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Chemical processes involved in the sol–gel preparation of an aluminium oxohydroxide gel from aluminium nitrate in organic medium

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Hydrolysis of aluminium nitrate in propan-1-ol leads to an aluminium oxohydroxide optically clear spinnable material as well as a slightly elastic, monolithic gel. The propanol has several roles in the hydrolysis. It dissolves the Al nitrate, induces the decomposition of the nitrate ions through nitric acid and promotes the hydrolysis and condensation of Al^{III}. Furthermore it reacts with nitric acid and/or its decomposition products resulting in formation of various oxidised derivatives of propan-1-ol. The products of the gel preparation, *i.e.* the organic compounds formed during heating of the aluminium nitrate–propan-1-ol mixture were investigated by gas chromatography as well as tandem MS techniques and UV–VIS spectroscopy. The coordination sphere of Al^{III} and the role of the organic compounds in building up the gel network has been studied by ^{27}Al MAS NMR and IR spectroscopy.

Introduction

The main aim of our research is to prepare refractory alumina fibres and ceramic monoliths by sol–gel methods that can replace high energy consuming melting technology. The basic step in the sol–gel preparation of alumina is the preparation of a gel containing aluminium oxohydroxide.

The widespread method to produce Al oxohydroxide gels is *via* hydrolysis of aluminium alkoxides.[1] The disadvantage of this precursor is the too fast hydrolysis that is difficult to control. In the first step of the preparation boehmite precipitates which has to be peptized to turn it into a sol. A transparent gel can be obtained from the sol by evaporation of the solvent. Another preparation procedure is to increase the pH in a solution of an inorganic Al salt by NH_3 or Al metal[2,3] which can result in a gel-like material in one or two steps. In this case the main problem is the large amount of anion that remains in the gel and this method generally does not yield a transparent gel.

In our work we have chosen inorganic Al salts as the starting material, since to produce spinnable (from which fibres can be drawn) product the hydrolysis should be controllable and precipitation must be avoided. It was also required that during the hydrolysis step the anions escape from the system to the largest possible extent. Nitrate, which decomposes readily, proved to be convenient in this respect, moreover the solubility of crystalline aluminium nitrate is high. We found that crystalline aluminium nitrate can be hydrolysed in propan-1-ol without precipitation. In absence of any basic agent, strong spontaneous hydrolysis of Al^{III} takes place in this alcohol–water mixed solvent. This hydrolysis method has rarely been mentioned in the literature. According to the interpretation of Akitt,[4] in such a medium the dissociation of nitric acid is disfavored resulting in a decrease of acidity in the system. Decreasing acidity will induce hydrolysis of Al^{III} and the subsequent condensation processes [eqn. (1) and (2)].

$$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(OH)_n(H_2O)_{6-n}]^{(3-n)+} + n\ H_3O^+ \qquad (1)$$

$$2\ [Al(H_2O)_5(OH)]^{2+} \rightarrow [Al_2(OH)_2(H_2O)_{10}]^{4+} \qquad (2)$$

However in an alcohol–aqueous medium the above processes may differ. The majority of nitrate escapes from the system as nitrous gases formed by decomposition of nitric acid.

Experimental

Materials and methods

As precursor we used puriss $Al(NO_3)_3 \cdot 9H_2O$ and the solvent was p.a. propan-1-ol. The determination of Al^{III} content was performed by complexometry, while the NO_3^- ion was determined by measuring its absorption maximum at 300 nm on a Perkin-Elmer Lambda-15 UV–VIS spectrophotometer. Carbon content was investigated by elemental analysis. Gas chromatography mass spectrometry (GC–MS) experiments were carried out with a HP 5890 instrument, on an ULTRA 2 5% phenylmethylsilicon column using a heating program from 40–100 °C. The components were detected by a HP 5091 MS analyser. Atmospheric pressure chemical ionisation (APCI) MS and electrospray (ES) MS spectra were recorded on a VG QUATTRO instrument using *ca.* 1 weight% (wt%) aqueous solutions. In APCI, the solution is sprayed at high temperature by a hot gas flux, followed by a (crown) discharge ionisation. The solvent ions transfer protons to the sample molecules, thus the molecular ions appear at m/z (mass/charge) = M + 1 (where M is the molecular weight) in the spectrum. For ES ionisation the experiment is performed at low temperature. Owing to the high voltage, the charged species leave the solution, and can be detected at m/z = M. The structure of the positively charged ions, formed by both ionisation processes, were determined after a second collision induced fragmentation (CID).

Thermogravimetric (TG) and TG–MS experiments were performed in an He atmosphere, with a Mettler instrument connected to an electron impact ioniser and a quadrupole MS analyser. Using the TG-MS mode gases liberated during heating can be detected. The gas molecules are ionised and fragmented and fragment ions are detected in an m/z analyser. Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch DSC 200 instrument in an N_2 atmosphere. In all experiments the heating rate was 10 K min^{-1}.

