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Comment on "Dehydration of Gels and Glasses in the Systems B_2O_3-SiO_2 and ZrO_2-SiO_2 Prepared by the Sol-Gel Process from Metal Alkoxides"

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IN A recent communication Nogami[1] reports on the shrinkage of SiO_2, $B_2O_3{\cdot}SiO_2$, and $ZrO_2{\cdot}SiO_2$ gels at intermediate temperatures (200° to 700°C, temperatures too low for appreciable viscous sintering to occur) where shrinkage is postulated to result from condensation reactions:

$$\equiv M{-}OH + HO{-}M\equiv \;\rightarrow\; \equiv M{-}O{-}M\equiv + H_2O \qquad (1)$$

where, for example M=Si, B, or Zr. For a heating rate of 5°C/min Nogami observed that shrinkage, L, was proportional to time, t

$$L = kt = k(T-b)/a \qquad (2)$$

where k, defined as the rate constant* of Eq. (1), is given as

$$k = k_0 \exp(-E/RT) \qquad (3)$$

and t is related to temperature T by $T = at + b$. a is the heating rate (5°C/min) and b is the initial temperature of the gels (25°C). Reasonably linear fits of log (L/t) vs $1/T$(K) were used as proof that Eq. (1) was a zero-order reaction. It should be noted here that when T is a function of time, Eq. (2) must be replaced by

$$L = \int_0^t k[T(t)]dt' \qquad (4)$$

The integral can be evaluated approximately[2] so that Eq. (2) is replaced by

$$L = \left(\frac{R}{E}\right)\left(\frac{T^2}{T-b}\right)kt \qquad (5)$$

Since $T^2/(T-b) \approx T$ varies slowly by comparison to the exponential term, a plot of log (L/t) vs $1/T$ would be nearly linear where Eq. (5) applies. Nogami related E, the activation energy derived from the slopes of such plots, to the binding strength of the hydroxyl to the metal ion and found that k varied continuously in the systems B_2O_3-SiO_2 and ZrO_2-SiO_2.

This comment is intended (1) to explain why gel shrinkage may exhibit apparent zero-order kinetics, (2) to demonstrate that at intermediate temperatures considerable shrinkage may occur with no associated weight loss [thus not being explained by Eq. (1)], and (3) to emphasize that gel shrinkage depends in a dramatic fashion on the original gel structure (as pointed out by Nogami in an earlier paper[3]) and perhaps to a lesser extent on gel composition.

A reaction rate is said to be of zero order if the rate of the reaction is independent of the concentration of the reactants, so that the rate of change of the concentrations is a constant:

$$-(dc/dt) = k \qquad (6)$$

Zero-total-order reactions are very rare. The possible explanations for apparent concentration-independent behavior are that the rate of the reaction is limited by the input of energy which causes reaction, the surface area on which the reaction occurs, or diffusion of reactants to close proximities permitting subsequent reaction.[4] One example of a surface-area-limited reaction is the decomposition of nitrous oxide on a hot platinum wire. When the platinum surface becomes saturated at a given concentration of reactants, a further increase in concentration does not result in a corresponding increase in reaction rate.[5]

It should be emphasized that, for gels, condensation reactions Eq. (1) can occur both on the pore surfaces and within the bulk or "skeleton." The amount of shrinkage resulting from such reactions depends on the gel synthesis method employed.[6,7] This is demonstrated in Fig. 1 for three different silica gels. The colloidal gel, composed of a comparatively dense, anhydrous SiO_2 skeleton, exhibits little shrinkage below 800°C. Most of the observed shrinkage results from dehydration of the surface which occurs reversibly with a corresponding shrinkage due to the change in surface free energy:

$$\varepsilon = -(1-\nu)S\rho_s\Delta\gamma/E \qquad (7)$$

where ε=linear strain, S=surface area, ρ_s=skeletal density, $\Delta\gamma$=change in surface free energy, and ν and E are Poisson's ratio and Young's modulus of the skeleton, respectively. For a silica gel containing $\approx 100\ m^2/g$ of surface, changing from a completely hydroxylated surface ($\gamma = 15\ \mu J/cm^2$)[8] to a pure siloxane surface ($\gamma = 26\ \mu J/cm^2$)[8] results in a shrinkage of $\ll 1\%$ (see Fig. 1).

