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WHAT FACTORS CONTROL THE STRUCTURE OF SILICA AEROGELS ?

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Résumé : En modifiant les conditions de polymérisation dans la solution précurseur, il est possible de contrôler la structure des aérogels de silice. La porosité varie comme celle de matériaux dont la structure est constituée de grains jusqu'à celle de matériaux dont la structure est analogue à des polymères. Quand les gels sont réalisés à partir d'alkoxides, le pH est le facteur dominant qui détermine la structure. Dans le domaine de pH compris entre 8 et 12, le gel est constitué de particules ayant diverses rugosités de surface. Dans des conditions neutres, la polymérisation est auto-limitée, elle produit des polymères ayant une géométrie identique à celle de clusters au seuil de percolation. Dans des conditions acides, la structure est constituée par des polymères branchés hautement ramifiés. En utilisant le concept de géométrie fractale, différents processus de croissance sont identifiés et rendent compte de la structure observée. Ces processus incluent la croissance dite "Eden" (réaction limitée entre monomère et cluster) dans des conditions basiques et une croissance cluster-cluster dans des conditions acides. Une cinétique de type percolation est proposée pour rendre compte du processus mis en jeu dans des conditions neutres.

Abstract - By manipulating polymerization conditions in solution precursors, it is possible to control the structure of silica aerogels. Porosity varies from grain-like to polymer-like. When produced from alkoxides, pH is the dominant factor that determines structure. Under strongly basic conditions (pH > 12) compact colloidal particles are observed. In the range pH = 8-12, particles of varying surface roughness result. In the neutral range, polymerization is self-limiting, producing polymers with the geometry of percolation clusters at threshold. Under acidic conditions, highly ramified branched polymers are realized. Using the concept of fractal geometry, different growth processes are identified that account for the observed structure. These processes include Eden growth (reaction-limited monomer-cluster aggregation) under basic conditions and the cluster-cluster analogue under acidic conditions. Kinetic percolation is postulated for the neutral regime.

1 - INTRODUCTION

Although aerogels have been known for decades, there is little reported information on the structure of these materials or on the chemical and physical factors that determine structure. This paucity of data results from the fact that standard methods for characterization of porosity, such as nitrogen adsorption and mercury porosimetry, do not provide quantitative insight into the structure particularly in the regime of fine porosity. Direct observation techniques, such as transmission electron microscopy, on the other hand, are compromised both by the insulating nature of the sample and the fact that three-dimensional (3-d) information is difficult to extract from 2-d projections or slices. Although scattering techniques provide averaged 3-d information, until recently these data have gone unanalyzed due to the absence of even a rudimentary model through which structural parameters might be extracted.

Fractal geometry /1/ provides a new perspective from which to view the structure of porous materials /2/. Fractal geometry allows one to distinguish between polymeric and colloidal objects, for example, since they fall into distinct classes called volume (or mass) fractals and surface fractals /3/. Volume fractals are chainlike polymers or networks, where the chain can equally be either material or void. Volume fractals are characterized by a fractal dimension D that can lie between 1 and 3. $D = 1$ corresponds to a linear (i. e. 1-d) object so porosity with $D = 1$ could signify either cylindrical pores or linear struts. The opposite extreme, $D = 3$, could signify either bubble or grain-like porosity. In general, there is a grain or strut-like analogue for every bubble-like morphology. Few techniques, including scattering techniques used here, can distinguish these analogues if they have the same D .

Surface fractals are uniformly dense (i. e. $D = 3$), but have rough surfaces characterized by a surface fractal dimension D_s that can vary between 2 and 3. If $D_s = 2$ the object is smooth like a conventional colloidal particle or bubble pore. In the other extreme, $D_s = 3$ means the pore surfaces are exceedingly rough.

Most physical models assume volume fractal porosity with $D = 1$ or 3. As shown below these extremes apply to no known aerogels, accounting for the need for the more general description afforded by fractal geometry.

