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ORIGINAL CONTRIBUTION

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Preparation of an aluminum oxo-hydroxide gel in organic medium

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Abstract A new method has been developed to prepare aluminum oxo-hydroxide containing spinnable material and gel. Partial hydrolysis of $Al(NO_3)_3 \cdot 9H_2O$ in 1-propanol at 78 °C produces a spinnable, viscous mixture. The role of the propanol in the hydrolysis proved to be to decrease the polarity of the solvent. In this medium the dissociation of nitric acid is driven back and it decomposes to nitrous gases resulting in the increase of pH in the solution. The conditions have been optimized to obtain the highest hydrolysis degree and to avoid precipitation of basic aluminum nitrate. The resulting optimal temperature is 76–80 °C, the time needed is at least 15 h in the case of a laboratory scale preparation. Increasing the ratio of propanol: water and the concentration of Al(III) to the maximum value, leads to the decomposition of 54% of the initial amount NO_3^- ion. By careful drying, the decomposition continues to about 70% and a solid foam comes into existence from the viscous mixture. This foam is able to swell in water, the degree of swelling in mass is about 10. The drying of swollen gel was examined. The spinnable mixture most likely contains polymer chains built up by H-bonds, the foam and the gel probably contain platelets.

Key words Sol–gel – hydrolysis – $Al(NO_3)_3$ – spinnability

Introduction

The main purpose of the present study was to develop a rapid method for the preparation of an aluminum oxo-hydroxide containing material that could, in turn, be used for obtaining a transparent alumina gel (bulk or spinnable). We also intended to prepare ceramic fibers, films or monoliths by further heat-treatment.

The aluminum oxo-hydroxide gels are two-component systems with an infinite network built up from Al, O atoms, OH-groups and water molecules. The network can be built up from ribbonlike fibers as well as monodisperse spherical particles, it can be microcrystalline and partially or totally amorphous (e.g. x-ray indifferent) depending on the preparation process [1]. The network can be the result of different chemical processes, however all of them require acidic or neutral medium. These methods are included in the so-called sol–gel techniques.

At this time, the most wide-spread sol–gel method for obtaining an alumina gel is the hydrolysis of *aluminum alcoholates* (*aluminum alkoxides*) in water. In the presence of *large* amount of water the first step of the mechanism is the hydrolysis of –OR group to –OH, finally aluminum oxide hydroxide precipitate forms [2]. This precipitate must be peptized to a clear sol and gelled with evaporation of the solvent. Little work has been carried out concerning *low* water: Al(III) ratios.

The main disadvantages of alkoxides as precursors are the too fast hydrolysis which can hardly be controlled, the

time-consuming peptization and the higher cost. Alkoxides are not suitable precursors for direct preparation of a spinnable mixture because of their far too fast gelation. Fibers can be prepared from a viscous liquid if the viscosity reaches a certain minimum value and remains constant for a long period of time. The latest efforts in this field are devoted to the development of methods which offer a possibility of control over the hydrolysis process [3,4].

The other method for the preparation of alumina gels is based on the hydrolysis of *inorganic salts*. It is well known that in the aqueous solutions of different Al^{III} salts basic materials cause the formation of aluminum oxide hydroxide precipitate in an amorphous form. The first step of this process is the hydrolysis and condensation of two hexaaqua complex ions to dimeric complex cations and after that to other oligomeric species:

$$2\,[Al(H_2O)_6]^{3+} + 2OH^- \rightarrow [(H_2O)_4Al\overset{OH}{\underset{OH}{}}Al(H_2O)_4]^{4+} + 2H_2O\,. \quad (1)$$

In the sol–gel processes to increase the concentration of the OH^- ion in the solution of $AlCl_3$ or $Al(NO_3)_3$, NH_3 is often used. The precipitate is peptized to form a clear sol which can be gelled by the evaporation of the solvent [5].

The hydrolysis with metal aluminum is a method currently used as well. Hydrolysis at higher temperature results in a sol containing fibrillar particles. This product can then be used for preparing fibers or films [6,7].

The main disadvantage of the inorganic aluminum compounds as a precursors is the presence of large amount of anions which incorporate into the gel and are hard to remove even by heating. To decrease the amount of anions, it is necessary to include a washing step [8].

