

Transformation of Aluminosilicate Wet Gel to Solid State

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Optically clear, homogeneous, monolithic aluminosilicate gels were prepared directly from solutions of inorganic aluminum salt, tetraethoxysilane, and alcohol. The dried aluminosilicate gels show new special properties, e.g. piezoelectricity and variable porosity (1–2000 m²/g) due to the fractal-like gel structure. Ceramic products, which keep the chemical bonds and structure of the gels, were produced by heat treatment at 300–350°C. The processes that occurred during heat treatment were investigated by thermal analysis and mass spectrometry. The temperature limits of the gel state were determined by differential scanning calorimetry and small angle X-ray scattering. The collapse of the gel structure began around 350°C; however, the amorphous character remained until the temperature (ca. 970°C) of the phase transmission. © 2002 Elsevier Science (USA)

Key Words: aluminosilicate; gel; heat treatment; thermal analysis; SAXS; MS.

INTRODUCTION

The main purpose of this work was to prepare homogeneous amorphous aluminosilicate systems with aluminum content as high as possible. The aluminum content in the aluminosilicate systems prepared by a new sol–gel method was expected to significantly exceed that which can be achieved by traditional high-temperature melting methods (about 0.1 mole ratio of Al/(Si + Al) in glass (1–3). The ceramics with higher aluminum content may be used to produce highly efficient catalysts (4–6). The aluminosilicate systems prepared by our new sol–gel method show significant piezoelectric properties (7, 8). The Al atoms bonded to the gel network and the fractal-like gel structures play a deceive role for the piezoelectric property. With increasing number of bonded Al atoms, the piezoelectricity becomes more intense (8).

Homogeneous aluminosilicate systems with high Al content can be prepared from tetraethoxysilane and inorganic aluminum salt in organic medium by the new, low-energy-consuming sol–gel procedure. The effects of

preparation and chemical conditions on the gelation as well as the incorporation of Al atoms into the gel networks by chemical bonds were reported in previous papers (9, 10). Hydrolysis and condensation of aluminum nitrate and tetraethoxysilane in organic medium lead to an optically clear, elastic, monolithic, wet aluminosilicate gel. The final ceramic product can be obtained from the wet gel by heat treatment.

The aim of the present work was to study the processes of mass loss and phase transitions occurring under the drying and heat treatment of wet gels. The important task was to determine the temperature range of the gel state and the most suitable temperature required to form ceramics products remaining the gel structure. The standard methods used for the measurements were thermal analysis and mass spectrometry, the complementary methods were small angle X-ray scattering, X-ray diffraction, and different mass spectrometric methods.

EXPERIMENTAL

Preparation of Aluminosilicate Gels

The gels were prepared by a rapid sol–gel method, in one step without sol formation. Tetraethoxysilane (p.a. TEOS, Aldrich) and an aluminum salt (p.a. Al(NO₃)₃·9H₂O, Fluka) were dissolved in an organic solvent (p.a. 1-propanol, Aldrich). The composition used most frequently was: 1 mole TEOS, 1 mole Al salt, 6 mole 1-propanol, and 0–100 mole water. The gelation was performed by refluxing at about 80°C for 10–11 h. In a closed system this same process at 80°C required 20–22 h (9, 10).

Characterization Methods

Thermogravimetric (TG) and differential thermal analytical (DTA) signals were provided by a Mettler TA-1 thermoanalyzer. The derivative thermogravimetric (DTG) curves were numerically calculated using differentiation of smoothing splines from the TG data obtained in a

computerized data acquisition process. Experiments were carried out on ≈ 20 mg of sample measured in a 0.1 cm^3 alumina crucible and alumina powder used as reference material. The working gas was air at a flow rate of $\approx 75\text{ cm}^3\text{ min}^{-1}$ and 10 K min^{-1} heating rate was applied.

The thermal decomposition processes were studied by Balzers QMS 420 quadrupole mass spectrometer coupled to the thermoanalyzer via the GES 10 capillary inlet interface heated to about 120°C (TG-MS). The working gas was 6N helium at a flow rate of $85\text{ cm}^3\text{ min}^{-1}$. Mass spectral scans were made continuously at a scan rate of 100 ms amu^{-1} (atomic mass unit) and the electron impact (EI) mass spectra obtained at 70 eV were recorded.

Differential scanning calorimetry (DSC) measurements were carried out by Netzsch DSC 200 calorimeter equipped with data acquisition and evaluation system in flowing nitrogen atmosphere ($10\text{ cm}^3\text{ min}^{-1}$) at 10 K min^{-1} heating rate. The sample weight was $10\text{--}20\text{ mg}$ and a sintered Al_2O_3 crucible was used. The temperature and the heat flow response of the calorimeter were calibrated using 6N purity metals.