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^{27}Al MAS NMR measurements were carried out at room temperature on a Bruker Avance DRX-500 NMR spectrometer (11.70 T) at 130.3182 MHz; a 52 mm BB{1H}CP MAS probehead was used with a 7 mm ZrO_2/Kel-F rotor. After a 10 μs X pulse (flip angle *ca.* 90°) data were acquired during 125 ms followed by a 1 s relaxation delay. 128 FID were accumulated with a typical spectral width of 65360 Hz (501.05 ppm). Data processing parameters: line broadening 30 Hz, real spectrum sizes 16 K data points. ^{27}Al chemical shifts were recorded with respect to $[Al(H_2O)_6]^{3+}$ as an external reference. The IR spectra were recorded on a Bruker IFS 55 FT-IR spectrometer over the range 400–4000 cm^{-1} using the normal KBr method.

Gel preparation

The gel preparation steps[5] are shown in Fig. 1. The hydrolysis product (A) obtained after distillation of the majority of the solvent (step 1/b) is spinnable. During careful drying (step 2) the spinnability first improves, the viscosity increases and finally the viscous mixture (A) transforms into a solid transparent material (B). By adding water to product B, a slightly opaque hydrogel (C) can be obtained. At room temperature the hydrogel dries spontaneously while becoming optically clear resulting in formation of a glasslike xerogel (dried and shrunk gel) as end product.

During previous work[5] the preparation method was optimised to obtain, without precipitation, the highest hydrolysis degree of Al^{III} (OH/Al^{III} mole ratio), *i.e.* a low as possible nitrate content. In step 1 the maximum decomposition ratio (60%) of the nitrate ions can be reached using propan-1-ol and $Al(NO_3)_3{\cdot}9H_2O$ in a 4.5:1 mole ratio and a 48 h reaction time at 75–80 °C under reflux. During step 1/a, which is accompanied by an significant formation of nitrous gases, the weight of the mixture decreases by 10%. At step 1/b the decrease in weight is a further 50% and 81% of the initial carbon is removed. During step 2 the nitrate content decreases further and finally the NO_3^-/Al^{III} mole ratio reaches 0.85, *i.e.* only *ca.* 30% of the initial amount of nitrate remains in the system. The carbon content in product A and B is 19 and 6% of the initial amount, respectively. The chemical compositions of the products are listed in Table 1.

Table 1 Chemical composition and relative weight of different products during the gel preparation

	molar composition					
	Al	N	C	H	O	relative weight (%)
reaction mixture[a]	1.0	3.0	13.5	54	22.5	100
product A	1.0	1.2	2.6	15.5	13.8	40
product B	1.0	0.85	0.82	7.9	8.8	28

[a] The reaction mixture contains $Al(NO_3)_3{\cdot}9H_2O$ and propan-1-ol in 1:4.5 mole ratio.

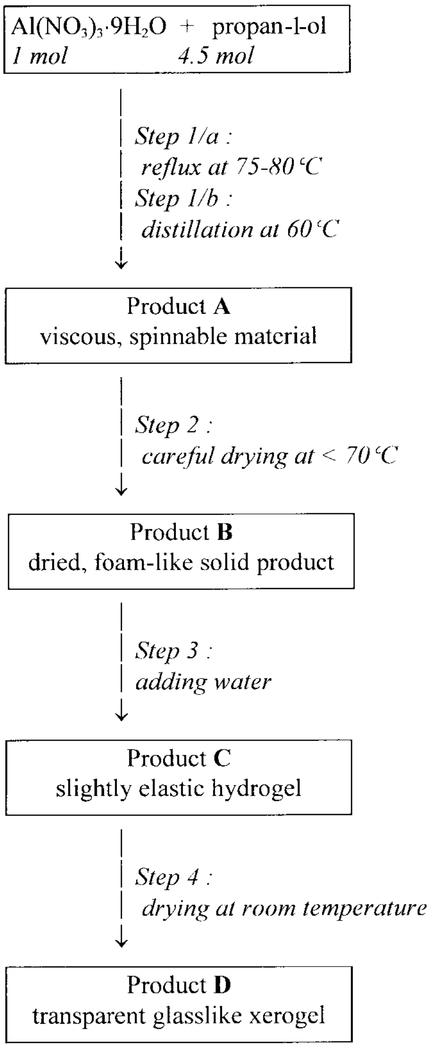


Fig. 1 The preparation process of aluminium oxohydroxide gel from aluminium nitrate in propan-1-ol

Results

Hydrolysis of aluminium nitrate in different alcohols and at various temperatures

