

Genesis of a Metal Oxide Gel by the Sol-Gel Process: Evidence from Scanning Electron Microscopy

Saloua Rezgui[†] and Bruce C. Gates*

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

Received August 30, 1993. Revised Manuscript Received January 6, 1994*

Scanning electron microscopy (SEM) was used to characterize the products of sol-gel synthesis with $\text{Al}(\text{O}-s\text{-Bu})_3$ and $\text{Mg}(\text{OEt})_2$ in the presence of acetic acid and *sec*-butyl alcohol. Water was not included among the reactants, but it formed in the synthesis mixture. The gel formed slowly and was crystalline. The material was observed at various stages of the sol-gel process, as illustrated by a single SEM image of a region of the sample. The image shows a honeycomb structure (which is not well characterized) that is the intermediate. The image also shows small particles that are formed from the honeycomb structure and indicates their coalesce into larger particles, which constitute the gel product.

Introduction

During a sol-gel synthesis, the reacting mixture evolves from a sol, in which there are individual particles more or less weakly interacting with each other, to a gel, which in essence becomes a continuous molecule occupying the entire volume.¹⁻⁴ As the sol particles grow and collide, condensation occurs and macroparticles form. The change is gradual as more and more particles become connected to each other.¹⁻⁶

Our goal was to characterize the intermediates in the formation of metal oxides by sol-gel synthesis. To facilitate the characterization at various stages of completion of the process, we used a homogeneous mixture of metal alkoxides chosen to ensure a relatively slow sol-gel synthesis and structures that were stable for characterization by scanning electron microscopy (SEM). The idea was to freeze the sample in the configurations in which it was formed at different stages of the sol-gel process by rapidly evacuating the solvent and observing the particle growth by scanning electron microscopy. The synthesis was done with only little water present (the water was formed in situ from acetic acid),⁷ because the volatile constituents in the product could be removed by evacuation at rates that were high in comparison with the rate of the synthesis and the rate of removal of water.

Experimental Methods

Materials Preparations. Aluminum *sec*-butoxide, $\text{Al}(\text{O}-s\text{-Bu})_3$ (98%), magnesium ethoxide, $\text{Mg}(\text{OEt})_2$ (99.9%), *sec*-butyl alcohol, *s*-BuOH (99+%), and glacial acetic acid (99.99%) were supplied by Aldrich.

[†] Current address: Laboratoire de Chimie des Matériaux et de Catalyse Hétérogène, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, Tunis, 1060, Tunisia.

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid. State Chem.* 1988, 18, 259.

(2) Hench, L. L.; West, K. J. *Chem. Rev.* 1990, 90, 33.

(3) Brinker, C. G.; Scherer, G. W. *Sol-Gel Science*; Academic Press: New York, 1989.

(4) Turner, C. W. *Ceram. Bull.* 1991, 70, 1487.

(5) Grubisic-Gallot, Z.; Schosseler, F.; Lixon, P.; Cabane, B. *Macromolecules* 1992, 25, 3733.

(6) Martin, J. E.; Adolf, D. *Annu. Rev. Phys. Chem.* 1991, 42, 311.

(7) Rezgui, S.; Gates, B. C.; Burkett, S.; Davis, M. E. To be published.

A mixture of $\text{Al}(\text{O}-s\text{-Bu})_3$ and $\text{Mg}(\text{OEt})_2$ was added to *s*-BuOH so that the atomic ratio $\text{Al}/\text{Mg} = 4$ and $[\text{Al}(\text{O}-s\text{-Bu})_3] = 1 \text{ M}$. The mixture was brought to reflux and stirred for 24 h; a homogeneous solution formed. Then acetic acid was added so that the ratio $[\text{HOAc}]/[\text{Al}(\text{O}-s\text{-Bu})_3]$ was 3. The resultant mixture was allowed to stand at room temperature for approximately 24 h. During this time, a gelatinous precipitate formed, but the process was not allowed to proceed to completion. A liquid (about 10% of the total volume) was still present.

