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Epitactic Nucleation of Spinel in Aluminosilicate Gels and Its Effect on Mullite Crystallization

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Control over the structure of hybrid (colloidal + molecular) aluminosilicate gels was utilized to demonstrate that precursor chemistry has a direct and controllable effect on the ~1000°C crystallization of spinel and mullite in molecular precursor systems. Synthesis or preparation conditions leading to the development of a cubic, transition alumina result in the epitactic nucleation of spinel at ~1000°C in gels that otherwise crystallize directly to mullite at ~1000°C. Thus, the preference for spinel nucleation in gels derived from solution precursor systems whose chemistries promote formation of transition alumina readily explains the reported inability to obtain substantial mullite yields at ~1000°C. Isothermal transformation kinetics of colloidal and hybrid gels show that in the absence of direct mullite formation at ~1000°C, the release of alumina from the spinel-type crystal structure becomes the rate-controlling step in the transformation. This necessitates higher temperatures for mullite formation and limits the kinetic enhancement possible with *extrinsic* increases in mullite nucleation frequency. [Key words: *aluminosilicates, gels, spinels, mullite, crystallization*.]

I. Introduction

A MULTITUDE of chemical precursor combinations and processes[1] have been investigated for the synthesis of mullite ($3Al_2O_3 \cdot 2SiO_2$) gels, precipitates, and powders. Although a wide range of molecular-scale structures are obtained, with few exceptions mullite phase formation from these chemical precursor systems follows one of two paths during heating. In some so-called molecularly mixed systems, mullite rapidly crystallizes from X-ray diffraction-amorphous gels at ~1000°C.[2-5] Alternatively, mullite slowly crystallizes at >1200°C from mixtures of an amorphous silica-rich phase and a poorly crystalline high-alumina (~$6Al_2O_3 \cdot SiO_2$[3]) phase commonly referred to as "spinel." The spinel evolves either (a) by the fast crystallization of solution-derived, XRD-amorphous gels at ~1000°C[6-11] or (b) slowly and continuously upon heating of colloidal-scale boehmite and silica above 500°C.[5,12-15]

It is important to note that seemingly comparable chemical precursor systems may exothermally crystallize either directly to mullite or to spinel at ~1000°C. The question of why spinel forms instead of mullite has been addressed only in the very general terms of alumina–silica scale-of-mixing or, alternately, the degree of Al–O–Si bonding in the precursor system.[1,3,10,16-21] The extent of ~1000°C mullite formation has been assumed to vary proportionately with the extent of Al–O–Si bonding in the gel. By parallel reasoning mullite crystallization temperatures above 1200°C have been attributed solely to processing-related alumina–silica segregation and the corresponding increase in diffusion distances.

The scale-of-mixing argument is based on the effect of the relative size and distribution of the aluminum and silicon precursors on diffusional processes. However, the scale-of-mixing concept fails to explain why gels generally do not crystallize to mullite at temperatures between ~1000° and ~1200°C.[21] The crystallization temperature and degree of reaction should vary continuously with diffusion distance and thus precursor scale, but the observed crystallization response is discontinuous. It is therefore apparent that additional factors must control the solid-state crystallization of chemical precursor systems.

To identify the factors influencing phase development requires an alumina–silica precursor structure that can be prepared with a range of scales. Such control has been elusive in processes employing salts and alkoxides because of the large differences in the hydrolysis and condensation rates of dissolved aluminum and silicon species.[1,18,22] An additional complication is the inability to directly quantify the scale of mixing. Consequently, phase development of gels is often interpreted by comparison to systems exhibiting the extremes of structure and crystallization behavior.[3] For example, direct mullite crystallization at ~1000°C is rationalized by maintenance of molecular-scale alumina–silica mixing during crystallization of gels with structures comparable to those of splat-cooled glasses. In contrast, complete inactivity in the ~1000°C range is characteristic of colloidal gels containing 10- to 100-nm-diameter boehmite and silica particles that follow individual crystallization paths below ~1250°C. The apparent homogeneities of precursors are therefore evaluated in retrospect (following crystallization) by comparison and "interpolation," though independent confirmation of gel structure is not available.

An alternate processing route allowing direct control over gel structure is to combine separately-processed gels having well established crystallization behaviors to form "hybrid" gels. Such an approach was originally developed to utilize control over mullite gel structures to tailor nucleation frequencies and thereby influence microstructure and transformation kinetics.[23,24] Hybrid gels, however, also allow for the examination of relationships between the ~1000° and >1200°C crystallizations of alumina–silica gels with far greater control than possible by changing cohydrolysis conditions of a single set of solution precursors.

In this paper we demonstrate on the basis of phase development, crystallization kinetics, and crystal chemistry of hybrid gels that the precursor chemistry has a direct and controllable effect on the formation of spinel at ~1000°C in molecularly mixed precursor systems. Furthermore, the formation of spinel directly impacts the apparent activation energy for mullite formation at >1200°C. In neither case is the scale of alumina–silica mixing preceding the reaction the controlling factor.

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II. Experimental Procedure

In earlier papers we reported on the general crystallization behavior and microstructural development of two different hybrid gel systems[23,24] In this paper we will use primarily "Type I" hybrid gels, in which the molecular and colloidal gels are combined with maximum homogeneity and thus maximum colloidal–molecular interfacial area (Fig. 1(A)), to illustrate what controls the development of spinel in a molecular precursor system and how this affects the formation mechanism of mullite. "Type II" hybrid gels exhibit more effective mullite seeding related to a change in gel design (Fig. 1(B)) and will be used to assess the role of nucleation in this mechanism.