To reveal the role of propan-1-ol and the chemical reactions taking place during the gel preparation, the process was performed under several different conditions. Beside the 'standard' method using propan-1-ol at *ca.* 75 °C, methanol and ethanol were used at 75 °C and propan-1-ol at 65 and 55 °C. As shown in Table 2, products after step 1 and 2 are characterised by the NO_3^-/Al^{III} mole ratio which gives an indication of the degree of hydrolysis of Al^{III}. The maximum water content of the hydrogel formed in step 3 is denoted by H, where $H=(m_{\mathrm{gel}}-m_{\mathrm{dry\ solid}})/\,m_{\mathrm{dry\ solid}}$. The solubility of aluminium nitrate in different alcohols strongly depends their polarity. The solubility of $Al(NO_3)_3{\cdot}9H_2O$ in 100 g of water, methanol, ethanol and propan-1-ol corresponds to 330, 207, 103 and 54 g while in butan-1-ol two phases separate. Above *ca.* 50 °C the decomposition of nitrate ions is appreciable in each case. At 75 °C in propanol the decomposition of nitrate after step 1 reaches 60%, in ethanol is 55% while in methanol only 25% of the initial nitrate content is lost. Moreover, when using methanol precipitation occurs in product A after some time. After the drying process (step 2), during which nitrate decomposes further, the difference between the products B prepared in ethanol or propan-1-ol decreases. In contrast to the similar degree of hydrolysis of the two products, their swelling in water differs markedly. The maximum H value in the hydrogels is 9 for preparation in propanol but is only *ca.* 1 when using ethanol.

The temperature was varied between 55 and 80 °C, while above 80 °C precipitation occurs.[5] The minimum temperature at which a clear solution can form in a reasonable time from an 1:4.5 aluminium nitrate propan-1-ol mixture is 55 °C. However the gel can not be prepared directly at this temperature as precipitation occurs after step 1. Upon treating the mixture at 65 and 75 °C the gel preparation process can be completed. On the basis of the NO_3^-/Al^{III} mole ratio, the decomposition of nitrate ions in step 1 can be determined and is 50 and 60% at 65 and 75 °C, respectively while after step 2 the extent of decomposition is very similar, 70 and 72%. The maximum H value of hydrogels do not show large differences between 65 and 75 °C. Large amounts of N=O containing compounds are observed by UV–VIS in the hydrolysis mixture prepared at 55 °C (spectrum not shown).

Table 2 Gel preparation under different conditions

	preparation condition			characterisation		
				NO_3^-/Al^{III} mole ratio		
solvent	T/°C	alcohol/H_2O mole ratio	$[Al^{III}]$/mol dm^{-3}	product A	product B	max. H value in product C
propan-1-ol	75	0.5	2.0	1.2	0.85	9
propan-1-ol	65	0.5	2.0	1.5	0.90	8
propan-1-ol	55	0.5	2.0	—[a] (precipitation)	—	—
methanol	75	0.5	3.0	2.3 (precipitation)	—	—
	75	1.11	2.0	3.0	—	—
ethanol	75	0.5	2.4	1.4	0.90	0.7
	75	0.7	2.0	1.5	0.90	0.9
	75	1.10	1.4	1.8	0.90	0.8

[a]The nitrate content could not be determined.

Organic compounds in the system

Organics in the distillate (GC-MS and UV–VIS). The overall composition of the distillate (obtained in step 1/b) has been determined qualitatively by GC–MS and results are shown in Table 3. The main component besides propan-1-ol is propyl acetate indicating the formation of acetic acid from propanol by a strong oxidation process.

For complementary results the UV–VIS spectra of the distillates (without dilution) were also recorded (Fig. 2). Above a broad band over the range 200–300 nm, an absorption band around 356 nm with a very characteristic vibrational structure can be observed and can be assigned to an R—ONO group, likely to be propyl nitrite a non-oxidised derivative of propanol. The distillate of the hydrolysis mixture treated at 55 °C has been found to contain the largest amount (*ca.* 2–3%) of this compound.

Organics in the gel products (tandem MS techniques). The spinnable viscous product has a carbon content of 10 wt%. To identify the organic compounds present, APCI MS experiments were performed. (It should be noted that mixed peaks, *i.e.* different molecules at the same M+1 value, are also present.) The main components are listed in Table 3. Besides propyl 2-hydroxypropionate (propyl lactate), 2-hydroxypropionic acid (lactic acid) and 2-hydroxypropan-1-ol can be detected in larger amount.

Product B contains *ca.* 5 wt% carbon. Accordingly, the amount of organic compounds observed in aqueous solution by APCI MS is less than in the viscous product and the spectrum is less complex. The two main components are acetic acid and propyl 2-hydroxypropionate (propyl lactate). The electrospray MS method is convenient to study charged species present in aqueous solution. The applied first ionisation is so mild that even weakly bonded complex ions remain intact. Table 4(a) shows the main components of the ESMS spectra of products A and B. As standards, solutions of different Al salts were investigated after addition of acetic acid.

