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Alumina gels that form porous transparent Al_2O_3

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Formation of a porous transparent Al_2O_3 from aluminium alkoxides has been previously reported. During the process, alkoxides are hydrolyzed and the resultant hydroxide is peptized to a clear sol. The sol then must be gelled and pyrolyzed to 500° C to obtain the aluminium oxide. This paper discusses the gel state and the requirements for the system to retain its integrity during the drying and pyrolysis.

Influence of electrolytes on the sol–gel transformation shows that there is a critical electrolyte concentration at which the gelling volume goes through a pronounced minimum. Deviation in either direction of this electrolyte concentration causes a sharp increase in the relative gelling volume and detrimentally effects the capability of the gel to retain its integrity. The sols that gel at concentrations less than ~4 g equivalent oxide per 100 ml do not retain their integrity during pyrolysis.

1. Introduction

Recently there has been considerable interest in studying metal organic-derived ceramics such as alumina. Formation of a ~64% porous yet transparent alumina from alkoxides has been reported [1].

Aluminium triethyl, $Al(C_2H_5)_3$, and aluminium isopropoxate, $Al(OC_3H_7)_3$, have often been used to prepare high purity alumina gels [2–6]. These gels are considered amorphous and are composed of small spherical particles which are chemically in very close association with water. Dehydration of such gels usually produces amorphous aluminas of small particle size and large surface area.

Aluminium alkoxide, $Al(OR)_3$, is readily hydrolyzed by water, producing aluminum mono- or tri-hydroxides [7]. Only the mono-hydroxide thus formed can be peptized to a clear sol; and when certain conditions are met the gel of this particular sol yeilds monolithic Al_2O_3 when pyrolyzed [8].

The first requirement for the formation of a gel is sufficient concentration of the sol. As the sol is concentrated the colloidal particle movement passes from a transitory to an oscillatory one and later ceases to be evident – a state where the sol has set to a gel. In some cases, electrolyte addition, hydration, and ageing also result in gel formation without the necessity for evaporation. The results presented here apply to unaged sols.

The sol–gel transition proceeds without any discontinuity in properties. Nevertheless, the viscosity of the system changes strikingly in such a short period of time and is often used as the sign of gelling. For instance, during boiling of the sol the bubbles will suddenly freeze and cease to ascend. Lewites took the time of solidification as the point where the sol is viscous enough not to flow out of an inverted test tube [9].

2. Results and discussion

2.1. Influence of electrolytes upon sol–gel transformation

The influence of electrolytes upon the sol–gel transformation must be sharply differentiated from their peptizing effect [8]. Quite apart from the fact that a minimum critical amount of certain acid electrolytes, e.g. HNO_3, HCl, is needed to peptize the hydroxide to a clear sol, the amount of electrolyte present in the sol determines the gelling point of the system as well as various properties of the oxide resulted from this gel.

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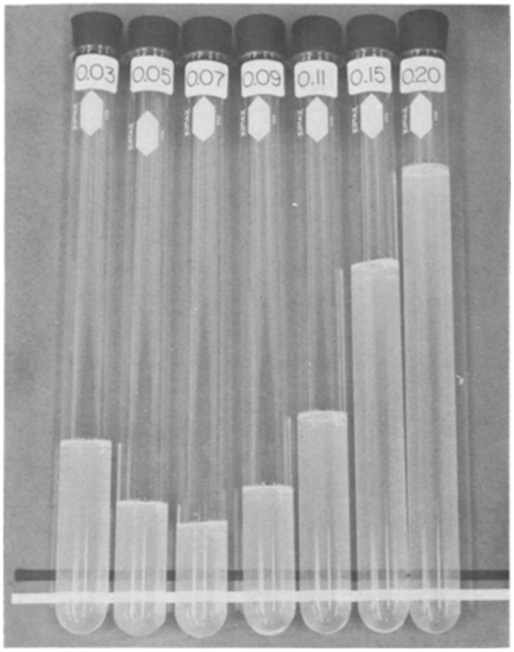

Figure 1 Effect of acid concentration on gelling point of sol.