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Fractals can be characterized by scattering techniques /4/. An incident beam (light, neutrons, or x-rays) impinges on a sample and the angular dependence of the scattered intensity is measured. For fractal objects, the intensity profile is always power-law when plotted versus the magnitude of the wavevector K ,

$$I \sim K^{-2D+D_s} \quad (1)$$

The quantity $P = -2D+D_s$ is called the Porod slope. Through Bragg's law, the parameter K can be related to a characteristic length L and the scattering angle θ ($K = 2\pi/L = 4\pi\lambda^{-1}\sin\theta/2$). By scanning θ , one effectively studies an object on different length scales determined by K^{-1} . Using a combination of light, x-ray, and neutron scattering, it is possible to probe scales between 1 Å and 1 μ.

It is usually possible to distinguish structures by the exponent in Eq. 1. Volume fractal porosity yields scattering curves with slopes between -1 and -3 corresponding to $P = -D = -D_s$. Smooth bubble pores give slopes of -4 as do their colloidal inverse, grains. Rough porosity corresponds to $P = -6 + D_s$, so slopes between -3 and -4 are expected.

In many cases it is possible to use fractal geometry to obtain greater insight into porosity than is available from the above rather general classification. In particular, fractal exponents, measured by scattering techniques, can be compared to those observed in computer simulations of polymerization processes /5/. In fact, the goal of this paper is to show that distinctly different structures are produced when silicon alkoxides are polymerized under different catalytic (pH) conditions. The premise is that structure can be traced to polymerization processes in the solution precursors. Although many factors can affect polymerization, pH is best understood and is the primary factor considered here.

Figure 1 is a schematic representation of the important reactions in silicate solutions /2,6/. Silica is essentially insoluble below pH = 8.5 (assuming alcohol solutions behave like aqueous solutions), so below this pH kinetic polymerization occurs far from equilibrium, exactly the regime where fractals are expected. In this kinetic regime, three classes of growth are postulated: Reaction-limited cluster-cluster growth (RLCA) under acidic conditions where polymerization is condensation-limited, and Eden growth (reaction-limited monomer-cluster aggregation) under basic conditions where growth is hydrolysis-limited. Near neutral conditions, polymerization seems best described as critical processes similar to percolation at threshold. Figure 1 is obviously highly schematic but follows the general framework outlined by Keefer /6/.

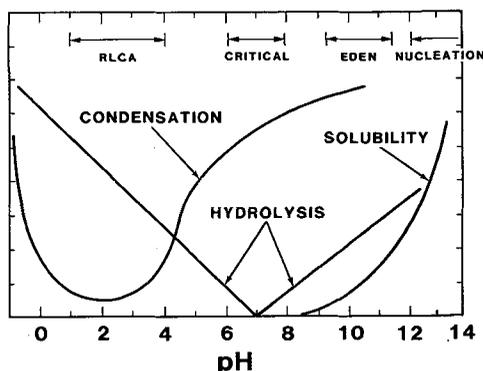


Fig. 1 - Schematic representation of the important reactions in silicate solutions. The ordinate is relative rate for the hydrolysis and condensation reactions but it is the saturation concentration for solubility.

Under exceedingly basic conditions silica is quite soluble so kinetic models, which are based on the assumption that Si-O-Si bonds do not dissociate, do not apply. In this regime, polymerization is adequately described by nucleation and growth, a thermodynamic model for phase separation near equilibrium. This model is adequately discussed in the literature /7/ particularly with regard to the production of Stöber silica colloids. Emphasis here, therefore, is on aerogels produced from the polymerization of alkoxides below pH = 12 in alcohol solution.

2 - BASE CATALYSIS

Most aerogels are produced by single-stage, base-catalyzed polymerization of TMOS or TEOS. The lower curve of Fig. 2, for example, shows the scattering curve /3/ for a commercial (Airglass, Staffanstorp, Sweden) TMOS aerogel produced at relatively high water silica ratio under base catalysis. The fact that the scattering curves approach slopes of -4 for a large K (corresponding to the short length scales) shows that the structures are uniformly dense and smooth below 20 Å. On longer length scales, a slope of -2 is observed, indicating network or volume fractal porosity.