In contrast to the alkoxide method, this procedure has not yet been successful in producing transparent monolithic gel.

We wished to find an inorganic salt that contains an anion which is unstable, and thus can be – at least partially – removed from the system easily. These criteria are fulfilled by both acetate or nitrate ions. The solubility of aluminum acetate in water is low, the mixture separates into two phases. Thus, $Al(NO_3)_3$ has been chosen as a precursor to prepare a spinnable mixture and to obtain a gel.

The purpose was to prepare the gel directly without precipitation and peptization. Therefore basic reagents cannot be used as hydrolyzing agents. The solution of the salt in pure water does not form gel even in the saturated state. Changing the solvent to propanol – the solubility of $Al(NO_3)_3 \cdot 9H_2O$ is excellent in it [9] – a spinnable viscous liquid forms and a transparent gel could be prepared by further treatment.

Experimental results

Materials and measuring methods

As a precursor we used puriss $Al(NO_3)_3 \cdot 9H_2O$, the solvent was a.lt 1-propanol. The determination of Al(III) was performed by complexometry, the NO_3^- ion was determined by measuring its n–π^* absorption maximum at 300 nm on Perkin–Elmer Lambda-15 UV-VIS spectrophotometer. The molar coefficient of extinction was $7.42 \pm 0.03\ mol^{-1}dm^3cm^{-1}$. This value was obtained by measuring standard solutions with altering NO_3^--concentration prepared from $Al(NO_3)_3 \cdot 9H_2O$ because of lack of data in the literature. Carbon content was determined by elemental analysis. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer.

Preparation of the gel

The process includes three main steps. First step is the hydrolysis of aluminum nitrate in 1-propanol at $\approx 80\,^\circ C$ with reflux. Interrupting the hydrolysis before the precipitation and evaporating the main part of the solvent an excellently spinnable viscous liquid can be directly obtained (Fig. 1). During further careful drying at 70 °C

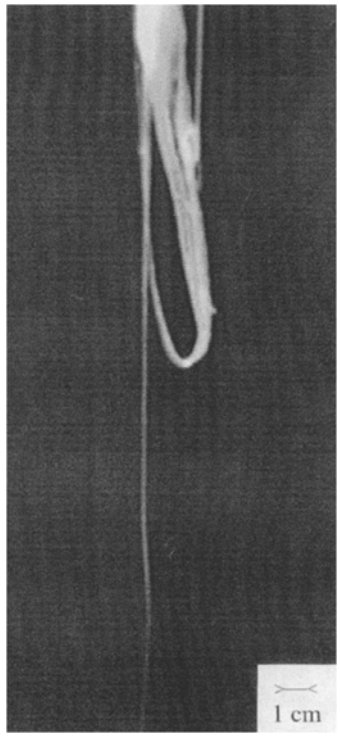

Fig. 1 The viscous, spinnable product

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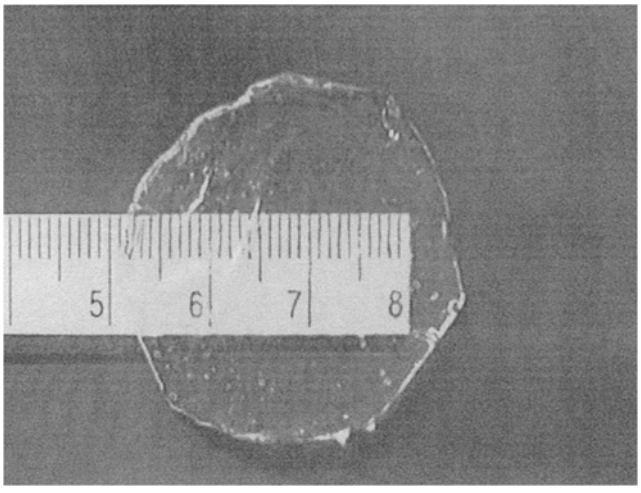