Table 4 (a) Main components in the ESMS spectra of solutions of products A, B and different Al salts after adding acetic acid

	M
product A	163, 181, 221, 235, 265, 307, 321, 379, 393
product B	163, 181, 265, 307, 321
Al^{III} salt + CH_3COOH	61, 121, 139, 157, 163, 181, 205, 265, 307

(b) Complex compounds of Al^{III} identified on the basis of the second fragmentation step

	M			
complex ion	$n=0$	$n=1$	$n=2$	$n=3$
$[Al(OH)_2(H_2O)_n]^+$	61	79	97	115
$[Al(OH)(OAc)^*(H_2O)_n]^+$	—	121	139	175
$[Al(OAc)_2(H_2O)_n]^+$	—	163	181	199
$[Al(OAc)_2(AcOH)_n]^+$	—	205	265	325
$[Al(OAc)_2(AcOH)_2(H_2O)_n]^+$	—	223	241	
$[Al(OAc)_2(AcOH)_2(AcOAc)_n]^+$	—	307		

The various ions in products A and B can be (partly) identified on the basis of the second fragmentation step. Although other organics have also been established by APCI MS, only complexes containing OH and acetate ions, acetic acid and water molecules [Table 4(b)] can unambiguously be identified. The relative amounts of different complex ions is not characterising as it depends on the dilution used in the measurement. In more dilute solution OH containing species dominate, while at higher concentration, the acetate and acetic acid containing complexes are dominant. In product A the spectrum is more noisy owing to the higher content of organics.

Table 3 Organic compounds in the different products of the gel preparation

		product A APCI MS		product B APCI MS	
t_r/s	distillate GC–MS		M+1		M+1
1.10	H_2O	acetic acid	61	acetic acid	61
1.90	propan-1-ol	propan-1,2-diol	77	propyl 2-hydroxypropionate	133
2.13	propyl formate	2-hydroxypropionic acid	91		
3.26	propyl acetate	2-hydroxypropyl acetate	119		
3.38	propyl nitrate	propyl 2-hydroxypropionate	133		
5.37	propyl propionate	1,1-dipropoxyethane	147		
6.95	dipropoxymethane	1,1-dipropoxypropane	161		
10.94	1,1-dipropoxypropane				

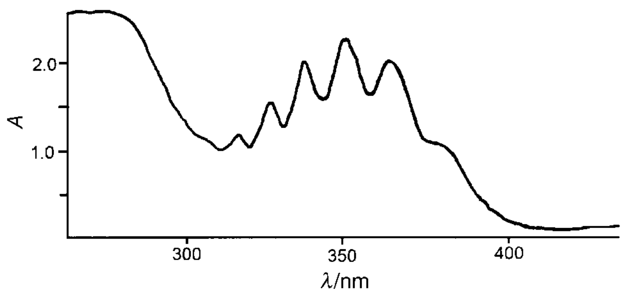


Fig. 2 UV–VIS spectrum of the distillate obtained in step 1/b

Study of the co-ordination sphere of Al^{III} in the gel products

^{27}Al MAS NMR spectra. Beside the viscous spinnable product and the elastic hydrogel, standard samples have also been investigated to aid in evaluation of the MAS NMR spectra. The standards used were boehmite (γ-AlOOH), a wet amorphous precipitate obtained from an Al^{III} containing solution upon adding NaOH, and an aluminium acetate gel produced by hydrothermal treatment of basic aluminium acetate.

MAS NMR spectra are shown in Fig. 3. The signal of the boehmite [Fig. 3(a)] is seen at *ca.* 8.5 ppm. The amorphous precipitate [Fig. 3(b)] shows two well separated, signals at 0 [$Al(H_2O)_6$] and 3.5–4 ppm. In agreement with the literature,[6–15] the latter can be assigned as Al atoms of dimers or oligomers, where the connections are established by shared OH and/or O (*e.g.* in trimers). The same two signals are essentially observed in the spectrum of aluminium acetate gel [Fig. 3(c)], which is explained by the fact that the coordination of acetate ions to the oligomers is preferred, and does not cause significant change in the chemical shift.[16,17]

Concerning the gel samples, the viscous spinnable product [Fig. 4(a)] shows a broad signal around 0 ppm with a small shoulder at 3.5–4 ppm indicating a low percentage of OH/O connections between Al ions. In contrast in the NMR spectrum of the hydrogel [Fig. 4(b)] the main signal occurs at 3.5–4 ppm which indicates the dominance of OH/O connections and thus the presence of oligomers in the sample.