(1) Type I Gel Synthesis

Preparation of the colloidal gel (73 wt% Al_2O_3, 27 wt% SiO_2) involves diluting a colloidal silica sol* in deionized water and slowly (~1 g/min) adding boehmite (γ-AlOOH) powder† while stirring vigorously. The final solids content is 20 wt%. After stirring for 1 day, concentrated nitric acid is added dropwise to lower the pH from ~8.5 to 3. This pH adjustment requires rapid passage through an intermediate pH regime of high viscosity caused by boehmite–silica heterocoagulation. Gelation occurs in 1 to 2 h. The wet gel is covered and kept for later use.

Preparation of the molecular gel is modified from Okada *et al.*'s procedure for their "SH" gel.[3] One hundred grams of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$)‡ is dissolved in 100 g of absolute ethanol by stirring overnight at 55°C, followed by cooling to room temperature and addition of 17.4 g of tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS).§ After stirring 2 to 3 h at room temperature, the clear solution is heated and stirred at 55°C under reflux conditions until gelation (~4 days). Absolute ethanol is added (~70 g) to allow the gel to be redispersed, and stirring is continued at 65°C under reflux conditions for another ~8 days to ensure complete cohydrolysis. This yields an opaque dispersion of the molecularly mixed gel in ethanol.

To promote compatibility of the molecularly and colloidally mixed systems the molecularly mixed gel dispersion is converted to an aqueous medium. Ethanol is evaporated at 70°C and a total of 400 to 500 g of deionized water is added as needed to maintain the system's volume. The dispersion is loosely covered and boiled at 100°C, which results in a gradual (~5 to 6 h) change from opacity to optical clarity. The dispersion is then cooled to room temperature and centrifuged at 2000 rpm for 25 min to remove any macroscopic gel heterogeneities. No significant settling of the gel occurs during centrifuging. The clear, aqueous dispersion is stable without adjustment of pH.

Hybrid gels were prepared by combining the molecular gel dispersion and the wet colloidal gel such that 25, 50, 75, and 90 wt% of the mullite totals would be derived from the molecular component. These Type I gels were denoted $25M_I$, $50M_I$, etc. Mixing was achieved by mechanically rolling (150 rpm, 2 days) polyethylene bottles containing the two wet gels and several Teflon-coated stirring bars. Deionized water was added to maintain low viscosity during mixing. Gels were dried at 90°C and crushed with a high-purity alumina mortar and pestle.

(2) Type II Gel Synthesis

In Type II hybrid gels the molecular gel units dispersed in the colloidal gel are made larger by forming clusters bound by hydrolyzed TEOS. The clear, aqueous molecular gel dispersion previously used in Type I hybrids is mixed with TEOS (and sufficient ethanol to obtain miscibility) to yield a mullite:excess silica weight ratio of 2:1. The mixture is stirred at 55°C under reflux conditions and gels in ~1 day. From this point the procedure is nearly the same as described above (i.e., dilution with ethanol, redispersion by stirring, heating at 65°C, ethanol-to-water conversion) with the exception of boiling and centrifuging. Boiling does not yield a clear dispersion as in the Type I gels, indicating a larger final particle/cluster size. To retain these clusters in suspension, centrifuging is limited to 5 min at 2000 rpm and is preceded by dilution of the dispersion to a solids content of ~4 wt% and its treatment in 150-mL batches with an ultrasonic horn for 90 s. Type II hybrid gels were mixed such that 5 and 10 wt% of the gels would be derived from this clustered (molecular gel + silica) gel following full transformation.

Note that because this modified seeding gel contains excess silica, the Type II hybrid gels vary slightly in composition (0M = 73 wt% Al_2O_3, $5M_{II}$ = 71.8 wt% Al_2O_3, $10M_{II}$ = 70.6 wt% Al_2O_3) relative to the Type I hybrid gels. Such variation can be easily eliminated by small compensating adjustments in the colloidal gel's alumina content. In the present experiments, however, hybrids were not adjusted in this manner to ensure a strictly constant reference for unseeded crystallization behavior and microstructure development. In the temperature range of solid-state alumina–silica reactions (<~1600°C), the kinetics and microstructure of mullite crystallization are affected far more by increased nucleation frequency than by small variations in bulk composition.

(3) Characterization

Differential thermal analysis (DTA) was performed on dehydroxylated (650°C) gel powders at a heating rate of 20°C/min to enhance crystallization exotherms. Crystalline phases were identified by X-ray diffraction (XRD) of samples following DTA heating to just above the relevant exotherms. Sintered gel microstructures (1000° and 1300°C for 2 h) were

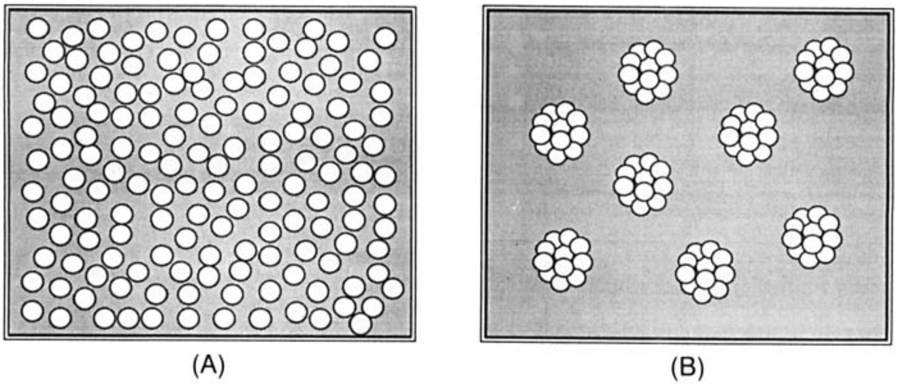
(A) (B)

Fig. 1. Schematics of hybrid gel structure types containing differing extents of gel interface: (A) Type I hybrid gels, (B) Type II hybrid gels. Circles represent molecular gel; shaded matrix represents colloidal gel.

