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The Effect of Copolymerization of Tetraethylorthosilicate and Aluminum Hydroxonitrates

A. A. Eliseev,* S. V. Kalinin,* V. I. Privalov,† A. A. Vertegel,* and Yu. D. Tretyakov*

*High School of Material Science, Department of Chemistry, Moscow State University, Vorobyovy Hills, 119899 Moscow, Russia; and
†N. S. Kurnakov Institute of General and Inorganic Chemistry, Leninskii Av., 31, 117907 Moscow, Russia

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Polymerization of tetraethylorthosilicate (TEOS) in the presence of aqueous solutions of aluminum hydroxonitrates ($Al(OH)_x(NO_3)_{3-x}$ ($0 < x < 2.5$) was investigated by means of optical spectrophotometry and ^{27}Al NMR. It was shown that gelation rate increases drastically in the system with $x > 2$. The effect is due to copolycondensation of aluminum hydroxocomplexes and TEOS. Aluminum species entering copolymerization reaction have proved to contain tetrahedrally coordinated aluminum. The effect discovered might be useful for the preparation of certain metal oxide–silica composites or silicate materials, such as mullite. © 1999 Academic Press

INTRODUCTION

Preparation of ceramic materials by chemical homogenization techniques is the traditional way to improve their reactivity, including sinterability, their catalytic activity, and their ability to participate in solid state reactions (1–4). One of the most widespread methods of chemical homogenization is the sol–gel method. The preparation technique for silica-containing multicomponent oxide materials, such as silicates and composites M_2O_Z/SiO_2 (M—transition metal), is usually based on the hydrolysis of a mixture of metal and silica alkoxides (5–6). However, due to significant differences between hydrolysis rates for silica and transition metal alkoxides, this method cannot be applied to the preparation of certain materials. To solve the problem the hydrolysis of $Si(OEt)_4$ (TEOS) in an aqueous solution containing metal nitrate was suggested. According to Refs. (7–11), the metal cation incorporates into the SiO_2 framework during gelation, thus forming a homogeneous precursor with a given composition and yielding the desired material after thermal treatment and/or chemical modification. Unfortunately, gelation times are rather long in this case and are comparable to those for acid-catalyzed hydrolysis of TEOS, imposing certain limitations on the applicability of this technique.

However, one can expect that the gelation rate may be substantially enhanced in the presence of *partially hydrolyzed* solutions of certain multivalent metal cations that contain polynuclear hydroxocomplexes of corresponding metals. Indeed, –OH groups in hydroxocomplexes possess greater nucleophilic strength than –OH groups in H_2O molecules in the first coordination sphere of metal or in pure solvent (12–13). In the present research we studied the processes of hydrolysis and polycondensation of TEOS in the presence of aluminum hydronitrates. Aluminum-containing species were chosen as the second component because of their well-known tendency to form Al–O–Si bonds in aqueous solutions (14), which may favor the process of gelation in this particular system.

EXPERIMENTAL

The scheme for the preparation of gels is shown in Fig. 1. The initial solutions of aluminum nitrate were prepared from solid $Al(NO_3)_3 \cdot 9H_2O$ (reagent grade) and distilled water. The solutions were treated with a calculated amount of sodium carbonate dissolved in a small amount of distilled water. The resultant solutions of aluminum hydroxonitrates were diluted with distilled water so that the concentration of aluminum in the final solutions was 1 M; the solutions were then kept for 1–2 weeks to achieve hydrolytic equilibrium. The degree x of hydrolysis in hydroxonitrates $Al(OH)_x(NO_3)_{3-x}$ was measured by pH-metric titration using a ChemCadet (Cole–Parmer) instrument with a combined Cole–Parmer 60648 electrode. The series of aluminum hydroxonitrate solutions with different degrees of hydrolysis x ($1.3 \leq x \leq 2.7$) was prepared. Henceforth, the samples are referred to as $Al - x$, where x stands for the degree of substitution of NO_3^- for OH^-.