Gas chromatography and mass spectrometry (GC-MS) experiments were performed with a HP 5890 instrument on an ULTRA 25% phenylmethylsilicon column using a heating program between 40 and 100°C . The components were detected by a HP 5091 MS analyzer. Atmospheric pressure chemical ionization (APCI) MS was recorded on a VG QUATTRO instrument using ca. 1 weight% aqueous solutions. In APCI technique, the solutions are sprayed at high temperature by a hot gas flux, followed by discharge ionization. The solvent ions transfer protons to the sample molecules, thus the molecular ions appear at m/z (mass/charge) = $M+1$ (where M is molecular weight) in the spectrum.

For the small-angle X-ray scattering (SAXS) measurements, we used a 12-kW X-ray generator and a pinhole X-ray camera with variable distance ($20.5\text{--}98.5\text{ cm}$) from the sample to the two-dimensional detector. The gels were covered in vacuum-tight foil to prevent drying during the measurements. The two-dimensional spectra were corrected for parasitic pinhole scattering, as well as for the foil scattering, and then radially averaged to give the scattered intensity, $I(q)$, as a function of the scattering vector,

$$q = 4\pi \sin(\theta/2)/\lambda, \quad [1]$$

where λ is the incident X-ray wavelength (1.54 \AA) and θ the scattering angle between the incident and diffracted beam. The curves are interpreted on the basis of fractal theory [6]. In case of supramolecular ordering, Bragg reflections occur at low scattering angles. The position of a diffuse maximum has been used to estimate the corresponding periodic

distance as

$$d = 2\pi/q_{\text{max}}. \quad [2]$$

RESULTS

Identification of the Organic Compounds in the Gels

Beside the inorganic components (aluminosilicate network, nonbonded but partly hydrolyzed Al ions, and nitrate anions), organic compounds (solvent and reaction products) can also be found in the gels. Oxidation–reduction reactions take place between solvent (1-propanol) and HNO_3 molecules obtained from nitrate anions (11). The gel curried at 80°C to evaporate the free solvent molecules has a carbon content of $4\text{--}5\text{ wt } \%$. The products of reaction formed during the gelation and the heat treatment have been identified qualitatively by GC-MS and atmospheric pressure chemical ionization (APCI) MS experiments. According to GC-MS technique, the main component beside 1-propanol and ethanol is the propyl acetate in the wet gels indicating the formation of acetic acid from propanol by a strong oxidation process. APCI MS measurements of wet gels supported these results. APCI MS investigation of the dried gels has mainly found propanol ($M+1=61$), 2-hydroxypropionic acid (lactic acid, $M+1=91$), and the various esters of lactic acid: methyl 2-hydroxypropionate (105), ethyl 2-hydroxypropionate (119), propyl 2-hydroxypropionate (133), ethyl 2-ethoxypropionate (147), and propene (43) (Fig. 1). Besides lactic acid, oxalic acid can also be formed in further oxidation processes and it can be detected at the same “ $M+1$.” The presence of lactic acid was proved to be much more probable than that of oxalic acid by applying different MS techniques (APCI and ESMS).

Thermal Analytical and Mass Spectrometric Measurements

Thermal analytical and mass spectrometric investigations were intended to reveal the thermal processes by which the nitrogen and the carbon content of the gel products were reduced. The chemical composition of gels used in the measurements has been characterized by 4.5 mole ratio of water/(Al + Si). Figure 2 shows thermal analytical (TA) curve for wet aluminosilicate gel. The mass loss of wet gels occurs in two main steps. The first step of mass loss is mainly attributed to the evaporation of solvent, the second is rather due to the thermal decomposition of nitrate content on the basis of thermal analysis of pure $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The exothermic peak above 300°C observed on the DTA curves indicates an exothermic oxidation reaction (e.g. combustion of organic compounds) occupied with mass loss. At the heating rate of 10 K min^{-1} ,