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‡Aldrich Chemical Co., Inc., Milwaukee, WI.
§Alfa Products, Danvers, MA.

characterized by SEM and TEM of unsupported thin gel films.[25] TEM samples were ion milled ($\theta = 11°$, 3.5 kV) for 1 to 2 h and carbon coated.

Isothermal heat treatments for kinetic analysis of the mullite transformation were preceded by calcining ~2 g of dried and crushed gel powders in a Pt foil pan at 600°C for 10 min to remove volatiles. Samples were rapidly transferred to and from the hot zone of a horizontal tube furnace maintained within ±2°C of the set point. The extent of mullite formation was measured by quantitative XRD using a CaF_2 internal standard. The ratios of the integrated intensities of the (120)–(210) mullite doublet reflection and the (111) reflection of CaF_2 were compared to mullite–CaF_2 calibration curves determined separately for each hybrid gel. The empirical equation $\alpha = 1 - \exp[-(Kt)^n]$, simplified from the Avrami model[26] for describing nucleation and growth transformation kinetics, was used to calculate rate constants (K, s^{-1}) and time exponents (n) from the weight fractions of crystallized mullite (α) in each gel as a function of time (t, seconds).

III. Results and Discussion

(1) Epitactic Nucleation of Spinel at ~1000°C

The DTA and XRD results for the molecular (100M) and the $90M_I$ and $75M_I$ hybrid gels are compared in Fig. 2. The intrinsic molecular gel (100M) crystallizes directly and fully to mullite with a sharp and intense exotherm (Fig. 2(A)). With the introduction of as little as 10 wt% colloidal gel ($90M_I$), however, only a trace of mullite forms during a similarly sharp but less intense exotherm (Fig. 2(B)). When the hybrids' colloidal gel content exceeds ~15%, the cubic spinel alone is detected above ~1000°C (Fig. 2(C)). In the absence of direct mullite formation, the associated exothermic peak intensities are substantially reduced.

Spinel formation during the ~1000°C exotherm is common in solution-derived gels, but has been attributed solely to heterogeneous alumina–silica mixing (i.e., the kinetic favorability of maintaining processing-related alumina–silica segregation). Considering the amount of alumina and silica in the $90M_I$ hybrid gel that is mixed on a scale known to permit direct mullite formation (Fig. 2(A)), we would have expected 90% mullite at ~1000°C if, in fact, the scale of alumina–silica mixing was a sufficient parameter for predicting phase development. The apparent discrepancy is explained by recalling that phase transformations depend on both kinetic and thermodynamic factors. Given adequate growth kinetics, crystallization of a metastable phase is not prohibited by thermodynamics if this phase is nucleated prior to a stable phase. In the present case it is proposed that after the boehmite component of the colloidal gel transforms to γ-alumina at ~500°C it serves as a substrate for the nucleation of metastable spinel in the hybrid gel. Epitactic nucleation of spinel on γ-alumina is favorable as spinel and γ-alumina are isostructural (i.e., both cubic) and have nearly identical lattice parameters (7.886 vs 7.906 Å, respectively[27]). Thus, when a suitable nucleant is available for spinel crystallization, the molecular gel is consumed by growth of the spinel and, hence, intrinsic mullite formation is precluded.

To further test whether the presence of a material of cubic structure is sufficient to direct the transformation of a molecular gel by epitactic nucleation, the molecular gel (100M) was mixed with various fractions of boehmite. This type of hybrid gel is equivalent to those above except the colloidal silica is intentionally omitted. The DTA traces and X-ray diffraction patterns of two such gels, the analogues of the $75M_I$ and $90M_I$ hybrids, were identical to those shown in Fig. 2. As expected from the presence of boehmite-derived γ-alumina and the behavior shown in Fig. 2, these gels' molecularly mixed components form the spinel–silica mixture rather than mullite at ~1000°C.

If epitactic nucleation of spinel on the cubic γ-alumina is the operative mechanism for the change in crystallization behavior of the molecular gels in the above experiments, it should be possible to effect the same change in a purely molecular system by inducing *in situ* γ-alumina formation. Boehmite can be produced *in situ* in such molecular aluminosilicate gels and zeolites[28] by rehydrating them after low-temperature calcination. In this experiment the molecular gel (100M) was calcined at 400°C for 1 h and then cooled to room temperature. Part of the dehydrated, amorphous gel was then immediately heated to 1000°C whereas another portion was rehydrated in humidified air for 24 h and then heated to 1000°C. The X-ray diffraction patterns of these two gels in Fig. 3 are seen to be strikingly similar to those of the 100M and $90M_I$ samples in Fig. 2. This experiment clearly demonstrates that the *in situ* formation of boehmite and its subsequent evolution to a cubic transition alumina directly promotes spinel crystallization.