Characterization of Materials. SEM. A mixture of gelatinous precipitate and liquid, from the interface between the liquid and the gel, was removed with a spatula and spread onto double-sided tape covering an aluminum specimen stub for mounting of the SEM samples. The sample was rapidly evacuated at room temperature, and then a 300-Å layer of gold was sputter deposited onto the sample with a BioRad Microscience Division SEM sputter-coating system.

The SEM characterization was done with an ISI-DS 130 dual-stage scanning electron microscope. The filament voltage was 20 keV, and the beam current was 100 mA. The images recorded with the freshly prepared sample were indistinguishable from those recorded with the sample that had been stored in air for a week.

X-ray Diffraction. X-ray diffraction data characterizing the dried gel were obtained with a Philips model PW 1729 diffractometer by using $\text{Cu K}\alpha$ radiation.

Results

Preparation. During the first step of the preparation, a homogeneous solution was formed. Acetic acid reacted with this solution, and the product was a gelatinous precipitate. Characterization of the chemistry is to be reported elsewhere.⁷

Characterization of Materials. Scanning electron micrographs characterizing the material are shown in Figures 1-5. The material dried in an oven at 70 °C or evacuated under conditions similar to those of the SEM experiment showed the same X-ray diffraction pattern, indicating a crystalline material.

Discussion

Chemistry of Sol-Gel Synthesis. The chemistry of this preparation is described elsewhere,⁸ and a brief summary is given here. Under the conditions of the first step of this sol-gel synthesis, the mixture of metal alkoxides

(8) Rezgui, S.; Gates, B. C., to be published.

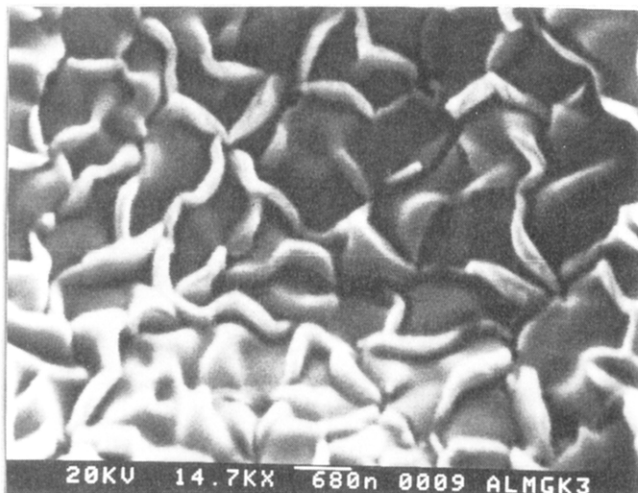


Figure 1. Scanning electron micrograph of mixed oxide of Al and Mg made by a sol-gel process. The image represents a part of the image in Figure 2. Similar images were observed for materials formed from the liquid in the pregenesis stage of the sol-gel process. This image shows a honeycomb structure similar to that of boehmite.

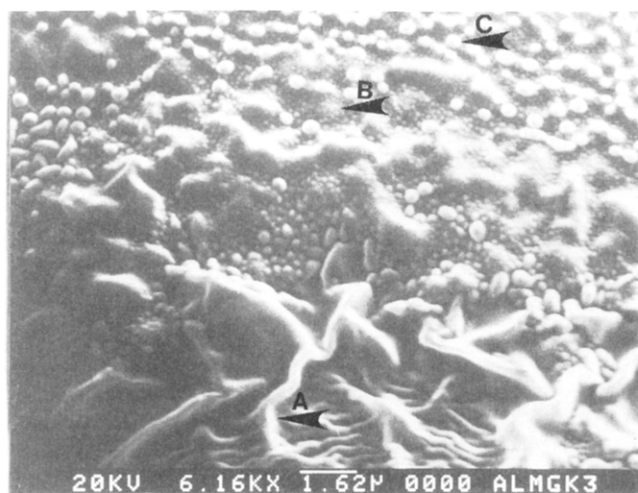
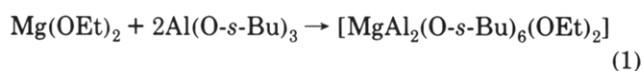