Fig. 2 The swollen gel

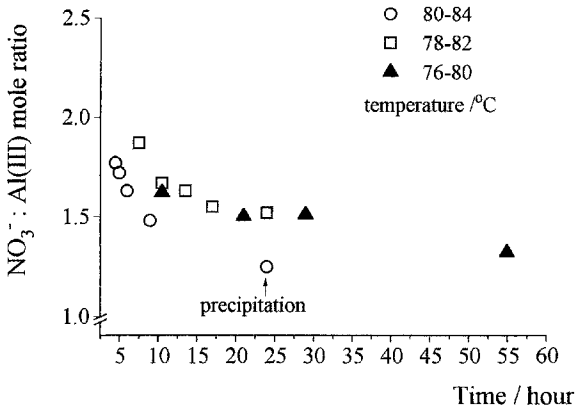

Fig. 3 Hydrolysis process of $Al(NO_3)_3 \cdot 9H_2O$ in 1-propanol at different temperatures

a solid foam with macroporous structure forms. This foam can swell in water and soft, generally transparent, slightly elastic gel comes into existence with the degree of swelling (mass ratio of the swollen gel and the solid foam) of about 10 (Fig. 2). At room temperature this gel gradually releases its water content; the result is a rigid, transparent, generally colorless dried gel.

The optimal conditions of the hydrolysis

Temperature

Aluminum nitrate is slightly soluble in C_1–C_3 alcohols at room temperature. At higher temperatures the solubility increases, dissolution becomes complete but at the same time the decomposition of NO_3^- ions begins by very intensive liberation of nitrogen oxides.

The optimum temperature range is about 76–80 °C because the higher the temperature the faster the reaction, but white gelatinous precipitate forms after 24 h in the case of about 100 g reaction mixture. At 78 °C this does not occur even after 48 h.

Time of the hydrolysis

For the characterization of the extent of hydrolysis we selected an easily measurable parameter, i.e., the mole ratio of the NO_3^- and Al(III) ions in the mixture. The lower the NO_3^- : Al(III) ratio the higher the (OH,O): Al(III) ratio. In about the first 5 h, the determination of NO_3^- ion is not possible because of the spectral interference due to other species (e.g. HNO_3, HNO_2, dissolved nitrous gases and even the reaction product of HNO_3 and propanol) in the solution. In this period the determination would have a large positive error (the measured NO_3^- : Al(III) ratio $\gg 3$). The change of NO_3^- : Al(III) mole ratio versus time in Fig. 3 shows that the rate of the reaction decreases considerably after some time. At 78 °C – in the case of about 100 g mixture – this time is 13–15 h. The mole ratio decreases after 24 and 48 h from 3 to 1.4 and 1.2 respectively at 78 °C in the reaction mixture with the optimal composition (see below). After this time a further considerable decomposition of the nitrate content cannot be observed but the possibility of the precipitation becomes more and more pronounced.

Based on these results the hydrolysis was carried out at 76–80 °C for 48 h (in some cases 24 h) because this way the highest hydrolysis degree could be achieved and we avoided precipitation.

The composition of the reaction mixture

We varied two parameters and measured their influences on the NO_3^- : Al(III) ratio (i.e., on the extent of hydrolysis) after a 24-h – long treatment at 78 °C. One parameter was the mole ratio of 1-propanol : H_2O which determines the polarity of the solvent (dielectric constant). The other was the initial concentration of the Al(III) (the amount of the NO_3^- ion is three times of this value).

The results are presented in Table 1 and in Figs. 4 and 5. It can be seen that decreasing either value causes the decrease of the decomposition of the NO_3^- ion, i.e., the extent of the hydrolysis. (It must be mentioned that the crystalline water of the salt as a minimum water content is a limiting factor for the achievable 1-propanol : H_2O ratio at a given concentration.) By this method the optimal 1-propanol : H_2O ratio was shown to be about 0.50 and

Table 1 The NO_3^-:Al^{3+} mole ratio in reaction mixtures with different compositions after 24 h treatment at 78 °C. " + " marks the compositions, which cannot be prepared from crystalline $Al(NO_3)_3$. The parameters which proved to be optimal are marked with bold frames

$c(Al^{3+})$ mol/dm^3	1-propanol:H_2O mole ratio						
	0.76	**0.55**	**0.47**	0.34	0.27	0.22	0.18
3.26	+	+	+	+	+	1.54	
2.6	+	+	+	1.44			
2.2	+	+	1.38				
1.9	+	1.40	1.46	1.59	1.69	1.78	1.98
1.7	+	1.55					
1.5	1.45	1.61	1.61	1.68	1.88	1.98	2.09
1.3		1.68					
1.1		1.91					
0.9		2.01					

initial concentration of the Al(III) about 2.0 mol/dm^3 (see Table 1).