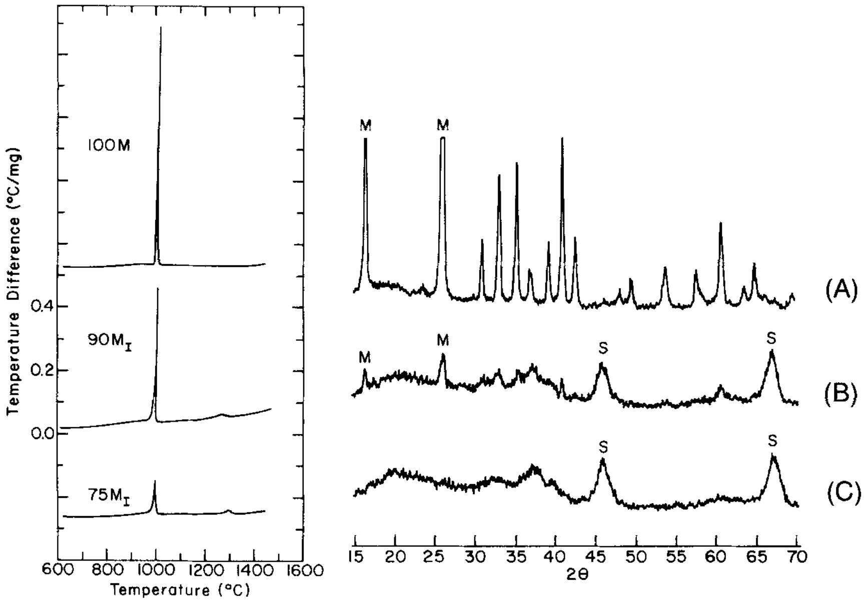


Fig. 2. Differential thermal analysis (20°C/min) and post-1000°C exotherm X-ray diffraction patterns of (A) molecular (100M) gel, (B) $90M_I$ hybrid gel, and (C) $75M_I$ hybrid gel; on XRD patterns, M is mullite, S is spinel.

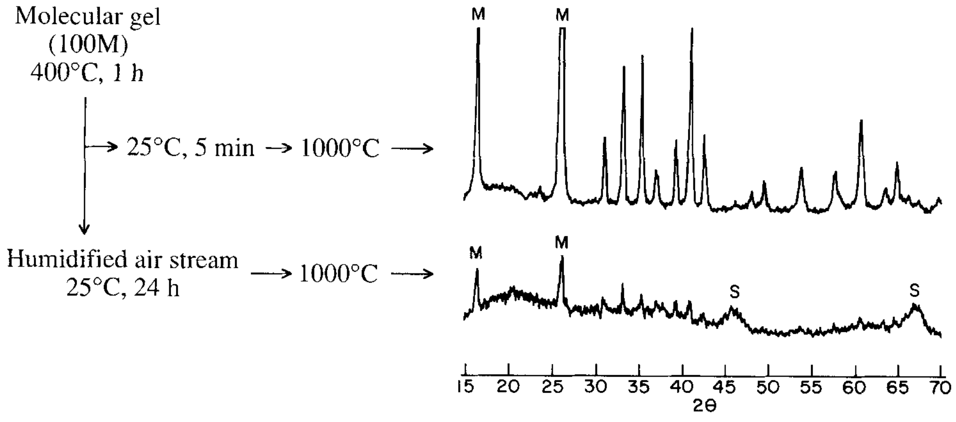


Fig. 3. Effect of post-calcination rehydration on 1000°C phase development of molecular (100M) gel; M is mullite, S is spinel.

The ability of the spinel to forestall mullite formation in the molecular gel requires both a high spinel nucleation frequency and a rapid spinel growth rate, both of which are influenced by gel processing. The growth rate is controlled by the diffusion kinetics of Al^{3+} and Si^{4+} in the crystallizing matrix, while in the present case spinel nucleation sites are provided by boehmite-derived γ-alumina intentionally added to the molecular gel. It is reasonable to project that nanometer-scale alumina-rich regions present in any "molecularly mixed" gel due to processing-related alumina–silica segregation will effectively serve the same function. Because the enhancement of spinel nucleation associated with even a few wt% segregated alumina is sufficient for spinel to dominate crystallization at ~1000°C (Fig. 2), direct mullite formation requires not only molecular-scale alumina–silica mixing, but nearly complete molecular-scale mixing. In light of such a stringent requirement, the inability of most sol-gel processes in the literature to yield substantial amounts of mullite at ~1000°C is readily explained by the difficulty of maintaining chemical homogeneity and the subsequent effect on spinel nucleation.

The favored formation of spinel in the published literature can be interpreted in terms of those chemical reactions and experimental conditions that lead to segregation of alumina and silica in alkoxide-derived gels.[1,3,18] The most commonly discussed parameters involve the concentration, pH, and rate of introduction of the water required for hydrolysis. Slowing the hydrolysis of the more reactive aluminum species, such as by adding acidic water in dilute water-in-alcohol solutions[29] or, at the extreme, by allowing reaction with atmospheric humidity[18] over a period of several months, promotes simultaneous (rather than consecutive) incorporation of aluminum and silicon into the gel. This, in turn, impedes formation of the alumina-rich spinel nuclei upon heating and allows mullite to crystallize at ~1000°C. In contrast, there are numerous reports of synthesis processes in which the hydrolysis of aluminum is accelerated by adding undiluted water of neutral or high pH. By promoting the formation of aluminum hydroxides (i.e., spinel nuclei precursors), it is inevitable that spinel first crystallizes when the precursor is heated to 1000°C. As a consequence of the recognized effect of localized γ-alumina formation on spinel crystallization, it is now possible to predict the crystallization path at 1000°C on the basis of the precursor chemistry.

