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Thermal transformation of alumina hydrolysates and gels synthesized from secbutoxyaluminium(III) modified with short-chain aliphatic acids dissolved in butyl ether

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Abstract

A combination of X-ray diffraction and thermal analysis was employed to characterise alumina hydrolysates synthesised from the hydrolysis of anhydrous trisecbutoxyaluminium (III). X-ray diffraction showed that the alumino-oxy(hydroxy) hydrolysates were boehmite. For boehmite the lamellar spacings are in the *b* direction and multiple *d*(0 2 0) peaks are observed for the unaged hydrolysate. After 4 h of ageing, a single *d*(0 2 0) peak is observed at 6.53 Å. Thermal analysis showed five endotherms at 70, 140, 238, 351 and 445°C. These endotherms are attributed to the dehydration and dehydroxylation of the hydrolysate.

Alumina oxy(hydroxy) gels were formed from the hydrolysates of anhydrous aliphatic acid modified trisecbutoxyaluminium(III). X-ray diffraction shows the gels were expanded above the (0 2 0) spacing of boehmite due to the incorporation of acid in the interlamellar space. The thermal analysis patterns of the acid modified gels were significantly different from that of the unmodified gel.

Keywords: Dehydration; Dehydroxylation; Differential thermal analysis; Differential thermogravimetric analysis; Alumina gel; Gibbsite; Boehmite; Thermogravimetric analysis; Trisecbutoxyaluminium(III)

1. Introduction

Alumina obtained through sol–gel processing is one of the most important ceramics commercially used today. Its uses include abrasives, refractories, chemical resistant coatings, bioceramic implants, and integrated circuit substrates. Thus it is important that the structure of alumina formed from the sol–gel process must be adequately studied. Alumina sols and gels are readily prepared by the hydrolysis of aluminium alkoxides such as trisecbutoxyaluminium(III) [$(s\text{-BuO})_3Al$ or ASB] [1,2]. Several phases of aluminium hydroxides exist according to the formula $Al(OH)_3$; these are gibbsite, nordstrandite and bayerite [3]. If the phase corresponds to the formula AlO(OH), then the phases are boehmite or diaspore [3]. Pseudoboehmite is a hydrated form of boehmite with slightly larger *d*-spacing. The chemical and structural make-up of the oxo-hydroxides formed from the hydrolysates depends on the conditions of the hydrolysis and the

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aging of the hydrolysates [4,5]. Ageing simply means the changes in phase as either the hydrolysate or the gel is left to stand in the presence of water. Such aging can affect the rates of peptisation of the alumina sols. Ageing of the oxo-hydroxides as gels causes structural changes in the sequence amorphous-pseudoboehmite–bayerite–gibbsite [1,2].

It is often necessary to synthesise ceramics with tailored properties for particular applications. In these instances the control of the reaction kinetics of hydrolysis and condensation is important. For the manufacture of these types of materials it is useful to modify the alkoxide precursors. Modification of precursors can be performed by coordination of the starting material with ligands. Metal alkoxides react with ligands due to their coordination unsaturation. For this to occur the metal expands its coordination via a nucleophilic addition. Such ligands as alcohols and acids may be used to react with the ASB. Chemical modifiers are substances which are used in controlling or retarding the rate of hydrolysis and condensation so that the desired material is formed whether it a gel, colloidal solution or precipitate [6,7]. The methodology is essential in the process of obtaining a metal sol that is suitable to be used in for example coating applications. Acids, chlorides, alcohols, bases, and chelating agents are all substances that effectively produce a new less reactive precursor [8].

Recent research has explored the thermal analysis of gels formed from the hydrolysates produced from $(s\text{-}BuO)_3Al$ and acid modified ASB [9,10]. This research produced hydrolysates and gels from ASB and the ASB was not necessarily free of water. In order to ensure the ASB and acids remain uncontaminated with water, the ASB and anhydrous acids were dissolved in dibutyl ether. This paper therefore reports the structural evolution of aluminium oxy(hydroxides) through the ageing of hydrolysates formed from ASB at 75°C. The effect on the structure of the alumina oxy(hydroxide) gels formed through the modification of ASB with short-chained organic acids is also reported.