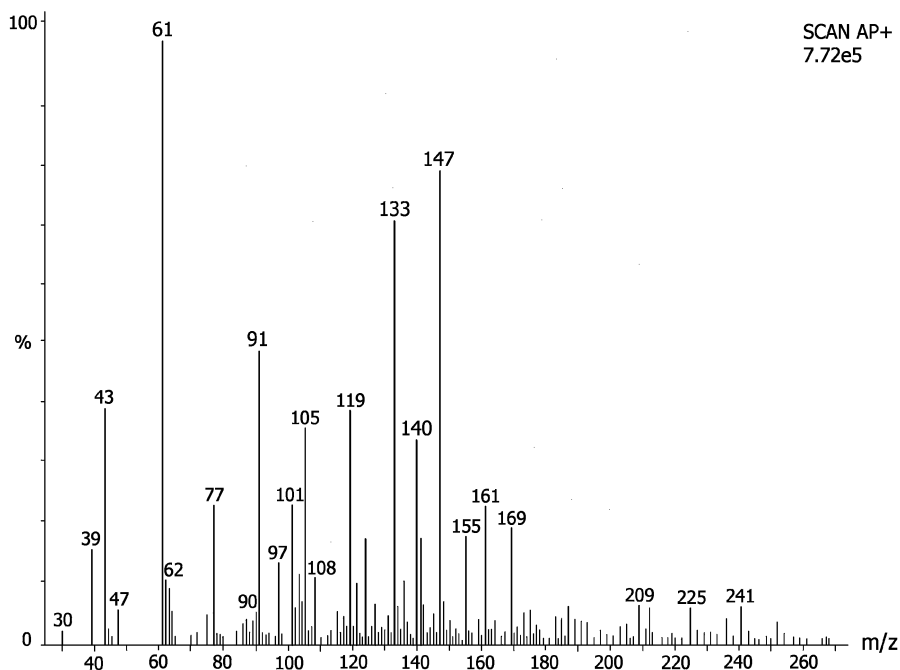


FIG. 1. APCI MS measurements of aluminosilicate gels with low water content (heat-treated at 100°C for 1 h).

the processes of mass loss occur below 500°C (Fig. 2). The exothermic peak between 970 and 980°C is attributed to the formation of crystalline mullite phase.

TG-MS measurements were performed to complete the thermal analysis. Figures 3 and 4 represent the removal of C-containing and N-containing fragments during the heating. The results of TG-MS investigation have been summarized in Table 1. The escape of C- and N-containing fragments occurs in two main steps supporting the results of thermal analysis. However, TG-MS measurements registered the third little step between 350 and 500°C more intensively than thermal analysis. The ratios of three steps detected by TG-MS are irrational. The ratio of first step is too low because the main part of free propanol content evaporates before the detection due to the evacuation at the beginning of measurements. CO₂ removes in the largest amount ($\approx 65\%$) at about 80–100°C. About 60% of CO molecules escapes in the second step, between 200 and 350°C. The majority of the CH fragments (e.g., C₂H₃⁺, C₂H₅⁺) evaporate from the gels below 100°C. The intensity of the thermal decomposition and the volatilization of N-containing fragments are highest at about 100°C (the first step) and the decomposition continues until 350°C in the second step. The water content evaporates in one step at $\approx 100^\circ\text{C}$.

The purpose of thermal analysis of aluminosilicate gels dried at different temperatures between 100 and 1500°C was to determine the temperature of the heat treatment required to dry the wet gels (Fig. 5). The heat treatment

took for 1 h in an open and closed sample holder, in an oven, the temperature changed between 100 and 1500°C increasing by 100°C steps. The mass of the heat-treated gel samples was 2–3 g. The chemical composition of gel used for the measurements was 1 mol TEOS, 1 mole crystalline

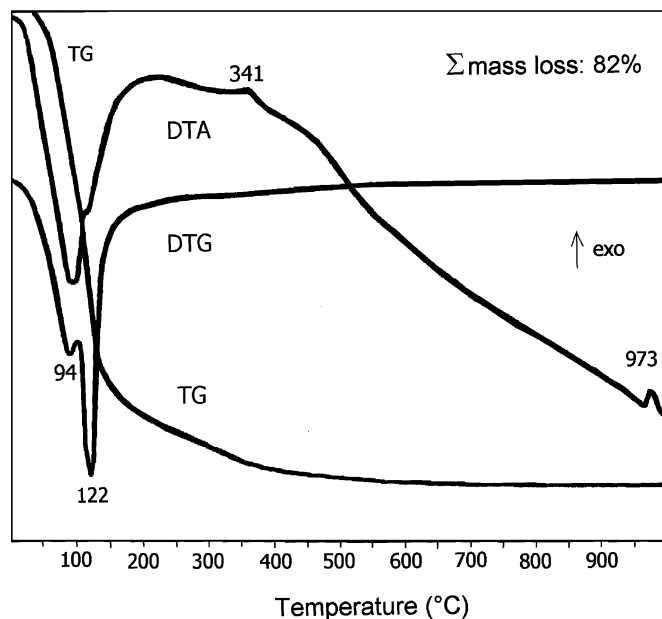


FIG. 2. Thermal analysis of wet aluminosilicate gel.