The complete prevention of alumina–silica segregation is especially problematic in dual alkoxide systems simply because water for hydrolysis must be added as a separate precursor. For example, even dropwise addition of water creates instantaneous, locally high water concentrations. Replacing the aluminum alkoxide with a hydrated aluminum salt such as aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) homogeneously distributes water from the outset in a loosely bound form that restricts its reaction. Although additional water, basic conditions, or insufficient time for cohydrolysis will still result in heterogeneity sufficient for spinel nucleation, mullite formation at ~1000°C has been achieved more readily from the aluminum nitrate nonahydrate–TEOS system[3-5,19,21] than from any combination of aluminum and silicon alkoxides.

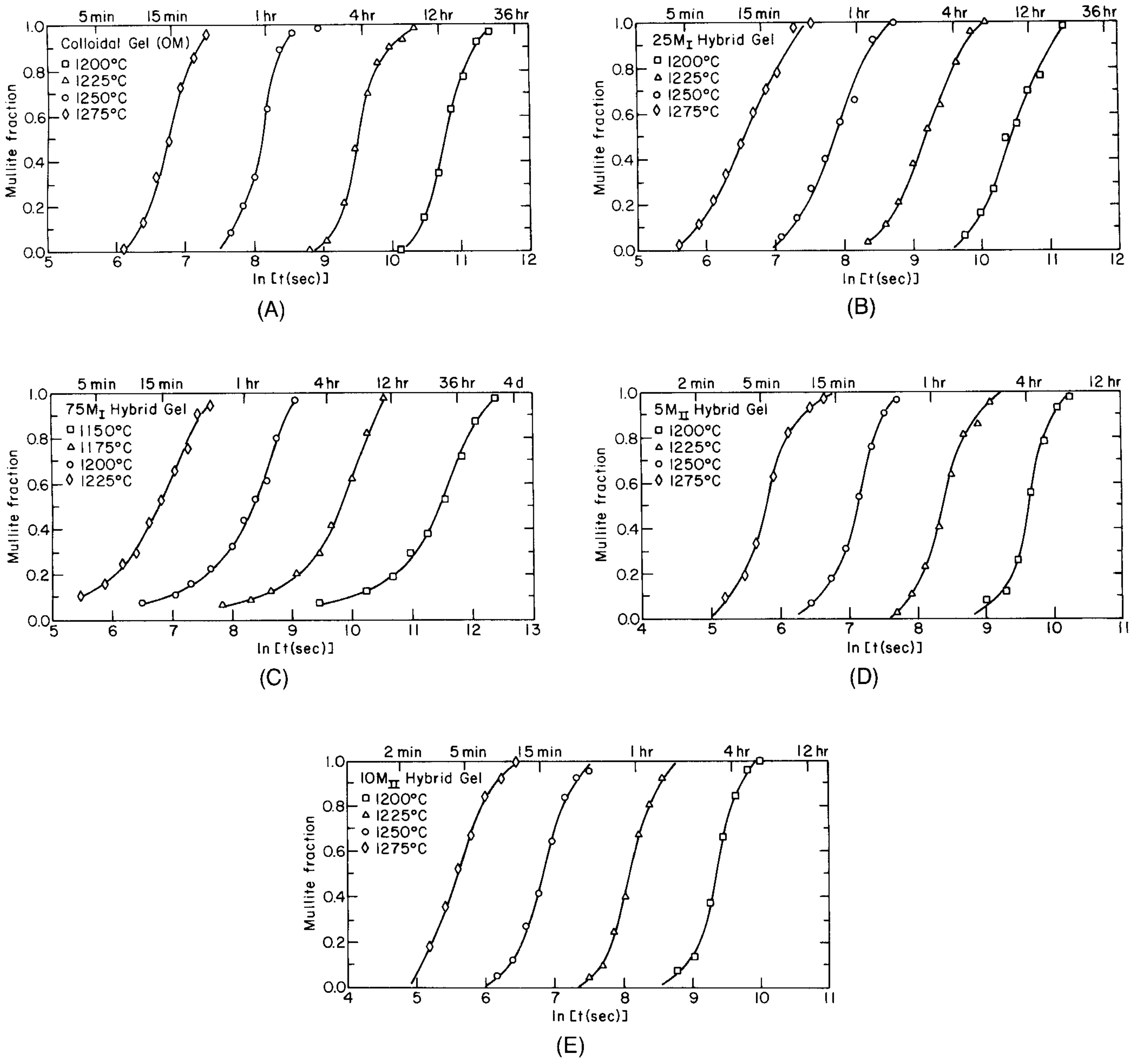
(2) Spinel Structure Effect on >1200°C Mullite Formation

As shown above, widespread spinel formation can follow from localized processing-related inhomogeneity, through purely interfacial interactions between isolated nuclei and an otherwise molecularly mixed system. Mullite crystallization requiring temperatures >1200°C is therefore more accurately attributed to prior formation of the spinel than to alumina–silica segregation per se. That is, the need for temperatures >1000°C does not necessarily reflect alumina–silica segregation throughout the gel prior to heating, but rather a decrease in effective diffusivities that occurs when the system is "stabilized" by spinel crystal growth at 1000°C. Factors affecting the stability of the spinel–silica mixture can be evaluated from the kinetics of the mixture's isothermal transformation to mullite.