Gelation was carried out by hydrolysis of TEOS in a water–ethanol medium (volume ratio TEOS : EtOH : aqueous phase = 1 : 3 : 1). Previously obtained $Al - x$ solutions were used as the aqueous phase. After gelation, the gels were aged for a period of $\sim$2–3 gelation times to ensure complete

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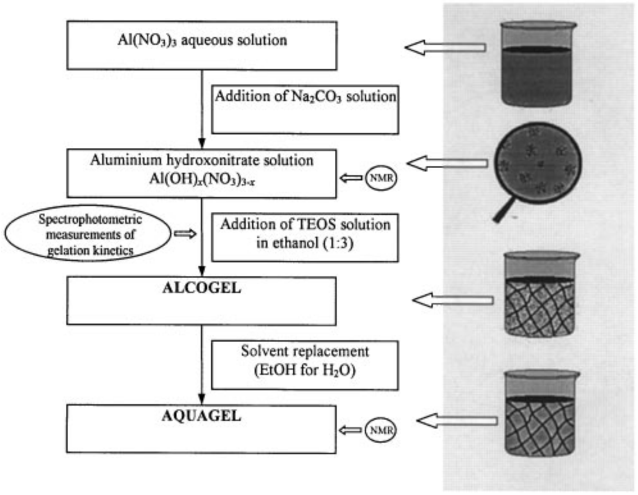

FIG. 1. Scheme of the synthesis.

condensation. The obtained alcogels were then washed with distilled water. There are two reasons for washing the alcogels: (1) If a large amount of EtOH remains in wet gel, it evaporates due to its high volatility. This may result in undesirable drying and cracking. Washing with a large amount of distilled water was carried out five times to ensure full solvent replacement, though no quantitative control of the amount of residual EtOH in aqua-gels was performed. (2) An alcogel contains large numbers of Na^+ and NO_3^- ions, which should be removed from the system. At the same time, according to the reference data (15), some NO_3^- anions may be incorporated into colloidal particles of aluminum hydroxonitrate and, therefore, full elimination of NO_3^- cannot be achieved by washing. The resulting wet aqua-gels were stored in hermetic plastic containers without any drying.

Gelation kinetics was studied by spectrophotometric measurements performed with a two-beam instrument KFK-3 in quartz cuvettes ($l = 10.0070$ mm) at wavelength $\lambda = 600$ nm. Kinetic experiments were carried out under isothermal conditions (precision, $\pm 0.1°C$).

^{27}Al NMR spectra for solutions and gels were obtained at 78.205 MHz with an MSL-300 (Bruker) spectrometer. All measurements were carried out at room temperature. During the measurements, samples (either aqueous solutions or wet gels) were placed in an ampoule 5 mm in diameter and 2 cm in height. Spectra were recorded after an excitation pulse of 15° (2 μs) was applied with an interval of 1 s between pulses. A 1 M aqueous solution of $[Al(H_2O)_6]^{3+}$ was used as the external standard (0 ppm) in all measurements. The number of accumulations was ~1000–6000.

RESULTS

The experiments revealed that hydrolysis of TEOS in the presence of aluminum hydroxonitrates $Al(OH)_x(NO_3)_{3-x}$ with high degrees of hydrolysis ($x > 1.9$) occurs very rapidly (gelation time ≈ 10–20 min), and the resulting gels are opaque although initial solutions were clear. At the same time, gelation time for the samples with lower degrees of hydrolysis ($x < 1.9$) is much longer (3–4 days) and transparent gels are formed, as in the case of conventional hydrolysis of TEOS in acidic medium. It should be noted that, according to literature data, the formation of transparent gels is characteristic of gelation limited by hydrolysis of TEOS, while opaque gels are formed when the kinetics of hydrolysis is limited by condensation processes (5). The opacity of gels is believed to result from considerable branching in the case of condensation-limited gelation and does not imply any phase separation.

The enhanced rate of gelation in the presence of aluminum hydroxonitrate with higher x values indicates that aluminum-containing species take part in polycondensation processes, probably by attacking TEOS molecules. The relatively short gelation time made it possible to study the kinetics of this process by means of optical spectrophotometry. The temporal dependence of optical density vs time for aluminum hydroxonitrate solutions with $x > 1.9$ is shown in Fig. 2.

