Preparation of Mullite Dispersed Silica Ceramics through Sol-Gel Processing

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SYNOPSIS

Mullite-dispersed silica ceramics were prepared through sol-gel processing by the use of tetraethoxy silane, aluminium nitrate and aluminium isopropoxide as the Si and Al sources where HCl and HNO_3 were the catalyst. Effect of the starting materials, solvents and catalysts was examined on the gelation time or temperature of mullite precipitation. Apparent activation energy of gelation ranged from 80 to 95kJ/mol. The presence of Al in the sols elongated the gelling time suggesting the formation of chelate bonds between Al and Si-OR or Si-OH bonds.

1. INTRODUCTION

Glass and ceramics are conventionally prepared by melting or sintering the starting materials at high temperatures. However, homogeneous glass cannot result when the melts experience phase separation[1] or the system is so refractory that the batch melts only at very high temperatures; ceramics will neither be obtained when they consist of crystalline phases that are unstable or decomposed near the sintering temperatures. Sol-gel processing is advantageous because the glass or ceramics that cannot be available via the conventional methods are obtained at lower firing temperatures by the use of solutions in which atomic level homogeneity is kept during preparation.[2] In this process hydrolysis and condensation reactions of organic and inorganic compounds takes place in the starting solutions resulting in gels that can be calcined to ceramic materials. Suppose gelation proceeds in a homogeneous mixture (a sol) of a component easy to become gelled and metallic ions that form highly ionic metal-oxygen bonds. The former component will construct a gel network, whose voids are occupied by the metal ions.

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The former component will construct a gel network, whose voids are occupied by the metal ions. The metal ions are held in the gel without being squeezed out by syneresis as gelling proceeds if they are strongly bonded to the gel matrix component. Subsequent proper heat treatment of the gel will lead to glass or glass ceramics in which ionic microcrystallites are homogeneously dispersed. Moreover, the control of the microcrystalline phase and their size or shape enables the preparation of multi-functional ceramic materials that have high thermal stability or strength. For example, refractory coatings and fibers of high chemical or thermal resistivity are thus prepared.[3] New such materials can be developed only with basic understanding of the sol-gel process. In the present work we have prepared silica ceramics dispersed with mullite particles, and studied the effects of the factors such as the raw materials, gelation temperature, solvent, and catalyst on the rate of gelation, microstructure of the obtained gels and thermal stability of the xerogels.
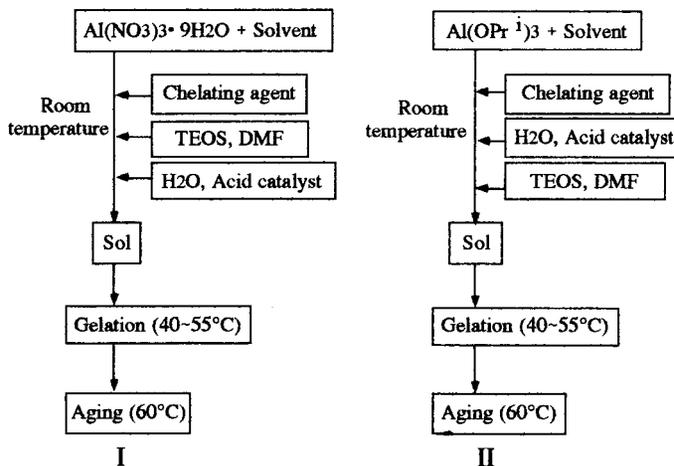
Fig. 1. Procedure I and II of preparing precursor gels.

2. EXPERIMENTAL

Aluminium nitrate ennea-hydrate $(Al(NO_3)_3•9H_2O)$ and aluminium isopropoxide $(Al(OPr^i)_3)$ were the sources of aluminium while tetraethoxy silane (TEOS, $Si(OEt)_4$) was that of silicon where Pr^i and Et denote $CH(CH_3)_2$ and C_2H_5, respectively. At mixing the raw materials in preliminary experiments aluminium hydroxide was precipitated and the sol became opaque. With 0.8 to 1.4 mol of H_2O_2 or acetyl acetone (acac-H) per Al the solutions were found stabilized. In the following, therefore, 1 mol H_2O_2 or acac-H per Al was added to the starting solutions. Chelates were probably formed between those additives and Al atoms. In order to find optimum conditions under which least pieces of cracks were produced in the gels after drying at 60°C, precursor gels were prepared under various conditions. The starting solutions also contained N,N-dimethyl formamide (DMF) as a drying control chemical agent (DCCA[4]) which gave gels of better quality.