The result of this hydrolysis process is a slightly viscous liquid that could only be drawn or gelled after evaporating some part of the solvent.

Further treatment of the hydrolysis product

Evaporation of the solvent

We examined the hydrolysis products prepared by the optimal composition. The further treatments were performed on different scales, by various drying procedures.

The structure of the obtained product is influenced by the temperature and the time of distillation i.e., the amount of the removed solvent. First a spinnable mixture can be obtained whereas after extended drying a solid foam forms.

At room temperature and atmospheric pressure the mass of mixture gradually decreases and reaches a constant value after some weeks, the exact time depends on the mass and the surface area of the sample. The same decrease in mass can be attained by about 15-min distillation in vacuum at 60 °C as well. The decrease of mass is about 50% in this period of the drying, while the consistence of the product becomes very viscous and spinnable. It can be characterized chemically, for example, by the equivalent Al_2O_3 content and the ratio of NO_3^- and Al(III) ions (Table 2). It is noteworthy that the Al_2O_3 content, i.e., the chemical compositions of the spinnable products prepared by various procedures are almost the same. On the basis of this fact, the spinnability could be linked to a definite composition. Carbon content measured by elemental analysis indicates the presence of some organic residue

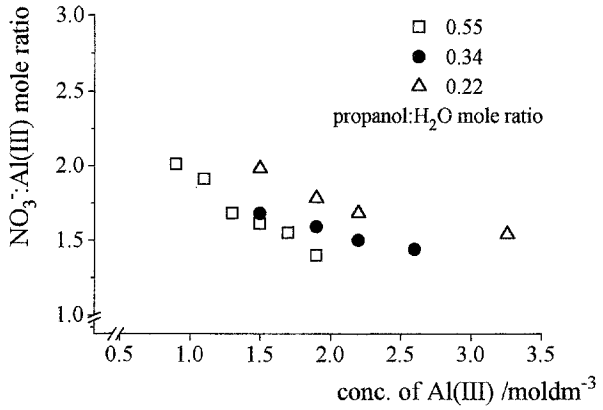

Fig. 4 Dependence of the NO_3^-:Al(III) mole ratio on the inital concentration of Al(III). The mixtures with different compositions were treated at 78 °C for 24 h

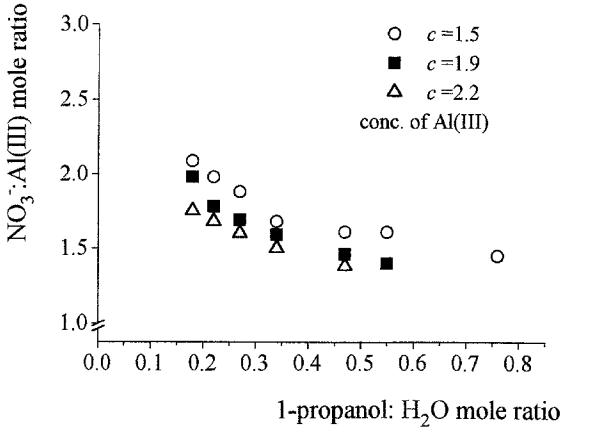

Fig. 5 Dependence of the NO_3^-:Al(III) mole ratio on the 1-propanol: water mole ratio. The mixtures with different compositions were treated at 78 °C for 24 h

(Table 2). The compounds can be propanol, propyl formiate, acetate, propionate, propyl nitrate and ethers in small amount, all of which proved to be present by capillary gas chromatography – mass spectrometry, infrared and ultraviolet absorption measurements [10]. The amount of the C-atoms is about 18% of the initial value.