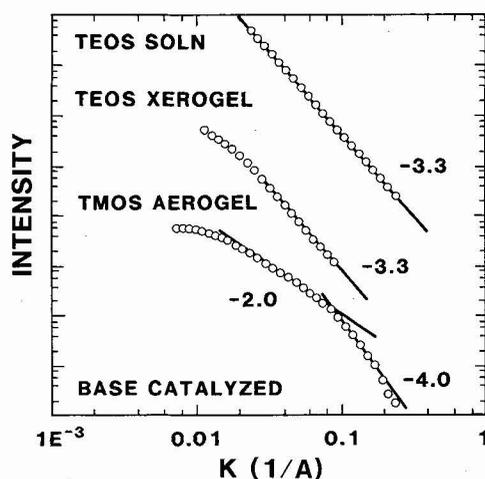


Fig. 2 - X-ray scattering profiles for base catalyzed silicates. The two upper curves demonstrate fractal roughness in both solution /6/ and xerogel /9/. The crossover in the lower curve /3/ from a slope of -2 to -4 is consistent with the structure postulated in Fig. 3.

Figure 3 shows the postulated structure of aerogels produced by base catalysis with aggressive hydrolysis: a network like structure of compact colloidal particles.

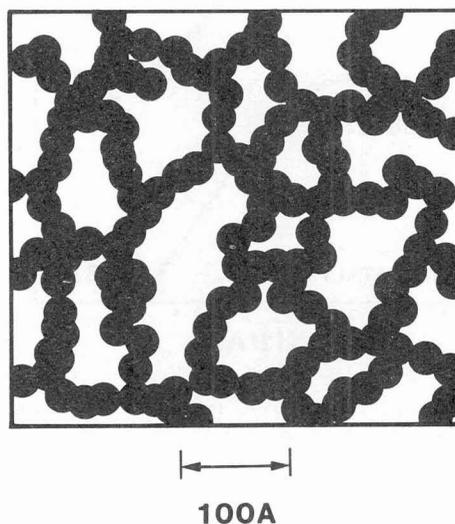


Fig. 3. Proposed structure for Aerogels produced under aggressive hydrolysis and base catalysis /3/.

Within the concept of reaction-limited kinetic growth, compact colloidal objects are expected when growth takes place by monomers adding to clusters (i. e. Eden growth). Although growth is almost certainly both kinetic and reaction-limited (as opposed to diffusion-limited) below $\text{pH} = 12$, the monomer-cluster (MC) condition appears to apply only under base-catalysis. Iler /8/ argues that the preferred condensation is between the most and least condensed species, a condition favoring MC reactions. Keith Keefe and I /9/, on the other hand, suggested that the preferred reaction mechanism (nucleophilic substitution /6/) favors MC processes. Finally, the fact that the polymerization is hydrolysis-limited (Fig. 1.) enhances MC polymerization since clusters will scavenge monomers as soon as they become activated by hydrolysis /2,5/.

The mapping on to the Eden growth model is reasonable only in the limit of fully hydrolyzed four functional monomers, as might be expected under strongly basic conditions in the presence of large amounts of water. As the water/silicon ratio W drops, hydrolysis is less probable, and the reacting species have unhydrolyzed or blocked sites that resist polymerization. In this regime, the growth process can be represented by a modification of the Eden model called the poisoned-Eden (PE) growth /9/. Although the basic Eden MC rules hold, some fraction of monomer sites are permanently blocked. Keefe's computer simulations show that the PE model produces rough colloidal particles /9,10/.

PE growth is expected under mild hydrolysis and base catalysis. The upper curves of Fig. 2, for example, show data for both a solution and its corresponding xerogel (air dried solution). The chemistry underlying these data favors milder hydrolysis (compared to the lower curve) through the use of: (1) TEOS rather than TMOS, (2) lower base concentration and (3) lower W . The observed slopes of -3.3 for both the solution and the xerogel indicate fractally rough porosity consistent with the packing of rough colloidal particles.