Figure 2. Scanning electron micrograph of mixed oxide of Al and Mg made by a sol-gel process. The image represents the interface between the liquid and the gel that had formed from the solution containing $\text{Al}(\text{O}-s\text{-Bu})_3$ and $\text{Mg}(\text{OEt})_2$ with acetic acid and the material formed as a result of evacuation of the liquid containing this mixture. The honeycomb structure evident in the lower part of the image is the same as that shown in Figure 1. The spherical particles evident in the upper part of the image are part of a gel. The intermediate region has some of the character of both of the regions mentioned above. This region is magnified in Figure 3.

reacts to give soluble aluminum-magnesium alkoxide complexes, as shown by Rai and Mehrotra:⁹



This structure does not account for all the aluminum present in the reaction mixture, and we infer that other aluminum-containing species were also present, including the aluminum alkoxide itself. When acetic acid was added to the homogeneous solution of the alkoxide mixture, some of the O-s-Bu and OEt ligands were replaced by OCOCH_3 ligands to give species such as, for example, $[\text{MgAl}_2(\text{O}-$

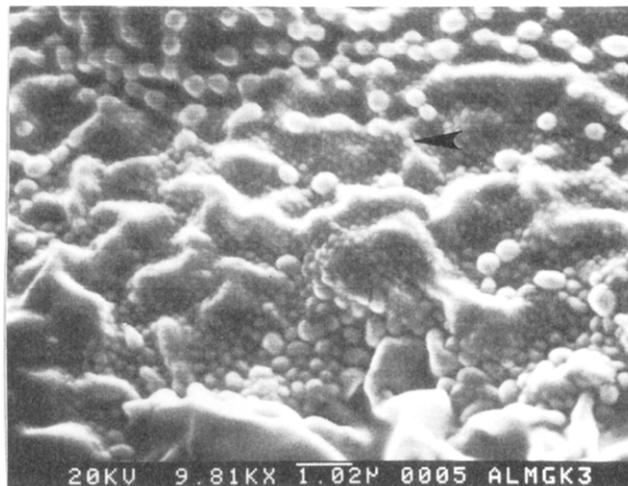


Figure 3. Scanning electron micrograph showing evidence of the genesis of the spherical particles constituting the gel. In this intermediate region of the solid, which is shown in Figure 2 and magnified here, both of the morphologies shown in Figure 2 are evident. The smallest spherical particles emerge from the honeycomb and become larger and separated from the honeycomb. The spherical particles grow at the expense of the honeycomb. This image is a demonstration of the mechanism of formation of the gel, which is composed of nearly homogeneous particles.

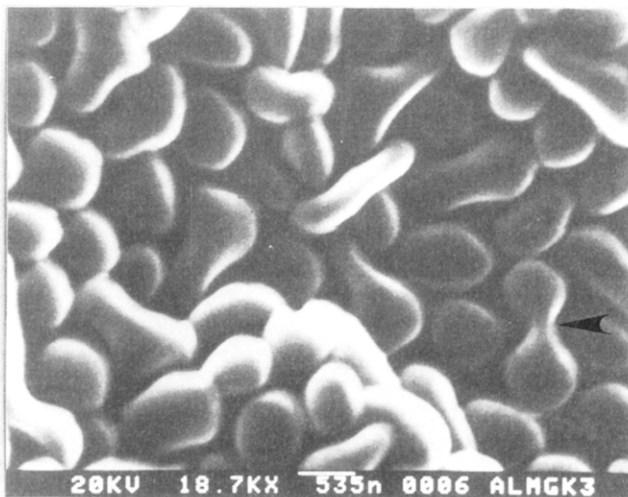
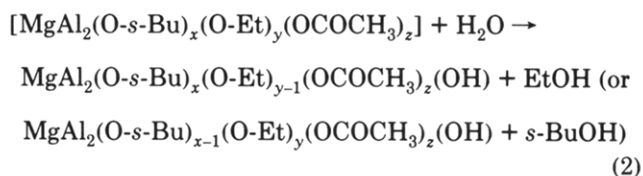


Figure 4. Scanning electron micrograph showing the gel in the final stage of formation. The particulate structure shown here is more fully developed than that shown in Figure 3.