Fig. 1 indicates the experimental procedure. The mixing ratios of the raw materials, solvents and additives were tabulated in Table 1. In a few experiments Al solutions were added to a TEOS solution after the hydrolysis of TEOS proceeded to some extent.[6] In the present study, however, the starting solutions were prepared by mixing solutions of the Al sources with TEOS.[7,8,9,10] $Al(OPr^i)_3$ could be dissolved in alcohols with the addition of acid. The sols were subject to gelation at 40 to 50°C and the gels were subsequently aged at 60°C for 24h. Thus obtained precursor gels were heated from the room temperature to 1300°C at a rate of 1°C/min. In the course of the treatment, they were held at 200, 400 and 600°C for 50h.

Table 1. (a) Starting materials and mixing ratios, and (b) cracking state of the xerogels

(a) Starting materials

Raw materials	Solvent	Chelating agent	Acid catalyst
$Al(NO_3)_3 \cdot 9H_2O$ $Al(OPr^i)_3$ TEOS $(Si(OEt)_4)$	Alcohols (ROH) R=Me, Et, n-Pr, i-Pr, n-Bu, n-Pen	Acetyl acetone (acac-H) H_2O_2	HCl, HNO_3, H_2SO_4 HCOOH (0.01, 0.1, 1, 5N)

Me: CH_3; Et: C_2H_5; n-Pr: C_3H_7; i-Pr: $CH(CH_3)_2$; n-Bu: C_4H_9; n-Pen: C_5H_{11}

(b) Cracking state of xerogels and optimum combination of the materials

Al source	Solvent	Cracking state*	Chelating agent	Acid, $H_2O/(Al+Si)$	ROH/ $H_2O/(Al+Si)$	DMF/ $H_2O/(Al+Si)$
$Al(NO_3)_3$ Procedure I	MeOH EtOH n-PrOH i-PrOH n-BuOH n-PenOH	⊙ ⊙ ⊙ ⊙ ⊙ △	H_2O_2	HCl (1N) HNO_3 (0.01N) 10	2	1
$Al(OPr^i)_3$ Procedure II	MeOH EtOH n-PrOH i-PrOH n-BuOH n-PenOH	△ △ ⊙ △ ⊙ △	acac-H	HCl (5N) HNO_3 (5N) 10	2	1

* Cracking state of xerogels dried at 60°C

⊙: No cracks; O: few cracks; △: cracked

3. RESULTS

3.1 Aged Gels and Additives

Table 1 (b) indicates correlation of the cracked state of the gels with combinations of the solvents or additives. The symbol O indicates the optimum combinations that gave crack-free dried gels. Better gels resulted from the iso-propyl alcohol solutions of aluminium nitrate and H_2O_2 as well as the n-butyl alcohol solutions of $Al(OPr^i)_3$ and acetyl acetone. Hydrochloric acid and nitric acid were appropriate for the acid catalyst for the present systems though the $Al(OPr^i)_3$ systems required more concentrated acid solutions for stable sols. Not only the pH of

Table 2. Gelation time and apparent activation energy

Starting Solutions	Acid:H_2O {pH}*	Gelation time, t_{gel} (h)**				Activation energy (kJ/mol)
		Gelling temperature (°C)				(ln t_0)***
		40	45	50	55	
Al(NO$_3$)$_3$	HCl (1N) {1.66}	60	38.3	24	14.6	80.0
(Proced. I)						(-26.8)
H$_2$O$_2$	HNO$_3$ (0.01N)	65	33.3	19	12.3	95.0
i-PrOH	{1.15}					(-32.4)
Al(OPr^i)$_3$	HCl (5N) {1.03}	45	24.7	18	8.8	89.0
(Proced. II)						(-30.4)
acac-H	HNO$_3$ (5N) {0.50}	43	20.75	16.25	7.3	95.0
n-BuOH						(-32.8)
TEOS•4H$_2$O•	HCl					55.4
4EtOH•HX [11]	HF					61.2
0.1Al(NO$_3$)$_3$•						
0.95TEOS•	No acid catalyst					89.2
6H$_2$O•4EtOH [7]						

{pH}*: initial pH of the starting solution.