2. Materials and methods

2.1. Synthesis of alumina hydrolysates, sols and gels

The $(s\text{-}BuO)_3Al$ as supplied was doubly distilled before modification. A solution of 0.1 M $(s\text{-}BuO)_3Al$ (ASB) was prepared in anhydrous doubly distilled dibutyl ether in a nitrogen atmosphere. The short-chain acids were dried over anhydrous sodium sulphate and a solution of 0.6 M was prepared in the dibutyl ether. These two solutions were then mixed slowly at 0°C to form the modified ASB solution. This starting material was then added, under constant vigorous stirring to demineralised water at 75°C, in a molar ratio of 1:100 alkoxide solution to water. A sample of each hydrolysate was taken for DTA/TGA analysis.

The resulting precipitates were washed several times with water to remove organic reaction products, namely alcohol, then diluted in water to give slurries with concentration of aluminium of 1:100 Al:water molar ratio. Hydrolysate slurries were agitated by the use of a magnetic stirrer at room temperatures to prepare the sol. Nitric acid dispersing agent was added in a ratio of 0.07 mole of HNO_3 per mole of Al. Samples of the sols produced were collected from the peptisation vessel and allowed to gel by solvent evaporation and by using a rotary evaporator at 25°C. Samples were dried under a nitrogen stream for 12 h before thermal analysis.

2.2. Thermal analysis

Differential thermal and thermogravimetric analyses of the crushed gels were obtained simultaneously using a Setaram DTA/TGA instrument, operating with a heating rate of 1.0°C per minute from ambient temperatures to 1350°C in air atmosphere. For comparison a commercially available boehmite known as "dispal" was used.

2.3. X-ray diffraction

The normal room temperature and temperature controlled XRD analyses were carried out on a Philips wide angle PW 3020/1820 vertical goniometer equipped with curved graphite-diffracted beam monochromators. The *d*-spacing and intensity measurements were improved by application of a self developed computer aided divergence slit system enabling constant sampling area irradiation (20 mm long) at any angle of incidence. The goniometer radius was enlarged from 173 to 204 mm. The radiation applied was Cu Kα from a long fine focus Cu tube, operating at 40 kV and 40 mA. The samples were measured in static air and in flowing nitrogen atmosphere at 15 l/h in stepscan mode with steps of 0.025° 2θ and a counting time of 1 s. Measured data were corrected with the Lorentz polarisation factor (for oriented specimens) and for their irradiated volume.

3. Results and discussion

The structure of sol–gel processes alumina has received much attention. It was found that amorphous aluminium oxy(hydroxide) is formed on the hydrolysis of ASB in water at 25°C. This amorphous AlOOH under ageing forms pseudoboehmite then bayerite via a dissolution re-precipitation process. However alumina precipitated from the action of 75°C water on ASB formed pseudoboehmite, which showed no ageing process. One such study was conducted by Pierre and Uhlmann [11,12]. The authors postulated that the structure of the resultant AlOOH formed from cold water hydrolysis of ASB was one of folded boehmite structure along the 0 2 0 planes of boehmite. This structure was then proposed to straighten during ageing of the amorphous aluminium oxy(hydroxide), which results in the formation of pseudoboehmite. Such a structure showed a X-ray diffraction pattern with the (0 2 0) peak for pseudoboehmite but not other peaks, which was attributed to the disintegration of long-range order but preservation of short-range order. It should be noted that the temperature of hydrolysis is 75°C. The reason for the selection of this temperature is that at and above this temperature a single phase is formed. If the hydrolysate is formed at 25°C, an amorphous aluminium oxy(hydroxide) is formed, which on ageing transforms to boehmite and gibbsite. Further ageing the mixture in the absence of alkali ions may transform to bayerite [13].