$s\text{-Bu})_x(\text{OEt})_y(\text{OCOCH}_3)_z]$, where $x + y + z = 8$. Other, related species are expected to have formed with the aluminum alkoxide, giving a mixture of metal alkoxide complexes with acetate ligands.

Water is produced by alcohol dehydration, which is catalyzed by the acetic acid.^{7,8} Water then precipitates in hydrolysis reactions that give ethanol and butanol, but water does not replace acetate ligands, as shown by results to be reported separately.^{7,8} We infer that water reacted with OR groups but not with acetate.^{7,8}

The hydrolysis reaction of a typical bimetallic species is represented schematically as follows:



(9) Rai, J.; Mehrotra, R. C. *J. Non-Cryst. Solids*. 1993, 152, 118.

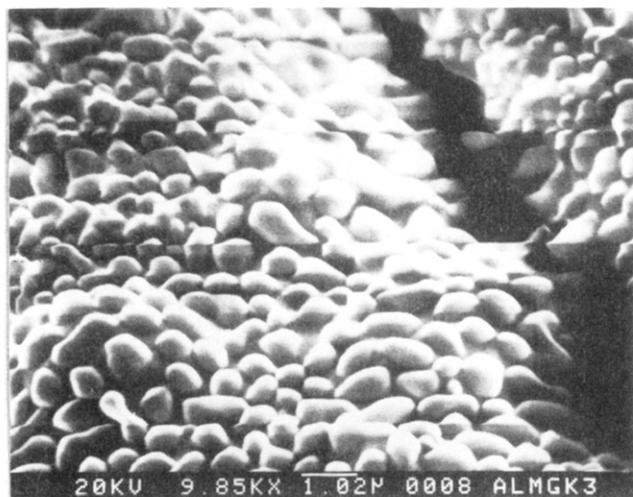
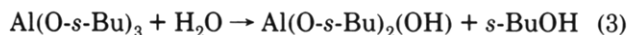


Figure 5. Structure of Figure 4 shown at a lower magnification to illustrate the homogeneity of the gel.

Similarly, the hydrolysis reaction of a typical aluminum-containing species, which would be expected to take place simultaneously, is represented as follows:



The species formed in eqs 2 and 3 undergo condensation. The kinetics of the whole process is mainly dependent on the kinetics of water formation, which results from alcohol dehydration and condensation reactions that occur as water is produced in the medium.^{7,8} Since our experiments were done with an excess of aluminum species, we postulate, building on this interpretation of the heterocoagulation process, that material grows outward from the inner core containing the bimetallic species as aluminum-containing species envelope the core by undergoing condensation, much as in a sol-gel synthesis involving only aluminum alkoxide and acetic acid in alcohol.⁷ Thus the gel microparticles are envisioned to grow outward from the bimetallic core, consuming the unconverted aluminum reactant, and the resultant material has a crystalline structure.

SEM Evidence of the Sol-Gel Process. Generally, in sol-gel synthesis, which takes place by a combination of hydrolysis and condensation reactions, polymeric material is formed from colloids. The gel formed in this kind of process typically consists of agglomerates of microscopic particles. The intermediate materials from which these particles are formed are for the most part not observable. What is remarkable about the SEM results of this work is that they provide evidence of structures from which the particles evidently grow because the gel formed is crystalline and therefore hardly affected by the experimental conditions and because the process is slow, allowing observation of the material at various stages of its preparation.

The SEM image of Figure 1 depicts a uniform honeycomb structure. The images of Figures 2 and 3 include the honeycomb structure and also spherical particles that are characteristic of a gel. The intermediate region shown in Figure 2 (and with a greater magnification in Figure 3) gives striking evidence of the emergence of very small and uniform particles from the honeycomb structure. For example, the regions marked with the arrows in Figure 3 show where the genesis of particles was occurring; the

honeycomb material was in the process of transformation into the particles in this part of the sample.

