bridging phenyl group as equivalent to a methylene group.

Given the values for  $C_j$  and  $n_{\theta_j}$  for each type of joint being considered,  $\lambda_j = -1$  for the terminal groups  $-\text{OH}$  and  $-\text{CH}_3$  and  $\lambda_j = 2/3$  for  $-\text{O}-$ ,  $-\text{CH}_2-$ , and  $-\text{C}_6\text{H}_4-$ . For the joint types considered in this work, the parameters related to the hardness index are given in Table S1 below.

**Table S1: Joint parameters for calculating rigidity index**

	OH	CH <sub>3</sub>	O	CH <sub>2</sub>	Ph
<b>Connectivity</b>	1	1	2	2	2
<b>Angle Constraints</b>	0	0	1	1	1
<b><math>\lambda</math></b>	-1	-1	2/3	2/3	2/3

For a silicate containing bridging (B) and terminal (T) groups (joints), the composition is  $\text{SiB}_{2-y/2}\text{T}_y$ . From Equation (S13) and  $\lambda$  from Table S1,  $h = (2/3)x_B - x_T$ . At  $h = 0$ , this becomes  $x_B/x_T = n_B/n_T = 3/2$ , which combined with the composition  $(n_B/n_T = (2-y/2)/y)$  gives

$$n_B/n_{\text{Si}} = 3/2 = 1.5 \quad (\text{S14})$$

The prediction from the simple form of rigidity theory is that silicate materials containing bridging groups similar to  $-\text{CH}_2-$  or  $-\text{O}-$  and terminal groups such as  $-\text{OH}$  and  $-\text{CH}_3$  will reach the rigidity transition when the number of bridging groups is 1.5 times the number of silicon atoms.

### Mechanical Properties

We follow Boolchand et al. (12) in positing that the mechanical properties (e.g. bulk modulus, yield stress) of nonporous materials with variable connectivity are functions of the hardness index:

$$\sigma = \sigma_{fc} f(h/h_{fc}) \quad (S15)$$

where the subscript  $fc$  indicates “fully connected” and  $f(1) = 1$ . Boolchand et al. found that for the nano-indentation hardness of carbon and silicon carbide films,  $f$  was closely approximated by a linear or power law form.

For the effect of porosity on the mechanical properties of a porous material we use a Gibson and Ashby (14) type expression:

$$\sigma_{gel} = \sigma (1 - \phi)^n \quad (S16)$$

Combining these we have:

$$\sigma_{gel} = \sigma_{fc} f(h/h_{fc}) (1 - \phi)^n \quad (S17)$$

For some yield stress,  $\sigma_{gel}^*$ , the gel will be able to resist the capillary forces causing collapse. There will then be a curve in  $(h, \phi)$  where  $\sigma_{gel}^* = \sigma^{dry}$  that separates regions where the gel is stable or unstable with respect to collapse:

$$\phi = 1 - \left( (\sigma^{dry} / \sigma_{fc}) / f(h/h_{fc}) \right)^{\frac{1}{n}} \quad (S18)$$

### Reaction Extent

For hydrolyzed organo-alkoxysilane precursors, we can write equations for the number of each type of bridging or terminal group as a function of an extent of reaction,  $n$ , and stoichiometric coefficients

$$\begin{aligned} n_{SiOH} &= n_{OH}^0 - 2n \\ n_{SiCH_3} &= n_{SiCH_3}^0 \\ n_{SiOSi} &= n_{SiOSi}^0 + n \\ n_{SiCH_2Si} &= n_{SiCH_2Si}^0 \\ n_{SiPhSi} &= n_{SiPhSi}^0 \end{aligned} \quad (S19)$$

where the organic groups are assumed inert under the conditions considered in this work.



For given precursors and extents of reaction, the hardness index as defined in Equation (S13) and the W index defined in Equations (S4-6) can be calculated. For a given hardness index, chosen for its influence on the mechanical properties of the gel, the extent of reaction can be determined, perhaps numerically, and then W calculated.

For the precursors considered in this work, the initial numbers of each type of joint (per silicon atom), necessary for calculating the composition and hardness index as a function of the extent of reaction, are given in Table S2. These are used to determine the composition at the rigidity transition which is then used to calculate W.

**Table S2: Initial number of joint types for calculating extent of reaction**

	H <sub>2</sub> O	OH	CH <sub>3</sub>	O	CH <sub>2</sub>	Ph
<b>TEOS</b>	90	4	0	0	0	0
<b>MTES</b>	90	3	1	0	0	0
<b>3R</b>	90	2	0	0	1	0
<b>3Me<sub>3</sub>R</b>	90	1	1	0	1	0
<b>PhB</b>	90	3	0	0	0	½
<b>MB</b>	90	3	0	0	½	0

#### Supporting Information References

References 1-18 are the same as in the main text.

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