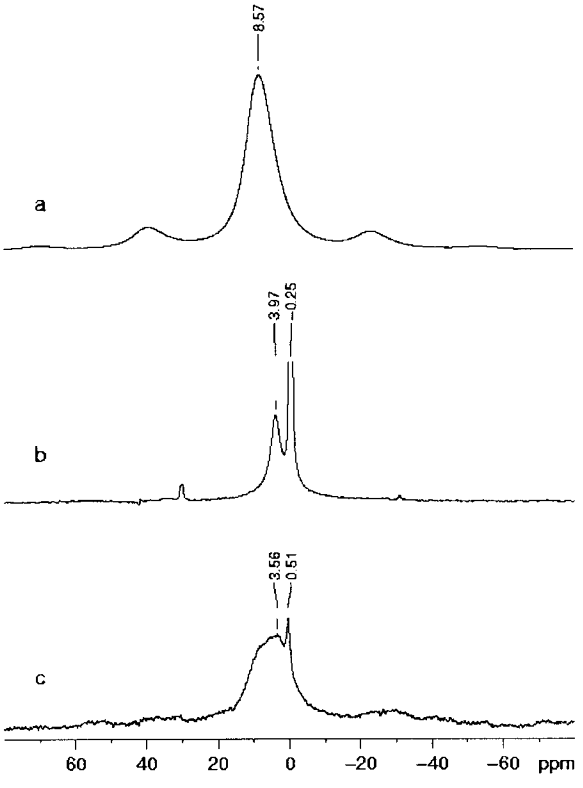


Fig. 3 ^{27}Al MAS NMR spectra of boehmite (a), amorphous hydroxide precipitate (b) and the aluminium acetate gel (c)

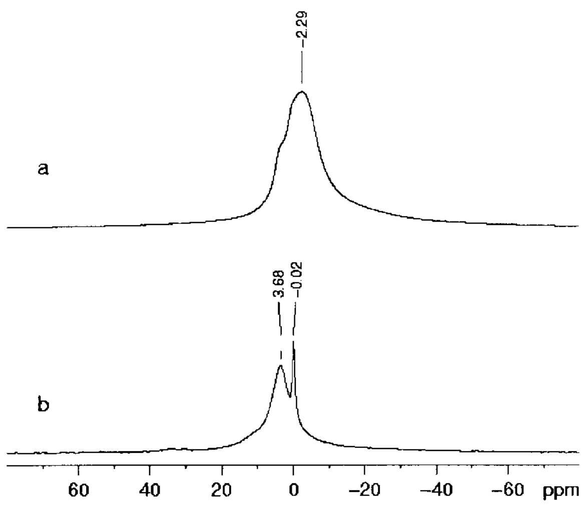


Fig. 4 ^{27}Al MAS NMR spectra of the viscous spinnable product (a) and the hydrogel (b)

IR absorption. IR spectra are shown in Fig. 5. The solid foam [Fig. 5(a)] and the xerogel [Fig. 5(b)] showed similar spectra. In the range of bonding vibrations of the OH group, two broad bands occur at 3400 and 3200 cm^{-1} indicating OH groups taking part in different bonding modes (*e.g.* in H bonds). Between 1800 and 1400 cm^{-1}, the weaker bands (besides the well known water vibration at 1600 cm^{-1}) belong to vibrations of organic C=O and CH groups. According to the literature bands at 1417, 1472 and 1595 cm^{-1} can be assigned to bidentate acetate ligands.[18,19] The methyl group of acetate ions absorbs[20] at 1050 cm^{-1}. The sharp band at 1384 cm^{-1} arises from the remaining nitrate content, while a band at 1160 cm^{-1} is due to Al—OH—Al.[21]

Chemical behaviour of products during heating

Thermoanalytical and TG–MS investigations were intended to reveal the thermal processes by which the nitrogen and the carbon content of the gel products was reduced. Fig. 6 shows DSC curves of products A and B while Table 5 and 6 contain results of the TG–MS investigations and the identification of the detected fragment ions, respectively. At a heating rate of 10 K min^{-1} the carbon can not be removed completely, and the samples are slightly grey even at 500 °C.

On the basis of TG–MS measurements the loss of organics of product A occurs in two steps. At *ca.* 100 °C, water, N- and C-oxides and smaller carbon containing fragments can be detected which form from the solvent, the nitrate and volatile ester or ether-type compounds. While this process is endothermic, at 300 °C an exothermic process occurs, accompanied

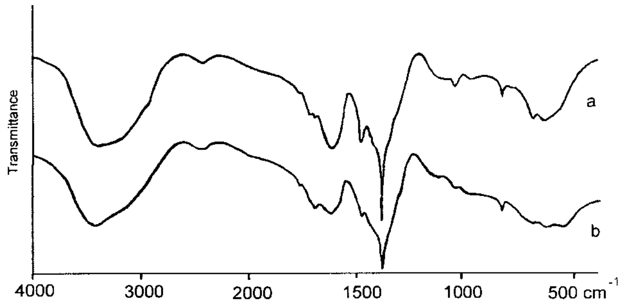


Fig. 5 IR spectra of the dried viscous product (a) and the dried hydrogel (b)

Table 5 Thermal processes observed in different products and compounds based on TG–MS results