The formation kinetics of mullite (i.e., the decomposition kinetics of the spinel) were quantified by fitting the mullite contents of heat-treated gels (Figs. 4(A) to (E)) to the Avrami model[26] for nucleation and growth processes. The rate constants for each gel's transformation were assumed to follow an Arrhenius temperature dependence (Fig. 5), and thus the apparent activation energy, E_a, can be derived from the slope. The apparent activation energy represents the energy barrier for all processes necessary for the transformation of the metastable spinel–silica mixture to stable mullite. Besides thermally activated nucleation, the apparent activation energy includes contributions from interface reactions (i.e., dissolution of silica and alumina species) and diffusional processes. Comparison of apparent activation energies for differently processed gels therefore indicates the relative stabilities of spinel–silica mixtures formed upon heating and yields insights into differences in rate-limiting processes related to processing.

The apparent activation energies for mullite formation in colloidal (0M) and hybrid (25M$_I$, 75M$_I$) gels are listed in Table I, along with mean time exponents, $\bar{n}$, and apparent rate constants at 1200°C. The apparent activation energy remains nearly constant, regardless of gel processing or phase development leading to the spinel–silica mixture. This suggests that there is a common thermally activated step that controls the transformation. The nature of the rate-limiting step can be deduced by examining the differences and similarities between each of the spinel–silica systems and by comparing these to literature reports.

The transformation kinetics of boehmite–silica gels have been reported by Wei and Halloran[30] and Li and Thomson.[31] Silica in the earlier studies was derived from acid-catalyzed hydrolysis of TEOS. This creates a branched, polymeric silica



(A) (B) (C) (D) (E)

Fig. 4. Isothermal mullite transformation curves at various temperatures for (A) colloidal (0M) gel, (B) 25M$_I$ hybrid gel, (C) 75M$_I$ hybrid gel, (D) 5M$_{II}$ hybrid gel, and (E) 10M$_{II}$ hybrid gel.

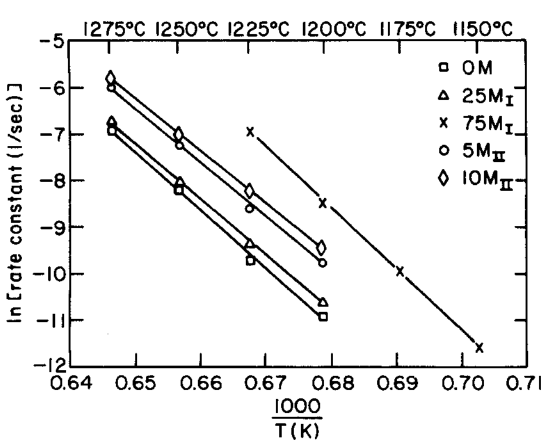


Fig. 5. Arrhenius plot of the apparent rate constants for the mullite transformation in colloidal (0M) and hybrid gels.

network[32] encompassing the boehmite particles, in contrast to the discrete 20-nm spheres of the colloidal silica used in this study. Pure silica gels formed from these different silicas are known to exhibit different transport properties (as evidenced by differences in their viscous sintering behavior) related to their hydroxyl contents.[33] However, comparison of the appar-

Table I. Apparent Activation Energies (E_a), Mean Time Exponents ($\bar{n}$), and Apparent Rate Constants at 1200°C (K_{1200}) for Colloidal and Hybrid Gels

Gel	E_a (kJ/mol)*	$\bar{n}$	K_{1200} (s^{-1})
Colloidal (0M)	1034 ± 124	3.5	1.75×10^{-5}
(Wei and Halloran[30])	1070 ± 200		
(Li and Thomson[31])	1028 ± 37		
25M$_I$ Hybrid	984 ± 71	2.7	2.42×10^{-5}
75M$_I$ Hybrid	1091 ± 71	1.6	2.08×10^{-4}
5M$_{II}$ Hybrid	960 ± 91	3.1	5.66×10^{-5}
10M$_{II}$ Hybrid	932 ± 49	3.3	7.75×10^{-5}

*Values from this study are 95% confidence intervals.

ent activation energy of the 0M gel in this study (1034 kJ/mol) to those of Wei and Halloran (1070 kJ/mol) and Li and Thomson (1028 kJ/mol) reveals a remarkable consistency. This suggests that the transformation rate is unaffected by variations in the nature of the silica phase or how the alumina and silica are combined during gel formation. Thus, it is concluded that the transformation kinetics are controlled by the alumina component.

The value of the time exponent, n, represents the nucleation conditions and the subsequent mechanism and dimensionality of growth for which the data best fit the nucleation and growth model.[26,34] The values of n for the colloidal gels range between 3.2 and 4.2, which is consistent with Wei and Halloran's conclusion of three-dimensional growth controlled by either short-range diffusion or reaction at the mullite interface. From transmission electron microscopy of a colloidal gel heated at 1300°C for 2 h (Fig. 6), mullite is observed to grow preferentially through the colloidal gel's amorphous silica phase and to characteristically envelop many (initially) unreacted spinel crystallites.[13,30] This growth path is consistent with silica not being involved in the rate-controlling step. Conversely, the engulfed spinel is physical evidence that mullite formation during the growth stage is limited by the removal of alumina from the spinel's cubic crystal structure. An analysis of Wei and Halloran's[30] microstructural observations and mullite growth kinetics in colloidal gels similarly led Sundaresan and Aksay[35] to propose this mechanism.