Much greater shrinkage is observed in metal alkoxide derived gels (*A* and *B* in Fig. 1), which is explained in part by condensation reactions occurring within the skeleton (as well as on the pore surfaces). This is by comparison an irreversible process which results in an increase in skeletal density[9] and a corresponding loss in weight. It is reasonable to suspect that condensation within the bulk is limited by diffusion of the individual reactant species, viz., hydroxyls, to locations where a second species is encountered (or perhaps by the diffusion of the byproduct water to a free surface). If the condensation reaction occurs rapidly compared to the diffusional processes, the rate of the reaction is diffusion limited and hence shrinkage is proportional to $\sqrt{t}$. Indeed replotting Nogami's[1] results according to†

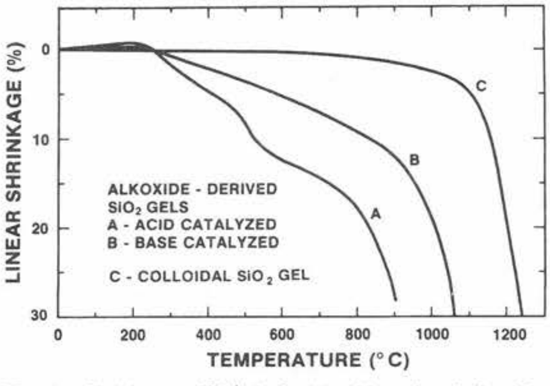

Fig. 1. Shrinkage at 2°C/min for (*A*) acid-catalyzed alkoxide-derived gel, (*B*) base-catalyzed alkoxide-derived gel, and (*C*) colloidal gel prepared from colloidal silica (after Ref. 4).

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*k was incorrectly defined as an equilibrium constant in Ref. 1.

†Replacing Dt with $\int_0^t D\,dt'$, as in going from Eq. (2) to Eq. (5), produces a term proportional to $\sqrt{T}$ on the right side of Eq. (8). However, this temperature dependence is too weak to influence the linearity of the resulting plot.

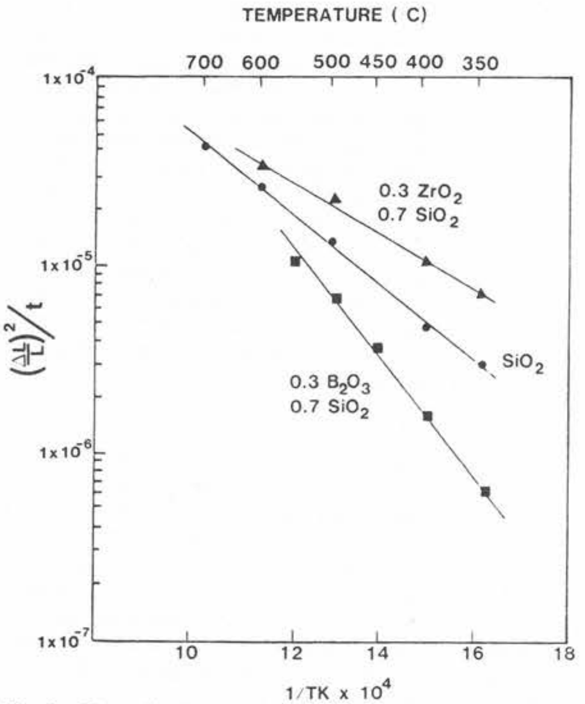

Fig. 2. Nogami's shrinkage data (Ref. 1) (5°C/min) plotted according to (shrinkage)$^2 \propto Dt$.