** and ***: ln t_{gel} = ln t_0 + ΔH/RT   (eq. 1)
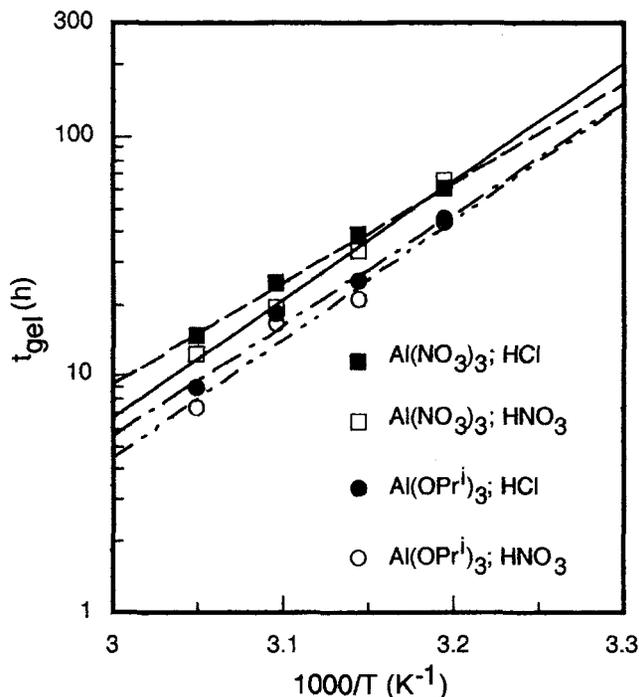
Fig. 2. Arrhenius type plots of gelation time (t_{gel}) as a function of gelling temperature.
The frequency factor and apparent activation energy are indicated in the rightmost column of Table 2.

the starting solutions for the optimum combinations but the gelation time are indicated in Table 2. Either sols from aluminium nitrate or $Al(OPr^i)_3$ became gels in 10~15h and 8~9h, respectively.

3.2 Apparent Activation Energy for Gelation

Fig. 2 represent the plots of the gelation time (t_{gel}) under the optimum conditions as a function of temperature. Table 2 shows the apparent activation energy for gelation ΔH after an Arrhenius type equation (1).

$$t_{gel} = t_o \exp (\Delta H/RT) \qquad (1)$$

The gelation time was shorter for the $Al(OPr^i)_3$ systems under any acid catalyst, and the nitric acid catalysis shortened the gelation time. The activation energy for an aluminium source was smaller for the HCl catalysis while the $Al(OPr^i)_3$ system gave a smaller activation energy under an acid catalyst. Table 2 also shows the activation energies for the systems $TEOS-H_2O-HCl$, HF after Colby et al.[11] and $TEOS-Al(NO_3)_3-H_2O$ after Bansal et al.[7] The activation energy of the present systems

Fig. 3. IR spectra of the gels strarting from $Al(NO_3)_3$ through procedure I.

was greater than that (82~110 kJ/mol[11]) for the gelation of the TEOS systems and was almost as large as that for the system $5Al_2O_3 \bullet 95SiO_2$ (89.2kJ/mol[7]). Comparing the t_{gel} between the system $5Al_2O_3 \bullet 95SiO_2$[7] and the present $10Al_2O_3 \bullet 90SiO_2$ system indicates the larger Al content shortened the gelation time.

3.3 Microstructure and Crystallization of the Gels

Fig. 3 represents IR spectra of the gels starting from aluminium nitrate. The as-dried xerogel has a strong band near 3000 cm[1] due either to O-H bonds of free water and silanol groups or to C-H bonds of organic groups. IR bands for Si-OR or Si-O-Si bonds are observed in the range from 1000 to 1300cm[1]. The 1600cm[1] band is due to free water and the C=O or C-N bonds of DMF cause a band near 1400cm[1]. These two bands disappear when the gels are treated at 600°C. A weaker band at 950cm[1] can be attributed to Si-O-Al bonds,[12] indicating that the Al atoms are already attached to the xerogel matrix. Formation of silica skeleton is completed after treating the gels at 1300°C since the 800cm[1] band corresponds to a symmetric stretching vibration of SiO_4 tetrahedra found for silica glass and other silicates. The following X-ray diffraction (XRD) experiment confirms this result. Fig. 4 shows crystalline phases identified by the XRD patterns of the gels after the treatment at temperatures indicated. In the gels from aluminium nitrate mullite appears at 900°C while mullite is precipitated at 1100°C in the gels from $Al(OPr^i)_3$. Heating the gels at 1300°C results in cristobalite irrespective of the Al source. Table 3 summarizes the