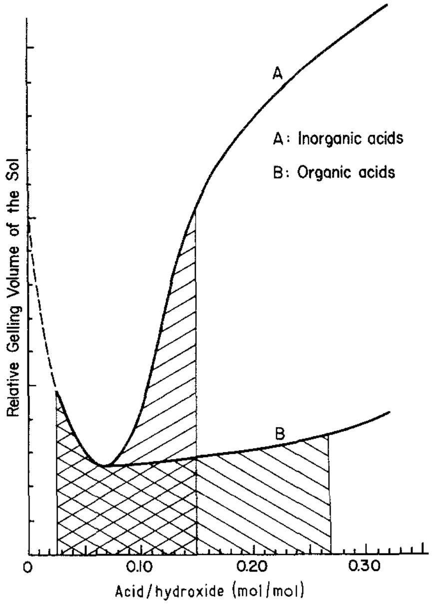

Figure 2 Range of gels yielding coherent transparent aluminimum oxide (shaded areas; above 0.1 mol inorganic, and 0.2 mol organic acids, the coherence is limited to films).

Fig. 1 shows the gelling volume of a sol containing different amounts of electrolytes. Initially a clear sol containing 5 g equivalent Al_2O_3 [or $\sim$6 g AlO(OH)] per 100 ml was prepared from 1.0 mol $Al(OC_4H_9)_3$ and 0.03 mol HNO_3. Seven 120 ml portions of this sol, each containing 6 g equivalent Al_2O_3, were taken and additional HNO_3 acid was added so that the samples contained a total of 0.03, 0.05, 0.07, 0.09, 0.11, 0.15 and 0.20 mol acid per mole hydroxide. Then these samples were boiled to the gelling point. As it is seen from Fig. 2 the gelling volume goes through a minimum when the acid concentration is about 0.07 mol per mol hydroxide. At the point where the minimum gelling volume occurs and equivalent Al_2O_3 concentration of about 25 g per 100 ml is attained, whereas the same sol will gel at concentrations as low as 2 to 3 g of equivalent alumina with higher electrolyte concentrations. This phenomenon holds true when any strong electrolyte, e.g. HCl, is used.

The initial decrease in the gelling volume is is caused by the effect of the acids on the electrical charge of the particles. As the acid is introduced, positively charged micella strongly absorbs anions of the acids and shifts towards a more neutral state, thus the interparticle repulsion is decreased. This makes it possible for the particles to approach each other closer and reduction in the gelling volume occurs. The increase of the gelling volume above 0.07 mol per mol hydroxide is due to electrolyte effect of the acids that can be induced even by neutral electrolytes. For instance, when NaCl was introduced into the sol as in the experiment explained above its effect on the gelling volume was the same as that of HCl or HNO_3 acid shown in Fig. 1. Exposure to ammonia or ammonia vapour will also cause precipitous gelling of these sols.

Organic acids such as acetic, even though they initially reduce the gelling volume, do not cause a subsequent sharp increase in the gelling volume since they are weak electrolytes, see Fig. 2.

2.2. Behaviour of the gel

At the gelling point the equivalent Al_2O_3 content of the system can be 4 to 25% by weight, depending on the electrolyte concentration. As a result, considerable shrinkage in size must necessarily occur during drying if the coherence is to be retained. Drying occurs in two stages: first, the gel shrinks to its final size of about 35 to 65% of the original dimensions (depending on electrolyte concentration), remaining transparent and non-porous; and, second, the gel is too rigid for further shrinkage to occur and begins to lose liquid internally with the formation of porosity. The gel loses 23% of its weight and becomes opaque during this second stage. However, after drying is complete transparency returns.

Rheology studies of the precursor gels indicate an almost ideal pseudoplastic behaviour. Shear-stress dependency of viscosity with a pseudoplastic constant of almost one has been measured for a gel prepared by hydrolyzing 1 mol $Al(OPr^i)_3$ with 100 mol H_2O at 75° C, peptizing with 0.1 mol acetic acid and concentrating to about 37 wt % equivalent alumina, see Fig. 3. It was found that these gels can be extruded quite easily when brought to the correct consistency. Tubes and rods as small as 0.2 mm in diameter were successfully extruded.

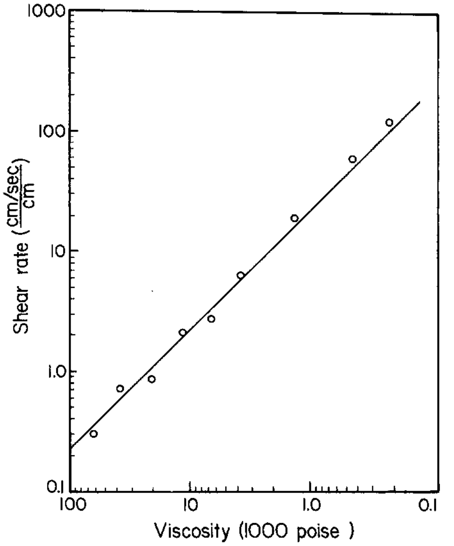

Figure 3 Shear-viscosity relation of a gel prepared by acetic acid and concentrated to about 37 wt % equivalent Al_2O_3.