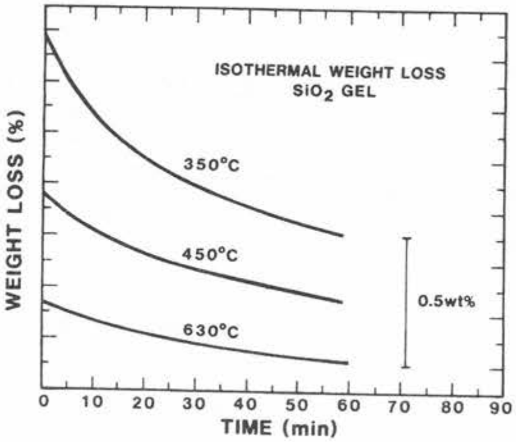

Fig. 3. Isothermal weight loss for SiO$_2$ gel B.

$$L = \sqrt{Dt} \tag{8}$$

where D, the diffusion coefficient, equals $D_0 \exp(-Q/RT)$ and Q equals the activation energy for diffusion results in an equally good fit to the experimental observations. This is shown in Fig. 2 for the three gel compositions investigated by Nogami (correlation coefficients in Fig. 2 >0.996), which demonstrates that linearity of such plots is a rather insensitive criterion for determining reaction kinetics.

Isothermal experiments provide a more sensitive means of distinguishing between zero-order reactions (fraction reacted is directly proportional to time) and diffusion-limited or higher-order reactions. Isothermal experiments performed on a large number of gels synthesized in our laboratory have not revealed $L = kt$ behavior at intermediate temperatures, nor do they suggest that Eq. (1) is a zero-order reaction. This is demonstrated in Fig. 3, which shows weight loss due to condensation (Eq. (1)) vs time for the silica gel composition B (composition B2 in ref. 10) held isothermally at three different temperatures. At the lowest temperature weight loss varies as approximately $t^{1/2}$ [weight loss (%)$=0.13t^{0.45}$; correlation coefficient$=0.98$], whereas after $\approx$20 min at the higher temperatures it varies approximately as e^{kt}. This suggests that Eq. (1) is initially diffusion limited and at higher temperatures eventually exhibits first-order kinetics.

To explain this behavior we propose that at lower temperatures condensation occurs predominantly in the bulk and is diffusion limited. At higher temperatures (where the skeleton is more fully densified), hydroxyls are located mainly on surfaces where Eq. (1) may obey first-order kinetics. Recent Raman results by Krol and van Lierop[11] can be interpreted to support this explanation. For a particular silica gel both hydrogen-bonded and isolated surface hydroxyls were observed below $\approx$500°C. At higher temperatures primarily isolated surface hydroxyls remained. Because of their varied environment, bulk hydroxyls will appear spectroscopically indistinguishable from hydrogen-bonded surface hydroxyls. This suggests that condensation of bulk and hydrogen-bonded surface hydroxyls is complete by $\approx$500°C. Above 500°C condensation occurs primarily between isolated surface silanols and may be first order in hydroxyl concentration according to our isothermal results. Further evidence which supports the idea that hydroxyls are located within the silica skeleton at low and intermediate temperatures includes reduced elastic moduli[12] and skeletal density[9] and increased coefficients of thermal expansion.[6,13] Heat treatments at temperatures up to 600°C cause the skeletal density to increase and the coefficient of thermal expansion to decrease. However, as described in the following paragraph, some of this behavior may be a result of structural relaxation.

Figures 4 and 5 demonstrate a second important concept in gel behavior. If shrinkage at intermediate temperatures depends only on condensation reactions, then shrinkage is directly proportional to weight loss. Figure 4 shows that for a particular silica gel (prepared under conditions which inhibit the extent of cross-linking) shrinkage does not necessarily depend on the amount of condensation. Whereas shrinkage in the region 250° to 400°C is proportional to weight loss, extensive shrinkage occurs between 450° and 600°C with little associated weight loss. Figure 5 shows that in this temperature range (450° to 600°C) shrinkage occurs exothermically with a corresponding increase in skeletal density. This behavior is explained by structural relaxation which occurs by diffusive motions of the polymeric network, resulting in reduced excess free volume without expulsion of water or other byproducts.[14] As shown by the repeat DSC (DSC-2) scan this process occurs irreversibly.