Temperature (°C)	Proced. I Al(NO3)3, HCl i-PrOH	Proced. II Al(i-PrO)3, HCl n-BuOH
	Cristobalite + Mullite	Cristobalite + Mullite
1300		
1200	Mullite + Amorphous	Mullite + Amorphous
1100		
1000		Amorphous
900		
800	Amorphous	

Fig. 4. Crystalline phases precipitated from the gels.

density, crystalline phases and mullite particle size, determined by XRD, for the gels treated at 1300°C. It is found that the gels turn into pore-free ceramics on heating at 1300°C since the density of the 1300°C gel (2.40g/cm³) is as large as that of the theoretical density of mullite dispersed silica ceramics of composition $10Al_2O_3 \cdot 90SiO_2$. Table 3 also showes that either of the Al sources produce similar ceramics when the gels are treated above 1100°C.

4. DISCUSSION

Precipitation of mullite never occurs in alumina-silica diphasic gels before they are heated above 1350°C[7] because Al and Si atoms should travel longer distance to accomplish reformation of the bonds. In the present study we have observed mullite in the gels heated at as low as 900°C. This suggests such greater structural modification is unnecessary because of monophasic nature of the present gels. This can be attributed to the presence of Si-O-Al bonds in the gels confirmed by the IR band near 900cm⁻¹. Moreover, the systems containing larger amount of Al became gel in shorter time. It is therefore considered that the formation of the Si-O-Al bonds is concerned with the apparent activation energy of gelation. Colby et al. observed[11] that the activation energy for the gelation of TEOS under HCl and HF catalyst was almost the same while shorter gelation time was for the HCl. They interpreted this result as showing that HCl is more active on hydrolysis of the Si-OR bonds resulting greater amount of silanol groups while HF is effective on condensation of the resulted Si-OH groups, and that the more silanol groups in the HCl-catalyzed sols enhance the frequency for a group to encounter the other.[11] In another words, the HCl catalysis has a larger

Table 3. A few properties of the gel-derived mullite ceramics.
Particle size of the precipitated mullite is shown.

Al source and procedure	Acid catalyst	Density (g/cm³)	Precipitated phase	Particle size of mulllite (Å)
Al(NO₃)₃	HCl	2.349	C + M	113
Proced. I	HNO₃	-	M	104
Al(OPrⁱ)₃	HCl	2.380	C + M	109
Proced. II	HNO₃	2.294	M	100

t_0 value of eq. (1) than the HF catalysis. The activation energy of Si-O-Si bond formation was given as about 55kJ/mol[7] and that of hydrolysis of Si-OR bonds was 19.4kJ/mol,[11] which are fairly smaller than the present data (80~95 kJ/mol). Since the gelation reaction involves many processes it is hard to give a strict meaning to thus obtained apparent activation energy, but we can at least point out that the presence of Al ions in the sol retards the gelation. Further interpretation of the present results should wait for much more accumulation of experimental results. However, we consider that some Al-bridged intermediates are formed by chelation between Al and Si-OR or Si-OH bonds in the course of gelation and that the chelates suppress the rate of hydrolysis and condensation of the Si-OR and Si-OH bonds. In the chelates the Al atoms are six-coordinated by oxygen atoms under the presence of water and pH lower than 6.[5]

5. CONCLUSION

Using tetraethoxy silane, aluminium nitrate and aluminium isopropoxide as the Si and Al sources, mullite-dispersed silica ceramics were prepared through sol-gel processing. Various alcohols were used for solvent while HCl and HNO_3 were the catalyst. Dimethyl formamide was added as a drying control agent. Optimum mixtures of these reagents were so determined as to resulting crack-free xerogels. Effect of the starting materials, solvents and catalyst was examined on the gelation time or temperature of mullite precipitation. Apparent activation energy of gelation ranged from 80 to 95kJ/mol and the presence of Al in the sols elongated the gelling time.

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