	T_1	T_2	T_3
product A	100 °C	220 °C	340 °C
Δm(%)	−41	−13	−14
main ions (m/z)	18, 28, 30, 44, 26, 27, 29, 31, 15, 43, 45	30	26, 27, 28, 30, 44
product B	100 °C	220 °C	300 °C
Δm(%)	−23	−19	−14
main ions (m/z)	18, 30, 44	30	28, 30, 44 (22),
$Al(NO_3)_3{\cdot}9H_2O$	120 °C	120–400 °C	
Δm(%)	−59	−20	
main ions (m/z)	18, 30, 44, 46	30	
$Al(OH)_{3-x}(OAc)_x$ $(2>x>1)$		295	315
Δm(%)	−3	−31	−32
main ions (m/z)		15, 29, 31, 41, 43, 45, 61	15, 26, 27, 43, 44, 22
Al acetate nitrate	150 °C	210 °C	315 °C
Δm(%)	−56	−11	−10
main ions (m/z)	18, 30, 15, 43, (45, 46)	30	16, 28, 30, 44

Table 6 Identification of the fragment ions detected during TG–MS investigation

m/z	ion	m/z	ion	m/z	ion
15	$CH_3^{\cdot +}$	28	CO^+ N_2^+	44	N_2O^+ CO_2^+
18	H_2O^+	29	$C_2H_5^+$	45	$HCOO^+$
22	CO_2^{2+}	30	NO^+	46	NO_2^+
26	$C_2H_2^+$	31	H_2COH^+	61	$CH_3COOH_2^+$
27	$C_2H_3^+$	43	CH_3CO^+		

by liberation of N- and C-oxides. To investigate this process, studies were performed on $Al(NO_3)_3{\cdot}9H_2O$, $Al(OH)_x(OAc)_{3-x}$ $(2>x>1)$, a solid mixture of these two salts [Fig. 7(a)] and on 'aluminium nitrate acetate' [Fig. 7(b)], which is a solid amorphous material prepared by drying a solution of the two salts. In the latter material the aluminium, nitrate and acetate ions can mix at a molecular level. The exothermic process at 300 °C appears in the DSC curve only in the latter case, and is not observed for a solid mixture of the two salts.

N-containing gases escape from product A in three steps. The majority is removed at 100 °C together with water (free nitrate ions) and at 220 °C nitrous gas liberation can be observed similarly to $Al(NO_3)_3{\cdot}9H_2O$. At 300 °C the remaining part of the N-containing material decomposes to nitrous gases in the exothermic process mentioned above. In the TG–MS spectrum of product B less carbon containing fragments are observed correspondingly to the lower organic content. At about 110 °C, water, N- and C-oxides escape. At 300 °C an exothermic reaction also takes place in this sample and N-containing material is also removed in three steps.

Discussion

Chemical processes

The fundamental process of the gelation is the hydrolysis of Al^{III} during which OH ions replace one or more water molecules in the first co-ordination sphere, followed by condensation of partly hydrolysed monomer giving oligomers.

The main role of the propan-1-ol is to dissolve the aluminium nitrate precursor, and to decrease the polarity of the system. Thus the decomposition of nitrate ions is promoted resulting in a decrease of acidity which causes hydrolysis. The degree of hydrolysis (OH/Al^{III} ratio) must increase parallel with the decrease in nitrate content. Investigation of the preparation process at various temperatures and in different alcohols shows that a minimum of 65 °C is required and a low polarity solvent (propanol or ethanol) is needed to lead to a sufficient extent of hydrolysis of Al^{III} to obtain transparent gel-like materials. At lower temperature (*e.g.* 55 °C) and in higher polarity solvents (*e.g.* methanol) the processes inducing the hydrolysis of Al^{III} can reach only an intermediate state (low extent of nitrate decomposition), furthermore precipitation occurs in both cases. Above 65 °C the final degree of hydrolysis of Al^{III} is *ca.* 2.1 in propan-1-ol. In ethanol the degree of hydrolysis after step 1 is lower than in propan-1-ol indicating slower decomposition processes due to the higher polarity of the solvent. During drying (step 2) the high concentration of Al^{III}, nitrate and hydroxide ions probably promotes decomposition which results in the same final degree of hydrolysis in both cases.

Chemical reactions also occur between propan-1-ol and the nitric acid and/or its decomposition products formed from nitrate ions. An outline of the chemical processes is postulated in (Fig. 8). Nitrosation of propan-1-ol can be regarded as an initial step since the amount of propyl nitrite in the distillate decreases with increasing reaction temperature. Nitrogen containing organic compounds (propyl nitrate and propyl nitrite) can be detected only in small amount in the distillate. Oxidising

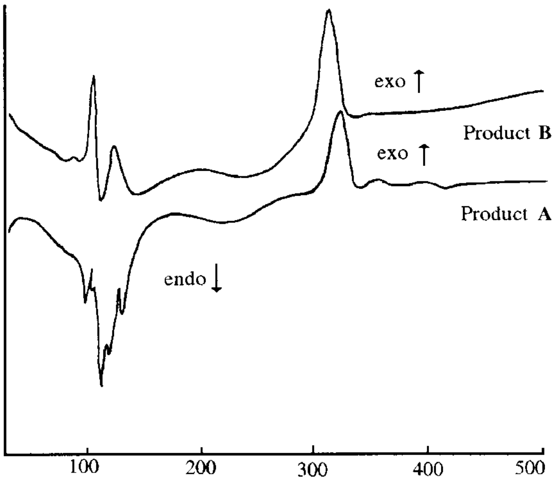


Fig. 6 DSC curves of the viscous spinnable product before (A) and after drying (B)