Eventually, of course, monomers will be exhausted and growth will be forced out of the MC regime in to the cluster-cluster (CC) regime /11/, otherwise gelation would not occur. Computer simulations of RLCA /12,13/, the CC analogue of Eden growth, give $D = 2.05 \pm .1$, consistent with the intermediate K regime in the lower curve of Fig. 2.

In summary, colloidal, or particulate aerogels with either rough or smooth surfaces are produced under base-catalyzed conditions. Particulate structures are favored because the reactions occur by MC processes. Depending on the aggressiveness of the hydrolysis, the resulting colloidal particles can have either rough or smooth surfaces.

3 - ACID CATALYSIS

Under acidic conditions, the rates of the hydrolysis and condensation are reversed. Now, reactive monomers are produced in a burst. Furthermore, there is no mechanistic argument favoring MC accretion. This situation leads to a classic realization of RLCA /2,5,11/. In solution, fractal dimensions close to 2 are observed (Fig. 4). For the corresponding aerogels, however, such low D 's, signifying high ramification, have not been observed, presumably because acid-catalyzed gels are highly polymeric down to molecular length scales. Brinker observed that these materials collapse even if critical point drying techniques are used /14,15/. The fact that aerogels cannot be successfully made from acid-catalyzed precursors is further evidence for the highly polymeric nature and low fractal dimension of the precursors.

Fig. 4 shows scattering data for an aerogel prepared by Brinker from an acid-catalyzed precursor /15/. The observed fractal dimension of 2.6 (compared to 2.1 in solution) is consistent with collapse of the polymeric network.

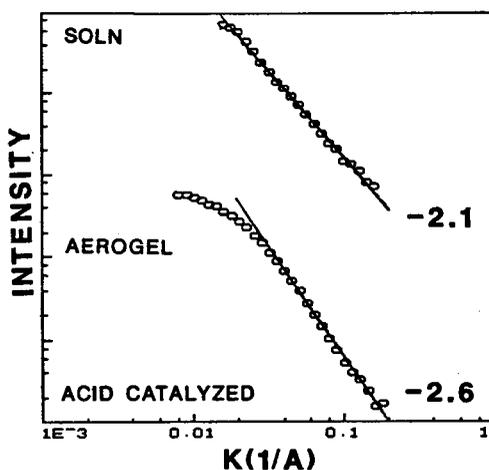


Fig. 4. Scattering profiles for acid catalyzed silicates /15/. The solution data are for TMOS with 10^{-3} M HCl. For TEOS Keefer /10/ observed the RLCA slope of -2 only at small K , suggesting an initial prejudice toward compact growth /11/.

4 - NEUTRAL AEROGELS

From Fig. 1, neutral polymerization corresponds to the extreme hydrolysis limit. Vacher, et al. /16/ showed that TMOS aerogels produced under neutral catalysis are polymeric (i. e. $D < 3$). Their data are reproduced in Fig. 5 and give a limiting slope of -2.7 . In an attempt to understand this observation, Al Hurd, Andrew Glines, and I studied the polymerization of silica under neutral conditions. In solution, we find fractal dimensions of 2.5, independent of the amount of water ($.5 \leq W \leq 4$) present in the system provided only that sufficient water is present to lead to gelation. It seems like the system settles on $D = 2.5$ regardless of the experimenter's attempts to change D by changing the water/silicon ratio W . Whereas under basic conditions the particles become more and more compact as W increases, there is no such effect in the extreme hydrolysis limit. This situation is reminiscent of the concept of self-organized criticality advanced by Bak, Tang and Wiesenfeld /17/.

Under neutral conditions, condensation reactions are fast, leading to immediate polymerization whenever an active, hydrolyzed site appears on a monomer or cluster. Clusters hibernate, awaiting activation by hydrolysis. The measured fractal dimension of 2.5, then, must represent the fractal dimension of the critical cluster which barely has enough active sites on its surface to allow continuous growth. Changing W changes the rate of growth but does not change the fundamental requirement that a certain level of branching is required. The system is self-limiting at the minimal level of branching required to sustain growth.