3.1. X-ray diffraction of alumino oxy(hydroxide) hydrolysates and gels

The X-ray diffraction patterns of alumina hydrolysates prepared from the modification of $(s\text{-BuO})_3Al$ in anhydrous butyl ether and aged for a range of times together with the XRD pattern of a standard boehmite are shown in Fig. 1. For boehmite the lamellar spacings are observed along the *b* direction and consequently the *d*(0 2 0) is the principal first peak. The

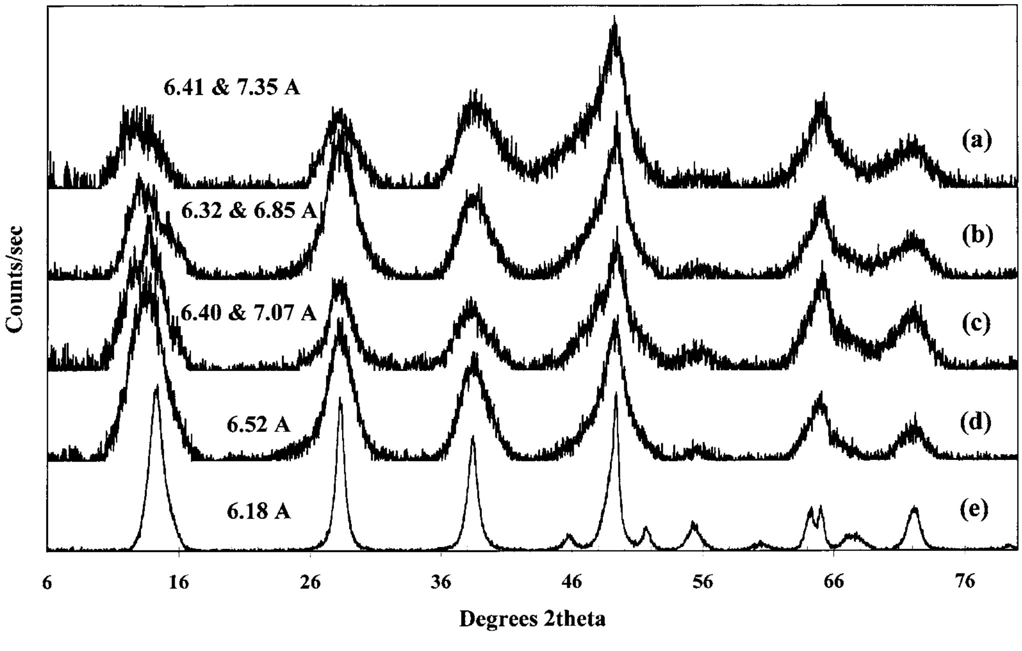


Fig. 1. X-ray diffraction patterns of (a) alumina hydrolysate at zero time; (b) 0.5 h; (c) 1 h; (d) 4 h; and (e) standard boehmite.

principal *d*-spacings for boehmite are observed at 6.15 (0 2 0), 3.14 (0 2 1), 2.33 (1 3 0), 1.84 (1 5 0), 1.45 (1 3 2), 1.43 (2 0 0) and 1.30 Å (2 2 1). The published values for boehmite are 6.12, 3.16 and 2.34 Å. The hydrolysates at the different times of ageing all show a pattern similar to that of boehmite. For the unaged hydrolysate and up to 1 h of ageing, multiple *d*(0 2 0) peaks are observed. At zero time, peaks are observed at 6.24, 7.53 and 9.9 Å. At an ageing time of 0.50 h, three peaks are observed at 5.72, 6.31 and 6.90 Å. After 1 h ageing time, peaks are observed at 6.14, 6.47 and 7.05 Å. After 4 h of ageing a single *d*(0 2 0) peak is observed at 6.52 Å.

As the hydrolysates are first formed, these materials are amorphous or non-diffracting and contain many stacking defects along the (0 2 0) direction. As ageing occurs, bigger crystals are formed and these defects are removed. The difference in the two spacings is attributed to the amount of water between the hydrolysate layers and the arrangement of these water molecules between the layers. The reason for the difference between the standard boehmite and the 4 h aged hydrolysate is attributed to the presence of water between the layers. The standard boehmite was spray dried and consequently most of the water has been removed. The kinetics of peptisation of these hydrolysates with nitric acid depends on the ageing of the hydrolysates. The 4 h aged hydrolysate is more easily peptised.