The $75M_I$ hybrid gel has an apparent activation energy for mullite crystallization of 1091 kJ/mol, despite the majority of the gel being molecularly mixed. An activation energy similar to those for colloidal gels is in accordance with theory for a common transformation mechanism, as the temperature dependence of the rate (i.e., E_a) should be independent of growth scale and geometry. The spinel–silica scale in the $75M_I$ hybrid gel is intrinsically set by short-range diffusion at ~1000°C, and is necessarily much finer (Fig. 7) than the extrinsic precursor/processing-dependent mixing in the colloidal gel. The Arrhenius plot for the $75M_I$ hybrid gel is therefore shifted to rate constants an order of magnitude greater than those for the colloidal gel. The proposed rate-limiting "release" of alumina from the spinel is not affected by the finer scale of spinel–silica mixing, although more alumina is available for mullite formation at any given temperature. This is based on the Kelvin equation, which predicts the increase in activity of a soluble species as the dimensions of its source decrease.

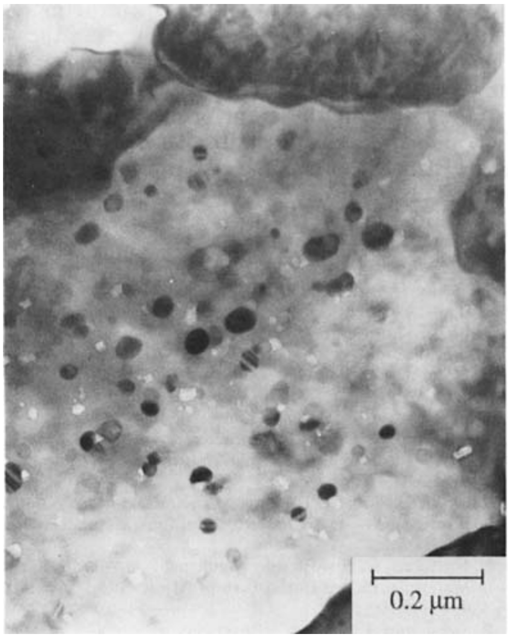


Fig. 6. TEM micrograph of the colloidal gel (0M) heated at 1300°C for 2 h. Dark intragranular spots are unreacted spinel within a mullite grain.

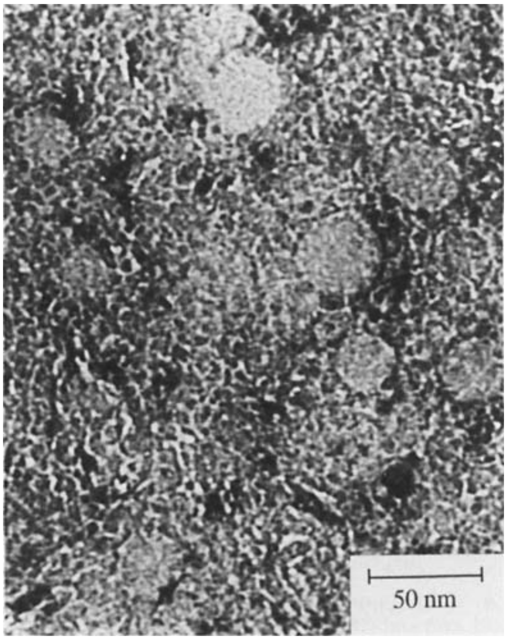


Fig. 7. TEM micrograph of the $75M_I$ hybrid gel heated at 1000°C for 2 h. Light circular features are from colloidal silica particles in hybrid's colloidal gel component.

Assuming the colloidal and $75M_I$ hybrid gels do, in fact, form mullite by the same mechanism, their time exponents can be directly compared. The much lower n values (1.6 to 1.8) calculated for the $75M_I$ hybrid gels then correspond to one- or two-dimensional growth.[26,34] This agrees with the finer-scale network morphology of these gels' spinel–silica mixtures, as the short-range diffusion responsible for spinel formation creates a system dominated by the spinel–silica interface. Mullite formation can therefore be completed entirely by a combination of two-dimensional growth along the interface and one-dimensional growth normal to the interface. In contrast, the more limited spinel–silica interface in the colloidal gels provides far fewer effective nuclei, necessitating the radial (three-dimensional) growth that proceeds preferentially through the amorphous silica-rich matrix.

The composition of the spinel crystallized at ~1000°C in molecular gels remains a subject of controversy. While most experimental evidence suggests a silica content of <10 wt%,[3,36,37] spinel compositions of $2Al_2O_3 \cdot SiO_2$[38] and $3Al_2O_3 \cdot 2SiO_2$[39] have been proposed. A spinel phase of stoichiometric mullite composition in the $75M_I$ hybrid gel would undergo a polymorphic transformation to mullite requiring a fundamentally different mechanism and apparent activation energy than those determined for the two-phase colloidal gel. The comparable apparent activation energies of the colloidal and $75M_I$ hybrid gels support the view that the spinel contains <10 wt% silica.

The $75M_I$ hybrid gel clearly cannot be considered a seeded colloidal gel, as a majority of its spinel–silica mixture forms at ~1000°C and its enhanced transformation to mullite results from this fraction's finer scale and higher intrinsic nucleation frequency. The $25M_I$ hybrid gel, in contrast, does remain predominantly colloidal, so the reduction in apparent activation energy to 984 kJ/mol from the colloidal gel's 1034 kJ/mol reflects extrinsically enhanced nucleation. The very small extent of this change can be attributed to the intermediate formation of the spinel (such that both the "seed" and "matrix" components of the hybrid gel crystallize mullite at over-