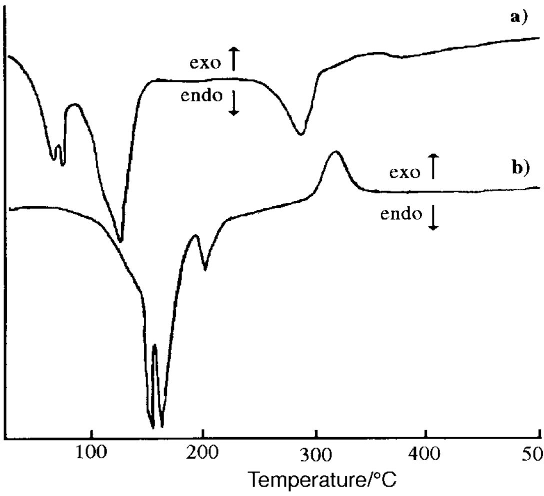


Fig. 7 DSC curve of the solid mixture of aluminium nitrate and basic aluminium acetate (a); DSC curve of the aluminium nitrate acetate salt (b)

processes follow or accompany the nitrosation and nitration and propanal, propionic acid and 2-hydroxypropionic acid are likely to form. These compounds can react with propan-1-ol, to give esters and acetals. Moreover, chain shortening also occurs to a large extent resulting in the formation of acetic and formic acid, which give propyl esters. A variety of ethers are also present. In earlier work, similar strong oxidation was observed upon treating propan-1-ol with dilute nitrous acid, when oxalic acid was shown to form.[22]

During step 1 the extent of the transformation of propan-1-ol can be estimated as 30% on the basis of the composition of the distillate and the carbon content of the viscous product (A). Considering the decrease in the amount of nitrate ions, the mole ratio of the transformed propan-1-ol and transformed nitrate ion is *ca.* 1 : 1.2 indicating that nitrate ions must decompose to a large extent through redox reactions with propan-1-ol. In the viscous product (A) propyl 2-hydroxypropionate (propyl lactate) and 2-hydroxypropionic acid (lactic acid) are the predominant compounds as established by APCI MS. According to ESMS complex ions containing only acetate and OH ions have unambiguously been identified, however lactate ions should also co-ordinate to Al^{III}.[7] One explanation for the absence of lactate complexes could be that the acetate/lactate ratio is much higher than shown in the APCI spectra, and thus the acetate complexes dominate in the ESMS spectra.

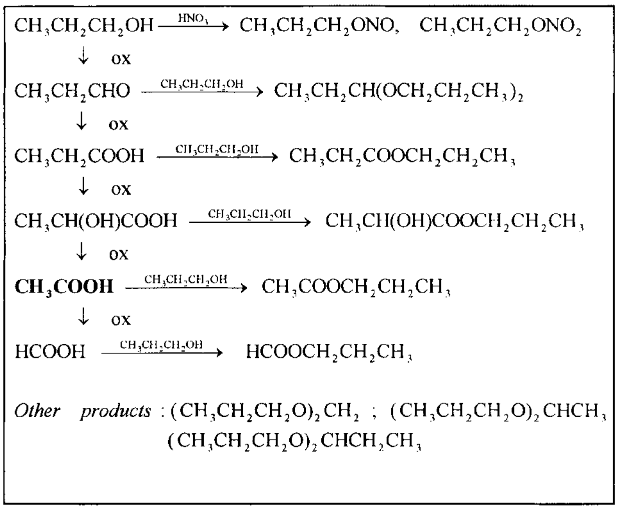
During drying (step 2) the total organic and the nitrate content decreases, the mole ratio of expelled carbon and nitrate being 3 : 1. The decomposing nitrate ions likely cause further oxidising processes and acetic acid (acetate ion) becomes the main organic component in the dried hydrolysis product (B) as established by APCI MS. In the ESMS spectra, acetate-containing complexes are mostly observed.

The thermal behaviour of products A and B gives further evidence for the presence of acetate ions around Al^{III}. The unexpected exothermic process (DSC) observed in gel products at 300 °C (in which water, nitrogen oxides and carbon oxides are all expelled together) can be explained by mixing of acetate and nitrate ions at the molecular level in the gel products.

Structural consequences

During generally used methods to prepare aluminium oxohydroxide gels, boehmite or boehmite-like structures form. This is not the case upon hydrolysis of aluminium nitrate in propan-1-ol as has been established by IR and MAS NMR spectra of the products.