During further careful drying at ambient pressure and 70 °C the viscosity increases and a foam-like structure forms – in this state the spinnability is excellent. (Fibers of more than 20 cm length and about 0.1 mm thickness can be drawn with a glassrod.) Finally, the spinnable foam solidifies. This solid foam is fragile, its skeleton is transparent. During this period the mass of the solid foam further decreases to about 30% of the initial value. The chemical composition of the solid foam varies in a greater interval than in the case of the spinnable mixture depending on the remaining water content. The amount of the carbon and

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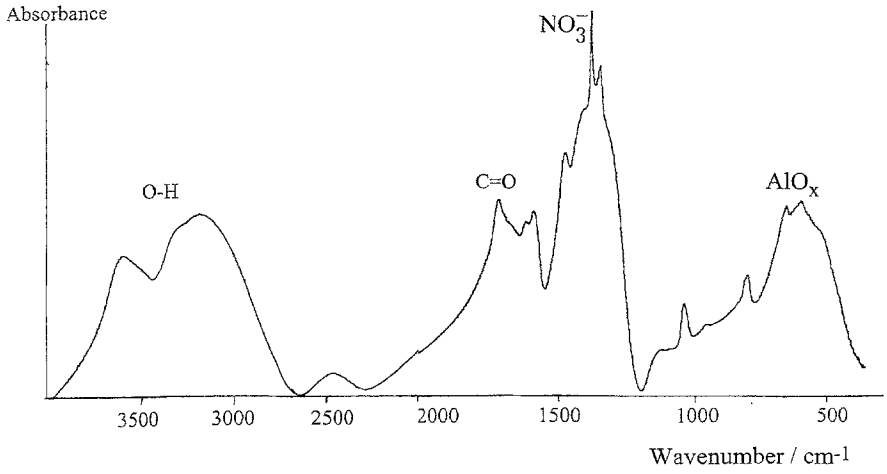

Fig. 6 Infrared spectrum of a solid foam in KBr pellet

the NO_3^- ion decreases. On the basis of elemental analysis and infrared spectroscopy organic residues (e.g. acetate groups) resulting in a 5% carbon content of the solid foam could be detected (see Fig. 6).

Swelling in water and drying of the swollen gel

The solid foam is soluble in water, the solubility depends on the drying process, but after some hours a slightly elastic transparent or opaque gel forms which is not spinnable. The maximum degree of swelling in mass is about 10. The swelling and gelation in 0.001, 0.01 and 0.1 mol/dm^3 HCl solution slows down as compared to that in water, it takes more and more time respectively, but the degree of swelling is similar. (In basic solutions a precipitation occurs.)

We examined the solubility of the solid foam in other solvents as well. We found it to be partially soluble in methanol, ethanol and glycol but gel did not form in any of these cases. In acetone and propanol the solubility is very low.

The chemical composition of these gels depends on the amount of the swelling water, at the maximum degree of swelling the equivalent Al_2O_3 is 3 (Table 2).

The mass and the volume of the gel obtained decrease to a great extent in an open vessel at ambient temperature and pressure, and finally the removal of the total amount of the swelling water can be observed. In Fig. 7 the extent of drying versus time can be seen in cases of gels with different degrees of swelling. First, the decrease of mass is linear when the water evaporates by diffusion. After a breakpoint on the curve the slope decreases due to the changed mechanism of evaporation. Because of the shrinkage of the network the water can liberate through the capillarities while the decrease of the total volume stops.

Table 2 Chemical composition of different products during the preparation process. The initial 1-propanol: H_2O ratio was 0.5, the conc. of Al(III) 2.0 mol/dm^3. The viscous product was analyzed when it reached the constant mass at room temperature. In contrast the swollen gels were examined at the highest degree of swelling

	Equ. Al_2O_3 Content m/m%	NO_3^- : Al(III) ratio	Carbon content m/m%
Reaction mixture	8.0	3.0	25.5
Viscous product	20 ± 0.6	1.2 ± 0.03	9–10
Solid foam	27 ± 3	0.90 ± 0.09	4–6
Swollen gel	3–6	0.90 ± 0.09	< 1*

* Estimated value.

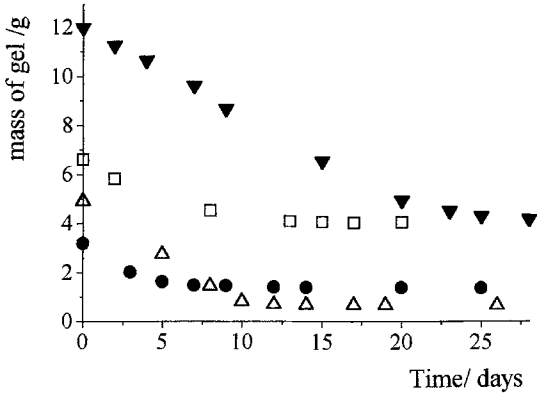

Fig. 7 Decrease of mass during drying of swollen gels with different degree of swelling and initial mass

During the first step of the drying process cracking may occur in a glass container due to the strong interaction between the gel and the glass-wall, it can easily be prevented by use of a plastic vessel. However at the second step the cracking can hardly be avoided.