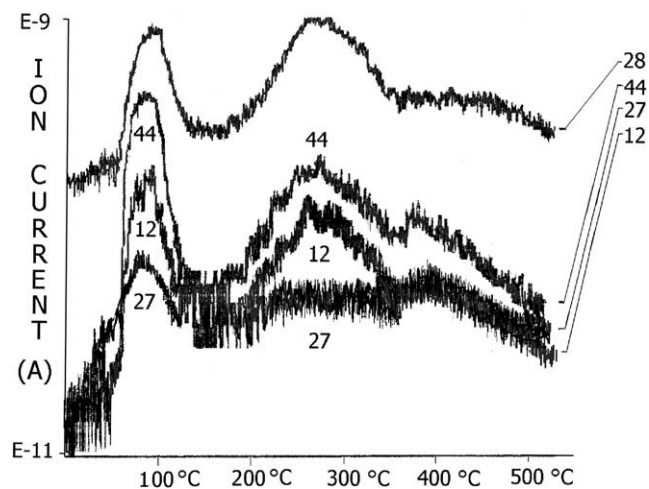


FIG. 3. Ion currents of C-containing fragments of aluminosilicate gels with low water content. 28: CO^+ , 44: CO_2^+ , 27: C_2H_3^+ as the most typical CH-fragments and 12: C^+ .

aluminum nitrate, and 6 mol 1-propanol. The 2 to 40-h heat treatments at 80°C in a strictly closed system caused no detectable change in the wet gels. At higher temperatures, $\geq 100^\circ\text{C}$, in a not strictly closed system, the results of the competing reactions can be detected due to the loss of the solvent and the other components (Fig. 5A). The concentrations of the reactants are necessary to achieve a characteristic value in the gels by mass loss. On the basis of the experiments, the concentration of the carbon content should achieve 4–5 wt % to speed up the reactions. Figure 6 represents the dependence of the reactions

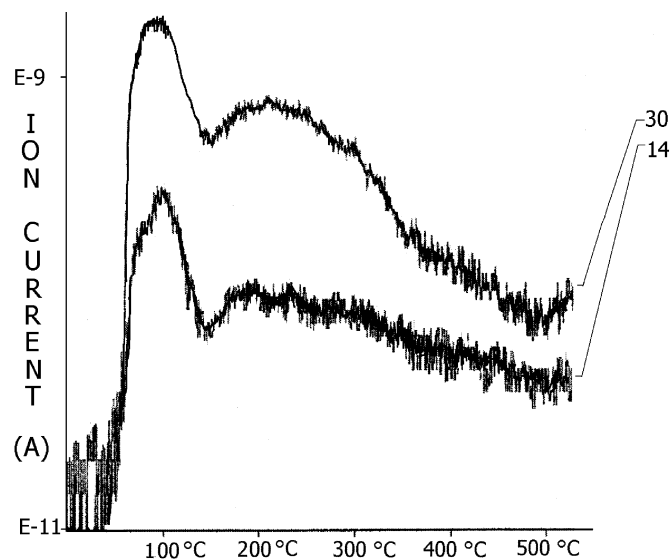


FIG. 4. Ion currents of N-containing fragments of aluminosilicate gels with low water content. 30: NO^+ and 14: N^+ .

TABLE 1
TG-MS Investigation of Wet Aluminosilicate Gels

Temperature ranges ($^\circ\text{C}$)	Mass loss (%)	Detected fragments in decreasing amounts
60–150	69 ± 3	H_2O^+ CO^+ CO_2^+ C^+ NO^+ N^+ C_2H_3^+ C_2H_5^+ (C_3H_5^+)
150–350	11 ± 1	CO_2^+ NO^+ CO^+ C^+ N^+
350–500	2 ± 0.5	CO_2^+ NO^+ CO^+ C^+ C_2H_3^+ (N^+)

Notes. Chemical composition of aluminosilicate gels used for measurements: 0.1 mole TEOS, 0.1 mole $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.6 mole 1-propanol. The time of heat treatment is 20 h at 80°C .

occurred by heating to 100°C on the water content of the gels. The duration of heat treatment was the same for every gel sample. The reactions are not intensive in the gel sample containing only crystal water of aluminum nitrate (Fig. 6A). The peaks on the DTA curve above 200°C are small. The intensity of reactions increases in the samples of about 5.5–7.0 mol water/(Al+Si) (Fig. 6B) and it diminishes in the samples of about 7.0–13.0 mole water/(Al+Si). In the samples of ≥ 14.5 mole water/(Al+Si), the reactions above 200°C , even the exothermic reaction, disappear (Fig. 6C). The processes of the drying and the escape of the reaction products are finished below 400°C (Fig. 5A). Any change cannot be observed on DTA and DTG curves of the gel sample dried at 400°C (Fig. 5B). Only the mass loss continues slightly between 400°C and 700°C .