^{27}Al NMR data for initial aqueous solutions of aluminum hydroxonitrates are shown in Fig. 3. One can see that for $x \geq 2$, the narrow peak at 60 ppm appears on the spectra. This observation is in good agreement with the reference data (15–18, 20), and the maximum at 60 ppm is usually ascribed to aluminum in tetrahedral coordination. Comparison of NMR spectra shown in Fig. 3 with that of corresponding aquagels in Fig. 4 demonstrates that in the latter case peaks at 60 ppm appear for lower degrees of hydrolysis. This indicates that the additional amount of aluminum in tetrahedral coordination forms in the course of gelation. The maxima for aquagels at 60 ppm are characterized by a much greater linewidth, which is typical for aluminum in a heterophase. Thus, one can assume that

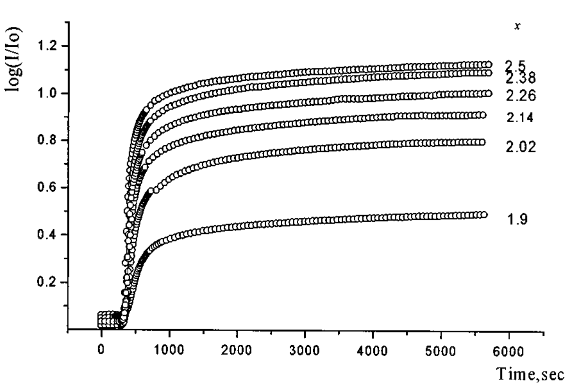

FIG. 2. Spectrophotometric studies of TEOS gelation kinetics in the presence of $Al(OH)_x(NO_3)_{3-x}$ solutions with different x at $\lambda = 600$ nm.

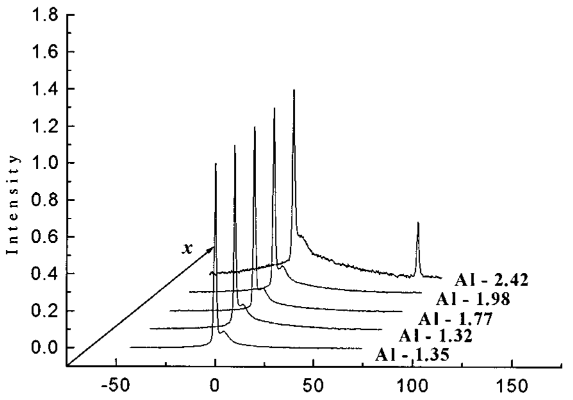

FIG. 3. ^{27}Al NMR spectra of a aluminum hydroxonitrates $Al(OH)_x(NO_3)_{3-x}$ with different degrees of hydrolysis x.

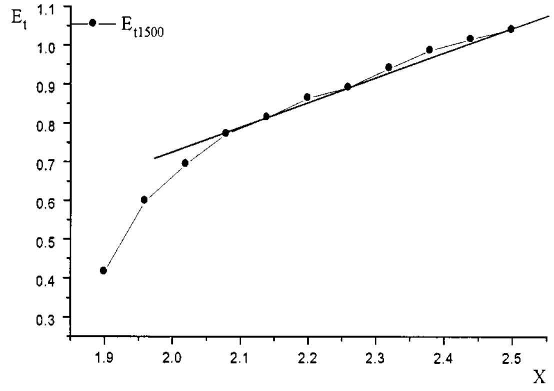

FIG. 5. Optical density E_{t1500} at $t = 1500$ s for the samples with different x.

tetrahedrally coordinated aluminum is incorporated into the silica network formed during polycondensation of TEOS. It should be noted that the maximum at 0 ppm corresponding to octahedrally coordinated aluminum exists on both series of the spectra. In both cases this peak remains narrow, indicating that octahedrally coordinated aluminum is present in a liquid phase. A relatively small peak at 4 ppm in Fig. 3 corresponds to oligomeric forms of aluminum hydroxocomplexes Al_3–Al_4 (15, 20). One can see that these forms do not appear in aquagels.

DISCUSSION

From data shown in Fig. 2 one can note that the temporal dependence of optical density in the course of gelation has the characteristic sigmoidal shape. The final optical density increases with the degree of hydrolysis of the initial aluminum hydroxonitrate solution. The dependence of optical density E_t measured at fixed $t = 1500$ s on the degree of hydrolysis x is shown in Fig. 5. We assume that the magnitude of E_{1500} is proportional to the degree of conversion in the polycondensation reaction in accordance with the Lambert–Beer law. One can see that for $x \geq 2$ the dependence is nearly linear. This fact leads to the assumption that certain aluminum species effectively participating in the gelation process are formed in the solutions with $x \approx 2$ and that their concentration increases linearly with x.