It is remarkable that in spite of the fact that during drying the total amount of swelling water evaporates, the foam does not reform. This dried gel can swell in water as well. The obtained monolith is hard but breaks easily.

Heat treatment of the dried gel

With heating the material up to 800 °C it remains amorphous based on powder XRD measurements; above this temperature it crystallizes to γ-, δ- and finally α-Al_2O_3. During the measurements carried out on thermogravimeter-mass spectrometer one can observe the removal of N and C content in two main steps, at about 100° and again at 300 °C, the total amount of the NO_3^- ion and the organic groups are removed by heating up to 500 °C. On the basis of IR measurements the formation of the AlO_x groups begins above 300 °C. The result of the heating in air is a powder that could be sintered to obtain monolithic ceramic body.

Conclusions

A transparent excellently spinnable aluminum oxo-hydroxide containing material has been prepared directly – that is without precipitation and peptization – by partial hydrolysis of $Al(NO_3)_3 \cdot 9H_2O$ in propanol.

The conditions have been optimized to attain the maximum degree of hydrolysis and to avoid the precipiation. These aims are best satisfied with the temperature 78 °C and 48 h of reaction time. The chemical composition of the spinnable viscous product obtained after the evaporation of the solvent is characteristic and very well reproducible; it contains 20 m/m% equivalent Al_2O_3, and the NO_3^- : Al(III) ratio is 1.2.

The assumed role of propanol in the hydrolysis is to decrease the polarity of the solvent [11]. The dissociation of HNO_3 is driven back in a less polar solvent. During heating the decomposition of NO_3^- ion begins, indicated by formation of nitrous gases. This process is accompanied by a pH increase according to the following reactions:

$$NO_3^- + H_3O^+ = HNO_3 + H_2O \quad (2)$$

$$2HNO_3 = 2NO_2 + 1/2O_2 \cdot \quad (3)$$

Thus, the decomposition of HNO_3 to nitrous gases induces the hydrolysis and condensation of Al(III) ions. In water the extent of this process is very small even at high concentrations of aluminum nitrate (at 80 °C max. 1% of NO_3^- content decomposes). In propanol less than 30% of the NO_3^- anions remain in the system after the drying, so the usual washing step for removing the major part of the anions is not necessary. The other 70% converts to nitrous gases during the hydrolysis and the drying, and a part of the initial N-content probaly exists in the gel as organic compounds, for example, propyl esters and propylnitrate. These compounds must be produced by the reaction of propanol with HNO_3 or nitrous gases as oxidizing agents.

The spinnability of the viscous mixture produced by hydrolysis can refer to existence of a chain-like structure [12]. The connectivity in the chain is probably maintained by shared OH^- ions and water molecules between the Al(III) ions and by H-bonds between the external OH groups and H_2O. This is indicated by the good solubility in water and the existence of different bonded OH-groups in the infrared spectrum of the solid foam (indicated by wide IR absorption of O–H bonds at higher energy, Fig. 6). The applied conditions (low pH, high concentration of Al(III), low water activity) are supposed to induce linear condensation of the Al(III) ions. This means that the condensation processes illustrated in Eq. (1) results in forming of a linear polycation instead of a planar structure [13].

During drying a fundamental change in the structure must take place, since the spinnability decreases gradually and the ability of network-forming increases. One possible explanation is that the condensation continues during drying, platelets form from the fibers and the system of this platelets can produce a gel in water.

By swelling a transparent monolithic gel can be obtained which is not spinnable due to its three-dimensional network. The gels with high degreee of swelling remain monolithic during the release of their water content, cracks generally occur only at the end of drying. During drying the gel loses the total amount of the swollen water, but the initial foam does not reform. This swollen gel could be the precursor – by suitable drying method – of the preparation of a ceramic body.

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