Differential Scanning Calorimetric (DSC) Measurements

DSC measurements were carried out in the wide temperature range in order to determine the temperature range of the gel state (Fig. 7). Since the DSC curves for aluminosilicate gels above 20°C are very similar to the curves of thermal analysis, the Fig. 7 represents the DSC curves in the range between 20 and -70°C . Crystallization in the gel with low water content cannot be observed by DSC investigation above -70°C (Fig. 7B). Certain structural ordering can be detected below *ca.* -36°C in the gel samples of ≥ 24.5 mol ratios of water/(Al+Si) (Fig. 7A). X-ray diffraction (XRD) measurements were performed to determine the upper temperature limit of gel state. Similar to the thermal analysis, XRD measurements also proved the formation of crystalline mullite phase at *ca.* 960°C .

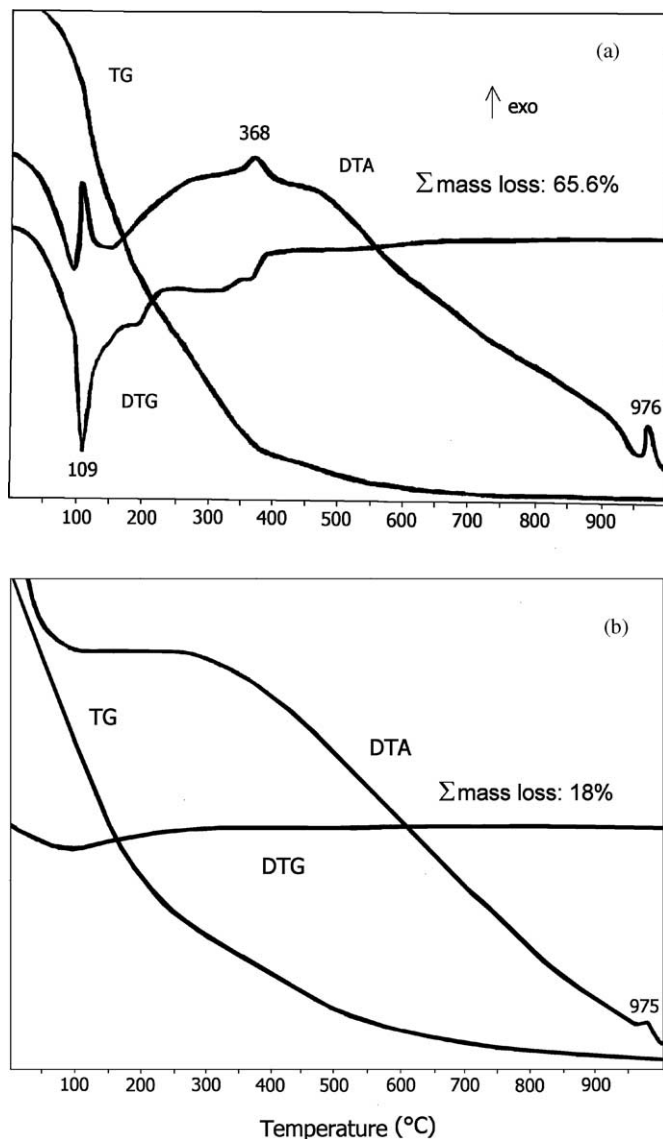


FIG. 5. Thermal analysis of aluminosilicate gels. A: dried gel (1 h at 100°C); B: dried gel (1 h at 400°C).