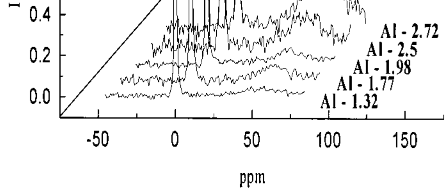

FIG. 4. ^{27}Al NMR spectra of aquagels obtained by copolymerization of TEOS with aluminum hydroxonitrates with different degrees of hydrolysis.

The dependence of the rate of polycondensation on the aluminum concentration in the aqueous phase was studied spectrophotometrically. In this case, we used solutions of aluminum hydroxonitrate with a constant degree of hydrolysis $x = 2.5$ and concentrations ranging from 0.05 to 1 M. The dependence of the reversed gelation time $1/\tau_{gel}$ on the aluminum concentration is shown in Fig. 6. Since the reversed gelation time is proportional to the rate of the reaction at the fixed degree of conversion, these data can be used to estimate the reaction order. The linear character of the dependence shown in Fig. 6 indicates that copolycondensation is the first-order reaction with respect to aluminum.

Activation energy of copolycondensation has been estimated by measuring gelation time as a function of temperature. The Arrhenius plot in coordinates $\log[1/\tau_{gel}] - 1/T$ is shown in Fig. 7. The value of activation energy was determined to be 72 ± 9 kJ/mol. It should be noted that according to the reference data (5), the activation energy for gelation of TEOS ranges from 40 to 80 kJ/mol depending on the pH value and the catalyst employed.

Thus, the spectrophotometric study of gelation kinetics demonstrates that aqueous solutions of $Al(OH)_x(NO_3)_{3-x}$ with $x \geq 2$ contain a cationic form of aluminum participating in polycondensation with TEOS. This reaction is of the

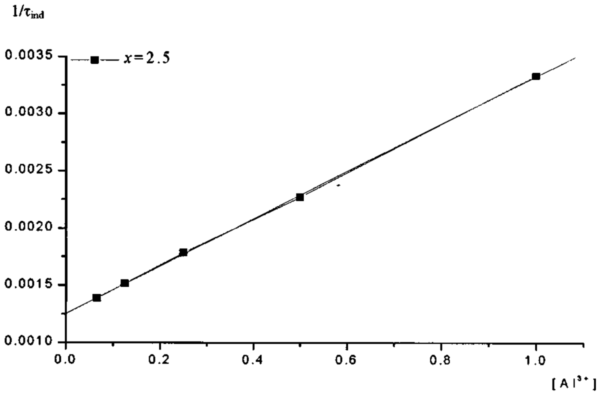

FIG. 6. Induction period of gelation as a function of aluminum concentration.

first-order with respect to aluminum. The value of activation energy obtained indicates that the process is reaction-limited rather than diffusion-limited.

It is well known that for acid-catalyzed hydrolysis of TEOS the limiting step is the nucleophilic attack of the water molecule on TEOS,

$$Si(OEt)_4 + xH_2O \rightarrow Si(OEt)_{4-x}(OH)_x + xEtOH, \quad [1]$$

while the following polycondensation of $Si(OEt)_{4-x}(OH)_x$ proceeds more rapidly:

$$2Si(OEt)_2(OH)_2 \rightarrow HO\text{–}[Si(OEt)_2]\text{–}O\text{–}[Si(OEt)_2]\text{–}OH + H_2O. \quad [2]$$

However, during hydrolysis in the presence of aluminum hydroxocomplex, the nucleophilic agent can be either the H_2O molecule or the OH^- group coordinated to the metal cation. According to the partial charge model (12, 13), the partial charge on the OH group in the H_2O molecule coordinated to the metal atom is necessarily higher than that in the noncoordinated water in the solvent and thus its nucleophilic strength is lower. However, the partial charge on the OH group directly coordinated to the metal can be lower than that in the free H_2O molecule and thus it can possess stronger nucleophilic activity.

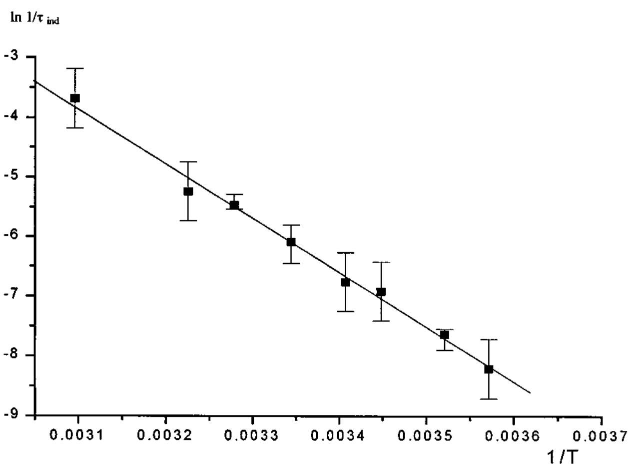

FIG. 7. Arrhenius plot for reversed induction period of gelation.