2.3. Pyrolysis

The chemical composition of dried gels closely corresponds to that of aluminium monohydroxide, AlO(OH), and therefore contains approximately 82 to 85 wt % equivalent of alumina. The material is more than 60% porous at this point. X-ray diffraction gives a wide, low intensity, delta aluminium oxide hydrate pattern. A more amorphous material is obtained if cold water is used during the initial hydrolysis of the alkoxides [7].

The capability of the gel to retain its integrity during the drying and firing may be due to the presence of a small amount of dissolved material in the sol [7]. When the sol is concentrated and gelled the dissolved material will condense and cement the colloidal particles together, giving a coherent body. Since the solid and dissolved parts have the same chemical composition, the granular nature of the structure diminishes during the firing, giving rise to a continuous phase. The ability of the system to stay coherent is optimized at 0.07 mol acid per mol of hydroxide, i.e. at the minimum gelling volume, and becomes restricted to films towards the higher limits of acid range, see Fig. 2.

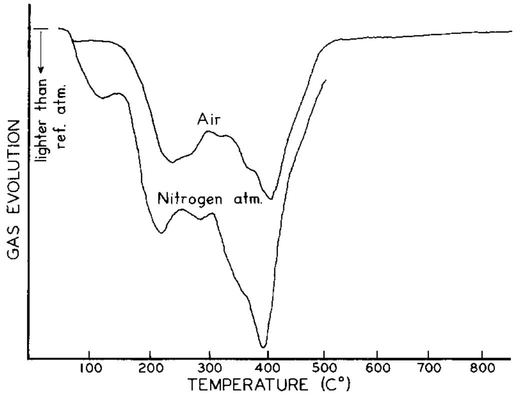

Figure 4 EGA curves during the pyrolysis in air and nitrogen with heating rate 10° C min^{-1}.

Fig. 4 shows evolved gas analysis curves of gel samples heated in nitrogen and air at the rate of 10° C min^{-1}. The gas (or mixture of gases) released has a density less than air, and gas release is completed by about 500° C. Oxygen from the atmosphere is apparently not required for pyrolysis since both curves are similar. When gel samples are heated in vacuum, pyrolysis shifts to slightly lower temperatures.

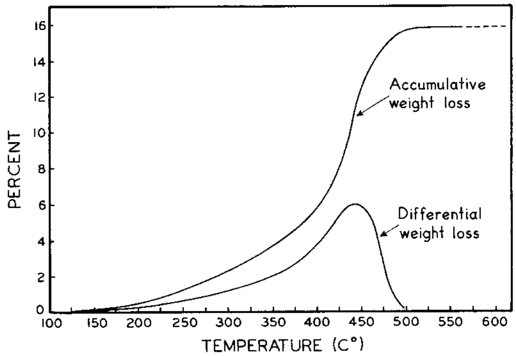

Figure 5 Weight loss during the pyrolysis with heating rate 10° C min^{-1}

The thermogravimetry curve shown in Fig. 5 also indicates essentially complete pyrolysis at about 500° C (note that these two curves are considerably different than those generated by either hydrates of alumina, or combinations of both).

A total weight loss of about 16% occurs between 150 to 500° C (loss below 150° C is insignificant). Most of this loss takes place between 375 and 475° C. The evolving gases are essentially water with small amounts of organics. It is in this range that extreme care must be taken to prevent fracture. Even at a heating rate of 2° C h^{-1} some fracturing may occur in large gels. Good uniformity of the furnace temperature is required without too much fluctuation. Coatings, films, and thin tubings show very little tendency to crack.

A heating schedule, which is inversely proportional to the rate of gas release, appears to work reasonably well. Nevertheless, if cracking is to be totally prevented, a thorough study of various heating schedules along with the uniformity of the gel and stresses formed during casting are needed. At the end of the heat-treatment a monolithic transparent active Al_2O_3 having some unique pore morphology results [1].

2.4. Effect of electrolytes on pore morphology

The pH measurements of the sol do not show a discontinuity at 0.07 mol acid concentration. However, the pore morphology of the resultant alumina reflects the optimizing effect of the acid–electrolyte interaction. Fig. 6 shows the pore volume and surface areas as a function of acid (electrolyte) concentration for the samples shown in Fig. 1. The gels were dried and fired to 600° C, and the surface area, pore volume and pore size distribution of the resultant alumina were tested by BET method. The pore volume goes through a maximum of 0.43 $cm^3\,g^{-1}$ (63 vol %) at about 0.07 mol acid per mole of hydrate whereas surface area decreases from 220 $m^2\,g^{-1}$ down to 160 $m^2\,g^{-1}$ as acid content increases. Fig. 7 shows that even though the poer radius with most volume (r_m) is somewhat larger at the 0.07 m acid concentrations the pore size distribution is most acute at this point.