Small Angle X-Ray Scattering (SAXS) Measurements

The purpose of SAXS measurements was to determine the gel structure in the function of heat treatment. The heat treatments were carried out in a not strictly closed vessel for 1 h at different temperature between 20 and 800°C. The SAXS curves for wet (directly after the gelation) and dried (1 h at 300 and 400°C) aluminosilicate gels prepared at low water content are shown in Fig. 8. A linear region with slope of -2.0 ± 0.1 can be observed on the log-log plot of SAXS data for wet gel indicating a mass fractal as gel structure (11). On the curve for aluminosilicate gel dried at 300°C, an inflection point and a broad shoulder up to 0.5 \AA^{-1} appear after a linear region at about $0.02\text{--}0.125 \text{ \AA}^{-1}$

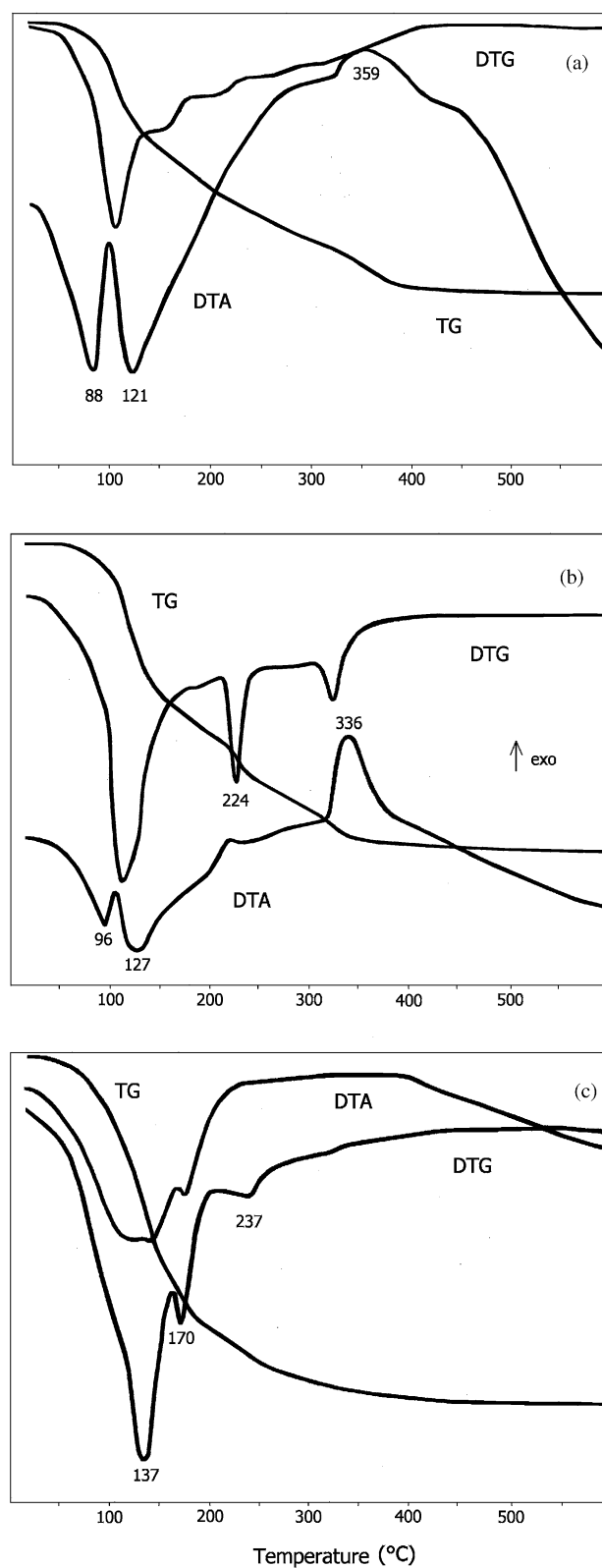


FIG. 6. Thermal analysis of dried (1 h at 100°C) aluminosilicate gels with various water content. A: 4.5 mol water/(Al+Si). B: 7.0 mol water/(Al+Si). C: 14.5 mol water/(Al+Si).

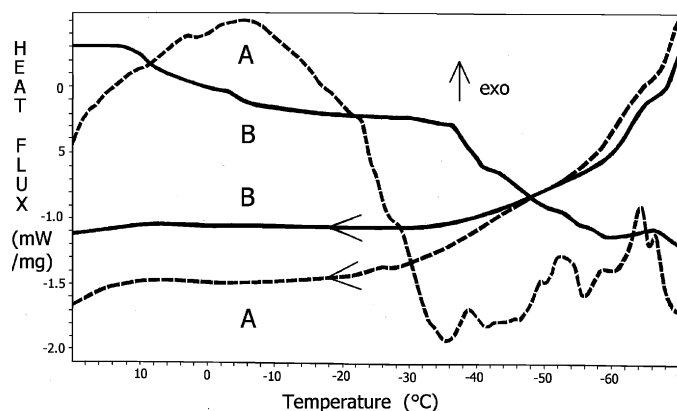


FIG. 7. DSC measurements of wet aluminosilicate gels with different water content. A: 4.5 mol water/(Al+Si). B: 24.5 mol water/(Al+Si).