Since the reaction in the presence of aluminum hydroxonitrate follows the first-order kinetics relative to aluminum, the reaction mechanism should include the attack of aluminum-containing specimen on a TEOS molecule. Such an attack may result either in hydrolysis according to Eq. [1] or in condensation with the formation of Al–O–Si bonds,

$$Si(OEt)_4 + [Al(OH)_x(H_2O)_y]^{m+} \rightarrow EtO\text{–}[Si(OEt)_2]\text{–}O\text{–}[Al(OH)_{x-1}(H_2O)_y] + H_2O. \quad [3]$$

The sharp growth of gelation rate for the systems containing aluminum hydroxonitrates with $x \geq 2$ alcogels indicates the change of the limiting step of the reaction. Another argument for the change of the rate-limiting step is the drastic change in the optical properties of alcogels containing aluminum species with $x > 2$ (see previous section). It should be mentioned that formation of opaque gel is characteristic for base-catalyzed hydrolysis of TEOS, for which the rate-limiting step is known to be polycondensation according to Eq. [2] (5, 19). However, in the case of gelation of TEOS in the presence of aluminum hydroxonitrates the rate-limiting step is unlikely to be polycondensation according to Eq. [3] because of the constant value of induction periods of gelation (see Fig. 2). In our opinion, the rate-limiting step for the systems under investigation is *hydrolysis* of aluminum with formation of certain hydroxocomplexes active in copolycondensation with TEOS, while polycondensation itself proceeds relatively quickly. This hypothesis accounts for both the first-order reaction with respect to aluminum and the constant induction periods of gelation.

One can assume that aluminum species participating in the copolymerization reaction contain aluminum in tetrahedral coordination. Indeed, the enhanced rate of gelation is observed for aluminum samples with degrees of hydrolysis $x > 2$. At the same time, ^{27}Al NMR studies of the aluminum hydroxonitrate solutions in the absence of TEOS (Fig. 3) demonstrate that the peak at 60 ppm appears for degrees of hydrolysis $x > 2$. The increase in the intensity of this maximum for aquagels as compared to corresponding aqueous solutions indicates an increase in the amount of tetrahedrally coordinated aluminum (Fig. 4). The peaks at 60 ppm for aquagels are significantly broader than those in Fig. 3, due to the lower mobility and stronger effect of dipole–dipole interactions of aluminum incorporated in the gel network. At the same time, peaks at 0 ppm remain narrow. This means that aluminum in octahedral coordination exists in the liquid phase and is not incorporated into the gel network. These data are in good agreement with the assumption of the copolycondensation of TEOS and aluminum hydroxonitrate and suggest that all aluminum incorporated into the gel matrix is tetrahedrally coordinated.

According to the reference data (15, 16), the only well-characterized aluminum hydroxocomplex containing tetrahedrally coordinated metal atoms is the tridecanuclear complex $Al_{13}O_4(OH)_{24}{}^{7+}$ having a Keggin-type structure. The maximum at 60 ppm seen in ^{27}Al NMR spectra of partially hydrolyzed solutions is usually ascribed to this polycation (20). Thus, one can assume that this polynuclear hydroxocomplex is responsible for the enhanced rate of the polycondensation in the system TEOS–EtOH–$Al(OH)_x(NO_3)_{3-x}$ ($x > 2$). Indeed, the calculation of the partial charge on the external OH groups in $Al_{13}O_4(OH)_{24}{}^{7+}$ gives a negative value of the partial charge: $\delta(OH) = -0.051$. At the same time, the partial charge on an external OH group for the octahedral complex $Al(H_2O)_6{}^{3+}$ is positive: $\delta(OH) = +0.058$. Due to the higher nucleophilic strength of the OH group in $Al_{13}O_4(OH)_{24}{}^{7+}$, this complex attacks a TEOS molecule more readily. The tendency toward formation of Al–O–Si bonds in tetrahedrally coordinated aluminum species (14) ensures the stability of the resulting gel network.

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