Furthermore, the growth of the particles is evident in Figures 2 and 3. The gradient in particle size is evidence of this growth, which may be an indication of coalescence of the particles. An image suggesting the coalescence of two particles is marked with an arrow in Figure 4. The condensation may be viewed as a surface reaction of two particles, whereby the splitting out of the condensation products (water or alcohol, for example) is accompanied by a bonding of the particles through creation of the network of polymer.

An image of larger particles is given in Figure 5; these are nearly uniform in size. The particles in this image are the largest that were observed in the sample. Thus, this region of the sample represents the final sol-gel product in these experiments.

Figure 1 is an image that is a magnified region of Figure 2, but no particles are evident. The honeycomb texture shown here was also observed in separate experiments to have formed from the liquid present over the gelatinous precipitate when the sample was evacuated under the same conditions used for the intermediate phase between the liquid and the gel. Thus we conclude that this region represents the sol-gel product at an early stage, which we call the pregenesis stage, i.e., that preceding the formation of the gel.

The exact nature of the material depicted in Figure 1 remains to be determined. We suggest the following interpretation:

Usually in gels formed from metal alkoxide, the hydrolysis reaction is very rapid and is completed at an early stage of sol preparation, especially when the sol formation is acid catalyzed. In our case, however, the liquid phase contains the species formed just before the condensation steps, namely, the alkoxide precursors $\text{Al(O-}i\text{-Bu)}_3$, $[\text{MgAl}_2(\text{O-}i\text{-Bu)}_6(\text{OEt})_2]$, the metal alkoxide complexes with acetate ligands such as $[\text{MgAl}_2(\text{O-}i\text{-Bu)}_x(\text{OEt})_y(\text{OCOCH}_3)_z]$, or $[\text{Al(O-}i\text{-Bu)}_{3-x}(\text{OCOCH}_3)_x]$ and the products of the hydrolysis reactions described in eqs 2 and 3. All these species are present in solution with $i\text{-BuOH}$, and, as a consequence of the chemistry, some water, as well as acetic acid, is also present in the medium. Acetic acid, water, and $i\text{-BuOH}$ form hydrogen bonds with all these precondensation species, in particular with the products of hydrolysis (MOH species), and the hydrogen bonds help to hold the molecules present in the sol stage together before condensation occurs. As the solvent evaporates, the solid network is drawn together to give a honeycomb structure, as shown in Figure 1. Formation of new bonds occurs as a result of condensation reactions, which increases the number of bridging bonds and causes a contraction of the sol to a gellike network. Since the evaporation of the solvent is fast, the final material does not have the same structure as that of the gel that has the time to grow and form an organized structure; thus we infer that this part of the material is affected by the removal of the solvent by evaporation (outgassing).

At a subsequent stage of the sol-gel process, the products of the hydrolysis will condense to give crystalline particles. Different sizes of the polymer particles were formed as the gelification occurred at different stages of the polycondensation process, as shown in Figures 2 and 3. The gel structure is formed of different units, e.g., primary particles about 100 nm in diameter (Figures 2 and 3), which

agglomerate to give secondary particles about 200 nm in diameter (Figures 2 and 3). Gelation is virtually complete when the secondary particles are linked to each other, forming large particles about 500 nm in diameter (Figures 4 and 5). Particles such as those observed in Figures 4 and 5 are also observed for the gelatinous precipitate when gelation is completed. We infer that the outgassing in this case does not affect the structure of the material because the particles are crystalline.

In summary, Figure 2 represents in a single image several stages of the sol-gel process. The honeycomb structure

(arrow A) is the intermediate from which the smallest particles are formed (arrow B), and these coalesce into larger particles (arrow C), which ultimately constitute the gel product. Thus several stages of the sol-gel process are illustrated by one region of the sample, which must have been near the gel-liquid interface in the sample prior to evacuation to remove the liquid.

Acknowledgment. S.R. was supported by a Fulbright Fellowship sponsored by AMIDEAST and was on leave from Faculté des Sciences de Bizerte, Tunisia.