with slope of -2.0 ± 0.1 . The distortion of the scattering curve is due to the modification of the fractal structure. On the curve for aluminosilicate gel dried at 400°C , broad peaks appear over the whole q -range of the measurement. The reflections on the scattering curve are attributed to structural ordering over a wide length scale (16–320 Å). The 230 and 43-Å corresponding periodic distances of structural ordering have been calculated from the position of diffuse maxima. The reflections on the SAXS curve indicate the collapse of the fractal structure. The heat treatment in an open system leads to the destruction of the fractal structure already at 100°C .

DISCUSSION

Chemical Processes of the Gelation and the Heat Treatment

The fundamental chemical processes of the gel preparation are the hydrolysis and the condensation reactions of TEOS and aluminum nitrate (9). During the gelation, there is no need for catalysis since the hydrolysis of Al nitrate provides the required acidic medium for the condensation reactions. The main role of 1-propanol is to dissolve the precursors (TEOS and aluminum nitrate) and to decrease the polarity of the system. The nitrate ions can be transformed into nitric acid molecules in a less polar medium and after that decomposed. Thus the decomposition of nitrate ions is promoted resulting in the decrease of acidity which causes hydrolysis reactions. During the heat

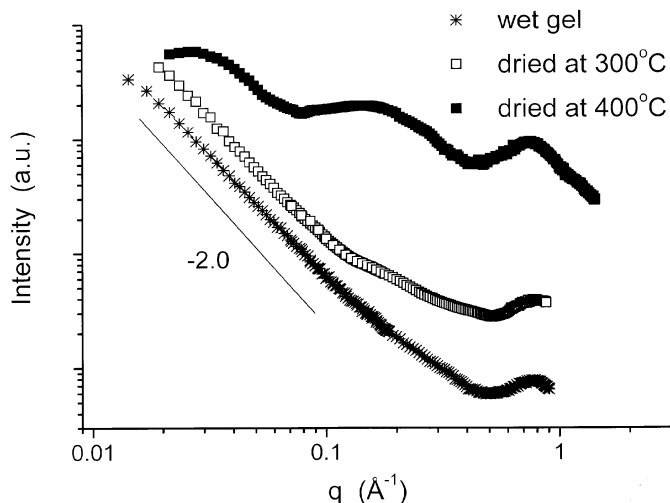
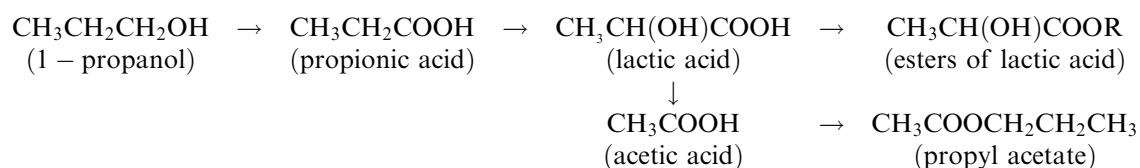


FIG. 8. SAXS measurements of wet and dried (1 h at 300 and 400°C) aluminosilicate gels with low water content.

treatment at 80°C , the decomposition of nitric acid molecules results in nitrous gases.

The nitric acid and/or its decomposition products in the larger concentration have a strong oxidation effect on 1-propanol. (In an earlier work, similar strong oxidation was observed upon treating 1-propanol with dilute nitrous acid, when oxalic acid formed (12).) The atmospheric pressure chemical ionization (APCI) MS and GC-MS investigation have found, besides 1-propanol and ethanol, propyl acetate as a main component in the wet aluminosilicate gels. Propanol comes from the solvent content of the gel, ethanol forms by the hydrolysis of TEOS, and propyl acetate should be the result of the oxidation processes of 1-propanol (and ethanol). APCI MS experiments have proved that further oxidation processes occur by the heat treatment $\geq 100^\circ\text{C}$ (Fig. 1). The thermal analysis has verified that the intensity of the oxidation processes depends strongly on the solvent concentrations in the gels (Fig. 6). The high solvent content hinders the reactions. The oxidation-reduction reactions occur mainly during the heat treatment. The mass loss contributes the oxidation processes because it helps to achieve a higher concentration of reactants (Fig. 6). The oxidation processes result in esters of lactic acid, lactic acid, and other oxidized products in the heat-treated gels (Fig. 1). An outline of the oxidation processes followed or accompanied by esterification reactions can be represented in the following:



[3]

Regarding the same upper temperature limit of the escape of N- and/or C-containing compounds, and of the gel state, the nonvaporizable organic compounds have a strong role in maintaining the gel structure. These organic compounds can establish connections around (as coordinated ligands) and probably between (as bidentate bridging ligands) the metal ions, especially Al ions. Our previous work proved the coordination of these organic compounds around and between Al ions in pure alumina gel (13).