Although Figs. 4 and 5 represent a rather dramatic example of structural relaxation occurring in a specially synthesized gel, we believe that structural relaxation is a common phenomenon for most alkoxide-derived gels. This hypothesis is based on results of small-angle X-ray scattering[10] and skeletal density measurements[6,9,15] which prove that alkoxide-derived gel-forming systems are weakly cross-linked compared to the corresponding melt-prepared glasses (permitting a wider range of network conformations) and densification studies which indicate that even at higher temperatures, where densification occurs predominantly by viscous sintering, structural relaxation can continue to occur, causing the shear viscosity to increase.[16]

In summary, we have shown that gel shrinkage at intermediate temperatures occurs by three mechanisms: (1) capillary contraction due to increasing surface energy as pore surfaces are dehydroxylated, (2) condensation-polymerization within the skeleton, and (3) structural relaxation. Since capillary contraction can only account for relative shrinkages of <0.01, extensive gel shrinkage which is accompanied by weight loss is expected to result primarily from condensation reactions within the skeleton. Although constant heating rate analyses do not distinguish between $t^{1/2}$ and zero-order kinetics for this condensation process, additional isothermal experiments suggest that, instead of a zero-order pro-

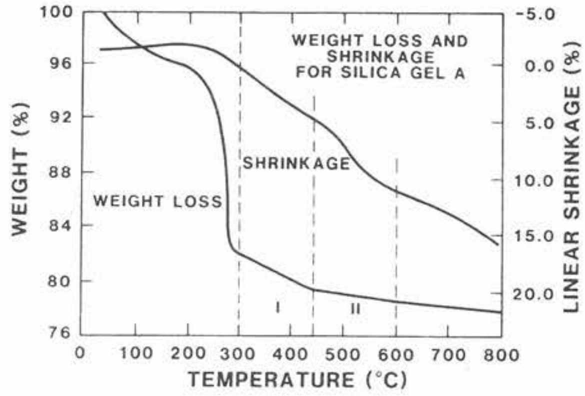

Fig. 4. Weight loss and shrinkage for SiO_2 gel A.

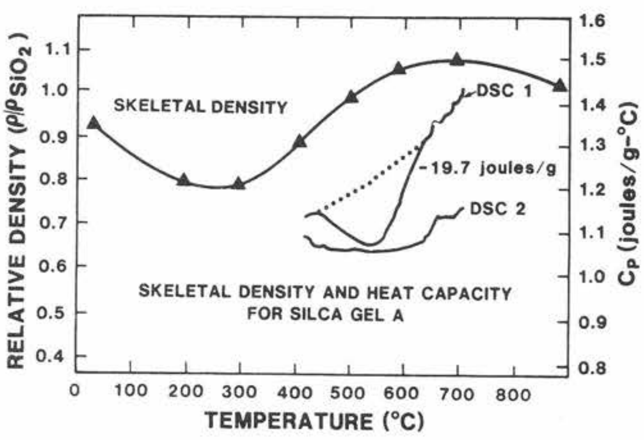

Fig. 5. Skeletal density and heat capacity for silica gel A. DSC-1 represents initial scan; DSC-2 is a repeat scan after specimen was cooled at 80°C/min.

cess, Nogami's shrinkage data are more reasonably explained by a diffusion-limited condensation process which causes shrinkage to be proportional to $\sqrt{Dt}$. In this case the continuous changes in k, observed as composition was varied in the binaries SiO_2-B_2O_3 and SiO_2-ZrO_2,[1] might reflect differences in the activation energy for diffusion of hydroxyls within the skeleton, as in fact postulated by Nogami.[1]

As the skeleton becomes more fully dehydrated, hydroxyls are located primarily on surfaces. Isothermal experiments suggest that condensation of surface hydroxyls may obey first-order kinetics.

Shrinkage at intermediate temperatures does not occur only by condensation reactions, however. We have demonstrated that variations in the gelation conditions can cause the contribution of structural relaxation to become quite significant. This points out that, because dramatic differences in shrinkage behavior can occur for gels of the same oxide composition prepared by different methods, differences which arise due to systematic variations in composition, e.g., in the B_2O_3-SiO_2 and ZrO_2-SiO_2 binaries, should be explained only after consideration of both the structural and chemical consequences of the compositional changes.

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