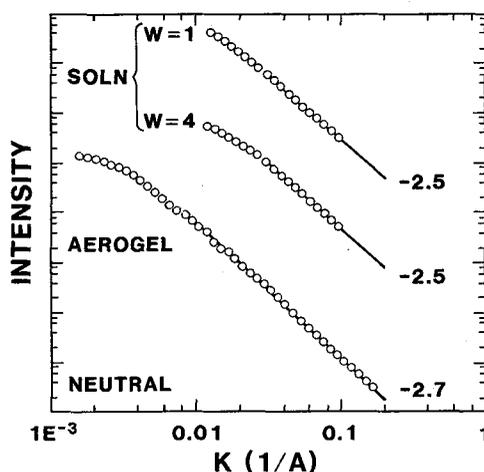


Fig. 5. Scattering profiles for neutral TMOS solutions /21,22/ and aerogel /16/.

Two models suggest that self-limiting growth requires a fractal dimension of 2.5. Alstrom /18/, modeled diffusion-limited aggregation (DLA) as a critical branching process in 2-d. His model, which does not allow circuits, gives a calculated $D = 1.6$, close to that observed in simulations of DLA in 2-d. From the DLA analogy, one expects $D = 2.5$ in a 3-d embedding space.

Alstrom's model does not allow circuits and cannot explain gelation. Critical branching with circuits is more closely related to percolation, a model in which clusters are produced by randomly occupying sites on a lattice. Although percolation /19/ is an equilibrium model not appropriate to kinetic growth, critical growth is very similar to Leath's algorithm for lattice filling /20/. In Leath's algorithm clusters are "grown" by starting from a seed site and randomly occupying sites neighboring the seed. Only a fraction P of sites are randomly selected. Further generations are similarly added on an ever increasing perimeter. If this algorithm is restricted to a single cluster, the cluster will always die (i.e. at some generation no perimeter sites are selected) if P is below the percolation threshold P_c . Above P_c , however, there is finite probability that every generation will survive so growth occasionally proceeds without limit.

If threshold percolation and critical growth are equivalent, then the growing clusters should have the topology and fractal dimension of the infinite percolation cluster ($D = 2.5$). If the fractal dimension is below 2.5, growth eventually ceases. If $D > 2.5$, growth is outside the hydrolysis limit and uniformly dense clusters corresponding to $P > P_c$ are expected (and observed /22/).

The above critical growth process might be described as kinetic percolation /21,22/. Kinetic percolation differs from normal percolation in that only threshold clusters is generated. All clusters are critical objects. Both MC and CC reactions are allowed just as the Leath algorithm can connect earlier generations to later generations. Finally, kinetic percolation generates a quasi-monodisperse distribution of cluster sizes in contrast to the strong power-law polydispersity of percolation. This difference accounts for the fact that the threshold cluster fractal dimension ($D = 2.5$) is observed rather than the ensemble averaged value ($D = 2.0$) expected in conventional percolation. Obviously, the mapping of critical growth to threshold percolation is speculative and needs to be tested by computer simulation.

5 - CONCLUSION

Depending on pH regime, at least four different models seem to be required to adequately explain observations on silicate solutions and aerogels. It seems, however, that these models may be part of a simpler, more general scheme that may eventually unify the present confusion. All of the structures discussed here (Eden clusters, PE clusters, critical clusters, RLCA's), for example, are found in ordinary percolation at different values of P . The problem is that percolation is an equilibrium model and the physics or chemistry relating percolation to kinetic growth over a wide pH range is absent. Perhaps the extensions of the idea of critical growth could provide the link. Outside the critical regime, it is reasonable that the other observed structures would arise. Below threshold, lattice animals with $D = 2$ are predicted in equilibrium percolation. It has been speculated that RLCA's are in fact lattice animals /11,23/. Above threshold, on the other hand, both compact clusters and rough clusters are found in percolation above threshold. In short, objects with all the observed fractal dimensions are found in percolation.

6 - ACKNOWLEDGMENT

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