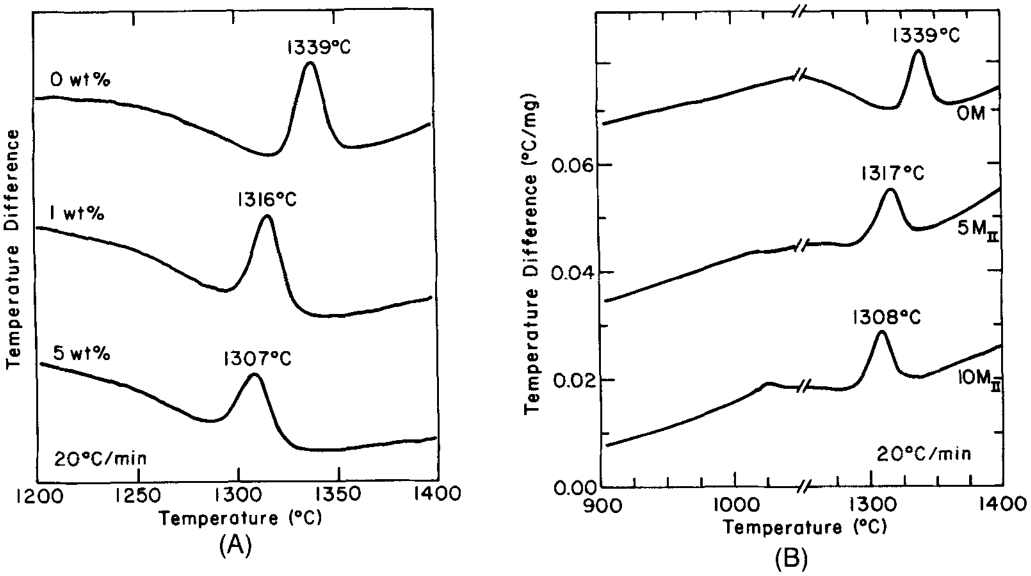


Fig. 8. Differential thermal analysis (20°C/min) of (A) colloidal gel containing crystalline mullite seed particles (0, 1, and 5 wt%, $d \sim 0.1$ μm) and (B) Type II hybrid gels.

lapping temperatures) and the subsequent dominance of E_a by the spinel effect that limits the rate of alumina availability for mullite formation.

(3) Seeded Nucleation of Mullite

The contribution of nucleation to E_a can be estimated by determining the maximum kinetic effect of seeding. To do this using hybrid gels, however, the effectiveness of nucleation control must be increased by designing hybrid gel structures to promote direct ~1000°C crystallization of mullite nuclei. In Type II hybrid gels this is accomplished by forming the molecularly mixed seeding gel into larger clusters to reduce the spinel's epitactic nucleation on the colloidal gel's γ-alumina (i.e., "spinel").[24] The DTA results in Fig. 8 show that the shifts in exothermic peak temperatures of Type II hybrid gels are comparable to those of colloidal gels conventionally seeded with crystalline mullite particles ($d \sim 0.1$ μm). Thus the small extent of the shifts—limited to ~35°C—is not related to insufficient "chemical" provision of mullite seeds in the hybrid gel, but to an inherently minor role of added seed crystals in the transformation process. In all cases, seeding effectiveness is more apparent in the sintered microstructures' reduced grain sizes[24] than in the DTA results.

The quantitative kinetic effect of $5M_{II}$ and $10M_{II}$ hybrid gel seeding is to reduce the apparent activation energy for mullite formation in the colloidal gel by ~7% and ~10%, respectively (Table I). For comparison, note that in the polymorphic $\theta \rightarrow \alpha$-alumina transformation,[40] seeding induces twice as large relative reductions in E_a and DTA peak temperature. The considerable amount of mullite seeding required to produce even a small effect on the colloidal gel's transformation kinetics is once again consistent with rate limitation related not to nucleation, but primarily to the availability of alumina as the spinel structure decomposes. Under these conditions, the first "free" alumina will be readily consumed by formation of intrinsic mullite nuclei at temperatures representing the lower limit for growth, so addition of extrinsic nuclei increases the number of potential growth sites but does not allow growth to proceed at significantly lower temperatures. Hence the relative change in incubation times with seeding ($\tau_{0,\text{seed}} \sim (1/4)\tau_{0,\text{unseed}}$) is an order of magnitude less than for a polymorphic phase transformation such as in the alumina ($\theta \rightarrow \alpha$) system.[40] The increase in the number of growth sites does enhance transformation kinetics by increasing the interfacial area of the mullite growth front, but induced changes to the system are nevertheless primarily microstructural.

IV. Summary

Factors controlling the transformation of aluminosilicate gels to spinel and mullite were examined using a variety of hybrid gels. It was demonstrated that the formation of spinel is promoted at 1000°C by epitactic nucleation on γ-alumina because of their close lattice matching and crystal structure similarity. This result allows one to interpret on the basis of the precursor chemistry whether mullite or spinel will form in molecular precursor systems. That is, those process conditions leading to chemical heterogeneity result in the segregation of alumina which in turn transforms to a cubic transition alumina. The transition alumina is then a substrate for the epitactic nucleation of spinel. Growth of spinel, however, proceeds regardless of the scale of alumina–silica mixing in amorphous material containing spinel nuclei. Thus while the formation of spinel is related to the relative scale of dispersion of the alumina and silica precursors, spinel formation is not due to segregation per se, but more fundamentally is attributed to the presence of nuclei which thermodynamically favor spinel formation instead of mullite. In the absence of direct mullite formation at 1000°C, the release of alumina from its spinel-type crystal structure becomes the rate-controlling step in the transformation. This necessitates higher temperatures for mullite formation and limits the kinetic enhancement possible with extrinsic increases in mullite nucleation frequency.

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