Thermal Processes of Nitrogen and Carbon Compounds of Aluminosilicate Gels

Summarizing the thermal analytical investigations it can be established that the carbon and nitrogen containing compounds remove from the gel during the heat treatment not only in volatilization and decomposition processes but in oxidation process, too. The water evaporates as usual in one step, around 100°C. Carbon containing compounds remove in three steps from the gels on the basis of TG-MS measurements (Figs. 3, 4). Taking the thermal analysis for the basis to determine the real ratios of the three steps, 80–95% of propanol content volatilize in the temperature range of 80–100°C depending on the solvent (especially water) content of the initial gelling solutions. The remaining carbon content (5–20%) escape in two steps between 150 and 400°C in oxidation reactions. The escape of nitrogen content, which corresponds to that of carbon content (Figs. 3, 4), also proves that the oxidation processes of 1-propanol occur by the effect of N-containing compounds.

Temperature Range of the Gel State

According to the DSC measurements in the temperature range of 20–−70°C, the gels prepared with low solvent content keep the gel state until −70°C (Fig. 7). Only in the gel samples of ≥ 24.5 mole ratios of water/(Al+Si) can some ordering below ca. −36°C be observed. Phase transition (formation of mullite) can only be detected by XRD or thermal analysis at 960–970°C. Beside the mullite phase, a significant amount of the gel samples remains amorphous even above 1000°C. (It should be mentioned that the chemical composition (Al/Si mole ratio of 1) of gels used in these measurements is not favorable to forming mullite phase.) In spite of this the crystalline phase only appears at high temperature; this high temperature is not considered as an upper temperature limit of the gel state. According to the SAXS measurements, the modification of the fractal gel structure begins at ca. 300°C in the gel samples (Fig. 8). The gel structure collapses up to 400°C; however, the amorphous character remains. The heat treatment at 100°C results in the same decomposition using an open system. Long drying leads to the collapse of

the gel structure even at room temperature in several months in an open system. The gel sample kept in a strictly closed vessel maintains its fractal structure even in several years.

Temperature of Heat Treatment

Keeping the gel state is very important in developing the special properties (e.g., piezoelectric effect, variable porosity in wide range) that strongly belong to the gel structure (7, 8). On the basis of the above-mentioned results, the heat treatment should be carried out in a not strictly closed system in order to slow down the drying processes and retain the chemical bonds and the structure of the gel samples. The first step of the heat treatment should be a cure of the wet gels at 80°C to remove the main part of the free solvent. The most suitable temperature for further drying of the gels is around 300–350°C to produce ceramic products with the structure characterizing the gel state. Below 300°C, too many C- and N-containing compounds remain in the samples to loosen the structure. Above 350°C, the gel structure collapses. Amorphous materials having some structural ordering can be prepared by drying between 350 and 950°C in an open or closed system.

CONCLUSIONS

Optically clear, homogeneous, elastic, monolithic, wet aluminosilicate gel can be produced by hydrolysis and condensation of aluminum nitrate and tetraethoxysilane in organic medium. Under the heat treatment required to obtain aluminosilicate ceramic products from the wet gels, evaporation, decomposition, and oxidation processes occur. The large extent (80–95%) of organic solvent (propanol) escapes in volatilization processes from the wet gel. The remaining carbon-containing molecules (5–20%) reacts with the compounds of nitrogen resulting in formation of various oxidized products (e.g., propyl acetate as main product). The nonvaporizable organic compounds have a strong role in keeping the gel structure by their connections around (as coordinated ligands) and probably between (as bidentate bridging ligands) the metal ions.

The temperature ($\approx 970^\circ\text{C}$) of the phase transition cannot come into consideration as an upper temperature limit of the gel state. However, the amorphous character remains, the gel structure begins to collapse at 300°C, and the collapse completes at 400°C. Regarding the upper temperature limit of the gel state, the temperature of 300–350°C proved to be the most suitable for drying to obtain solid ceramic products with gel structure. Keeping the gel structure is very important for the new special properties (e.g., piezoelectricity, variable porosity over a wide range) those depend strongly on the fractal-like structure.

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