NMR measurements show only octrahedrally coordinated Al atoms in the gels. In the spinnable viscous material, owing to the high organic content of the medium, a loose 'network' forms, where the connectivity is maintained probably through coordinated organic compounds (mainly acetate ions). The low water content of the medium hinders the formation of aluminium polycations, which are known to be present under aqueous conditions. Upon adding water to the dried viscous product, a hydrogel forms accompanied by a complete change of the coordination sphere of the Al atoms. Most Al atoms are involved in oligomers linked by OH, O and/or acetate ions. As is well known, acetate ions can co-ordinate as a uni- or bi-dentate ligand to Al monomers.[19] (log $K_1 \approx 1.5$)[16] but they display a greater tendency to form aqueous acetate complexes at higher temperature (80 °C).[22] However it has also been established that acetate ions show a stronger affinity towards dimers or oligomers,[16,17,23] where they can connect as bridging ligands to two Al atoms already linked by shared OH or O. It is also possible that acetate ions connected to coordinated water molecules can link together two Al atoms in two different oligomers; possible variations are shown in Fig. 9. Acetate coordination must play an important role in the formation of the gel products. In contrast to the high degree of hydrolysis of Al, no precipitate forms during the entire hydrolysis process. This can be explained by the hindering effect of acetate ions on precipitation by occupying coordination sites around Al ions. At the same time, the amount of acetate is not high enough to produce a basic acetate salt (the acetate/Al ratio is <0.4 on the basis of the carbon content). Investigation of the gel preparation process under different conditions (see Table 2) can prove this. Precipitation occurs when reacting propan-1-ol and aluminium nitrate at 55 °C; the low temperature does not allow the formation of a sufficient amount of acetate. Using methanol at 75 °C also results in precipitation. Formic acid (formate ion), the oxidised derivative of methanol can also coordinate to Al but then the high polarity of the water–methanol medium does not promote the formation of a sufficient amount of the oxidising agent nitric acid.



$$CH_3CH_2CH_2OH \xrightarrow{HNO_3} CH_3CH_2CH_2ONO,\quad CH_3CH_2CH_2ONO_2$$
$$\downarrow \text{ox}$$
$$CH_3CH_2CHO \xrightarrow{CH_3CH_2CH_2OH} CH_3CH_2CH(OCH_2CH_2CH_3)_2$$
$$\downarrow \text{ox}$$
$$CH_3CH_2COOH \xrightarrow{CH_3CH_2CH_2OH} CH_3CH_2COOCH_2CH_2CH_3$$
$$\downarrow \text{ox}$$
$$CH_3CH(OH)COOH \xrightarrow{CH_3CH_2CH_2OH} CH_3CH(OH)COOCH_2CH_2CH_3$$
$$\downarrow \text{ox}$$
$$\mathbf{CH_3COOH} \xrightarrow{CH_3CH_2CH_2OH} CH_3COOCH_2CH_2CH_3$$
$$\downarrow \text{ox}$$
$$HCOOH \xrightarrow{CH_3CH_2CH_2OH} HCOOCH_2CH_2CH_3$$

Other products : $(CH_3CH_2CH_2O)_2CH_2$; $(CH_3CH_2CH_2O)_2CHCH_3$
$(CH_3CH_2CH_2O)_2CHCH_2CH_3$

Fig. 8 The probable outline of the chemical reactions taking place in the aluminium nitrate propan-1-ol mixture at higher temperature

The importance of the organic compounds in the gel structure can also be verified by comparison of the different maximum water content of the hydrogels. This is much lower when hydrolysing aluminium nitrate in ethanol than in propanol. Since the degree of hydrolysis is similar in both cases, this difference can only be caused by the different organic compounds present in the gels (*e.g.* formate *cf.* acetate).

Conclusion

Upon treating aluminium nitrate in propan-1-ol optically clear, transparent homogeneous aluminium oxohydroxide gels can be obtained avoiding the formation of any precipitate. This preparation method is fast and easy, since the time consuming peptisation and washing step are not needed owing to the lack of precipitation and the spontaneous decomposition of the nitrate.

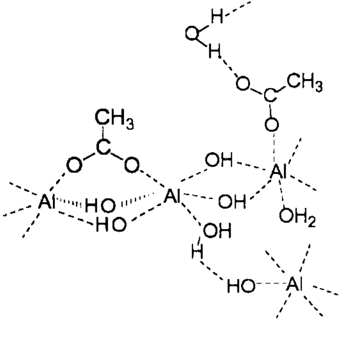


Fig. 9 The different ways of acetate ion coordination around Al^{III}

The role of acetate formed *in situ* during the gel preparation process proved to be important in gel formation. By occupying coordination sites acetate ions hinder precipitation during the preparation process. Furthermore, acting as a bidentate bridging ligand, acetate ions can establish connections in and between the Al^{III} oligomers from which the gel network is built up. The transparent spinnable mixture and the xerogel obtained by this method may be promising precursors in preparing high surface alumina fibres and ceramics.

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