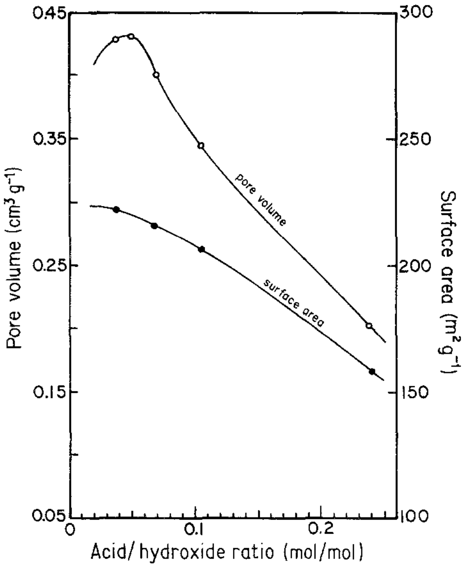

Figure 6 Effect of acid concentration of sol on pore volume and surface area of resultant Al_2O_3 fired at 600° C for 24 h.

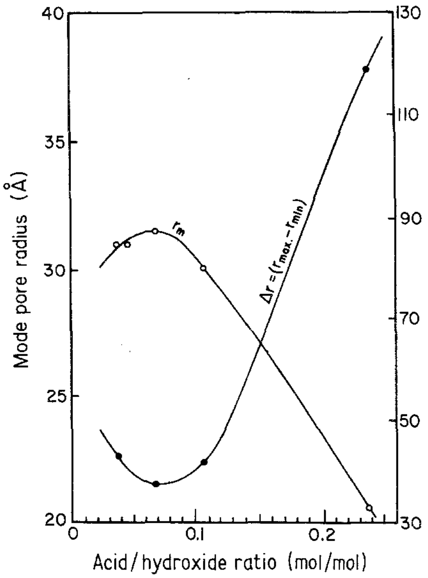

Figure 7 Effect of acid concentration of sol on mode pore radius (r_m) and pore size variation (Δr) of the resultant material fired at 600° C for 24 h.

It has also been found that non-electrolytes also influence the gelling point and pore morphology of the resultant alumina. According to Traube and Kohler capillary-inactive substances accelerate gel formation while capillary-active inhibit it [10]. We have found that replacing water by glycerin or glycols as dispersion medium (by adding the latter into the sol, then boiling the water off) causes gelling at lower concentrations of hydroxide, and the effective pore size of the resultant oxide is generally larger. On the other hand, partial replacement of water by an alcohol in the initial sol (by evaporating the water to the gelling point, then adding alcohol) results in smaller pore size (see Table I).

Characterization of resultant aluminium oxide along with its various properties is presented in another paper [1].

3. Conclusions

(1) A transparent monolithic active aluminium

TABLE I Effect of sol dispersion medium on the pore morphology of resultant alumina*

Dispersion medium	Average pore radius (Å)	Total pore volume (ml g^{-1})	Surface area (m^2 g^{-1})
Methyl alcohol	47	0.27	230
Ethyl alcohol	50	0.37	294
Water	55	0.57	423
Propylene glycol	71	0.52	293
Triethylene glycol	96	0.82	367

* Fired at 600° C

oxide can be produced from a clear sol obtained from aluminium alkoxides by a gel process. Relative gelling volume of the sol goes through a minimum at electrolyte concentration of about 0.07 mol per mol hydroxide. At this electrolyte concentration sol–gel transformation occurs at around 25% equivalent Al_2O_3. Deviation of electrolyte concentration in either direction causes a sharp increase in the gelling volume. Sols gelling at concentrations less than 4 g equivalent Al_2O_3 per 100 ml do not retain their integrity.

(2) The pore size distribution. transparency of the resultant aluminium oxide are also optimized at this electrolyte concentration.

(3) When brought to the correct consistency the gel can be extruded or handled in classical ceramic-forming methods. If the gel is in the form of film or coating less than 20 μm thick it retains its original size in two dimensions and shrinks only in the direction of thickness during drying.

(4) The gel shows a viscosity-shear rate dependency having a slope almost equal to one, corresponding to an ideal pseudoplastic material.

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