The X-ray diffraction patterns of the alumina gels formed from the peptisation of the alumina hydrolysates modified with acetic, propanoic and butanoic acid are shown in Fig. 2. The first peak (0 2 0) is the interlayer distance. The crystals are very small but the lamellar spacings are large. Hence the intensity of the *d*(0 2 0) peak is large compared with that of the other spacings. The unmodified gel synthesised from the 4 h hydrolysate described above shows a *d*(0 2 0) spacing of 6.37 Å. This corresponds to boehmite. A low intensity broad peak at 12.30 Å is also observed and is attributed to a bigger lattice spacing through two unit cells joined together. Differences are observed in the *d*(0 2 0) spacings for the aliphatic acid modified alumina gels. For the acetic acid modified gel, two *d*(0 2 0) peaks are observed at 8.82 and 10.34 Å (intense). These spacings do not correspond to that of boehmite. The *d*-spacings for the other reflections show some resemblance to that of boehmite. The reason for the observation of the two spacings is assigned to the presence and orientation of the

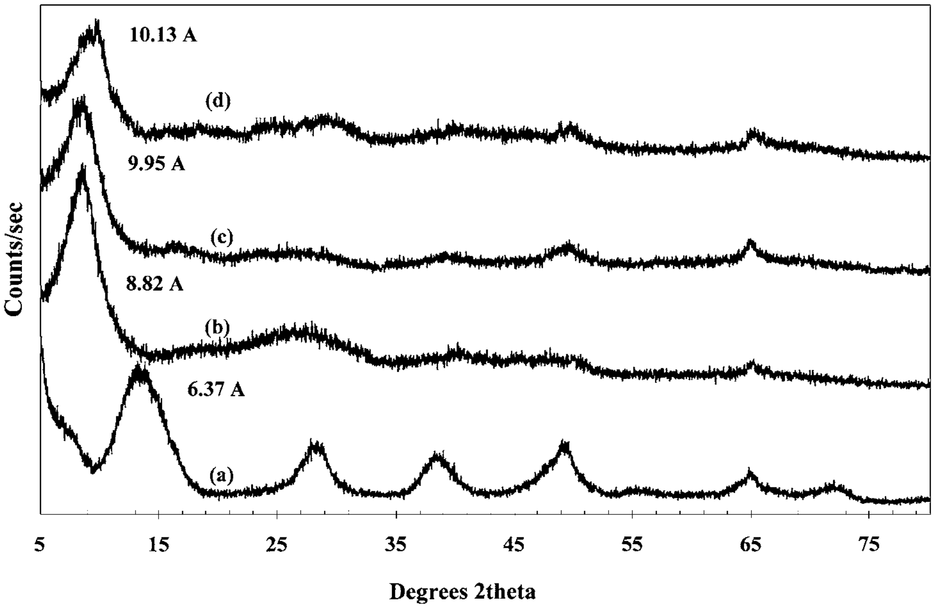


Fig. 2. X-ray diffraction patterns of (a) non-modified alumina gel; (b) acetic acid modified gel; (c) propanoic acid modified gel; and (d) butanoic acid modified gel.

acetic acid between the interlamellar spaces. The acetic acid molecule sits on the surface between the boehmite layers and prevents these layers collapsing. Since the acetic acid may have two orientations to the boehmite surface either parallel or perpendicular to the surface two *d*(0 2 0) spacings are observed. For the propanoic acid modified gels, two spacings are observed at 9.68 and 10.46 Å. For the butanoic acid modified gels spacings for the *d*(0 2 0) peak of 7.64, 8.90 and 10.09 Å are observed. It is proposed that the butanoic acid may take several different orientations within the interlamellar space of the boehmite-like layers resulting in the observation of three (0 2 0) spacings.

4. Differential thermal analysis of the alumino oxy(hydroxide) hydrolysates and gels

4.1. Thermal analysis of the aged hydrolysates

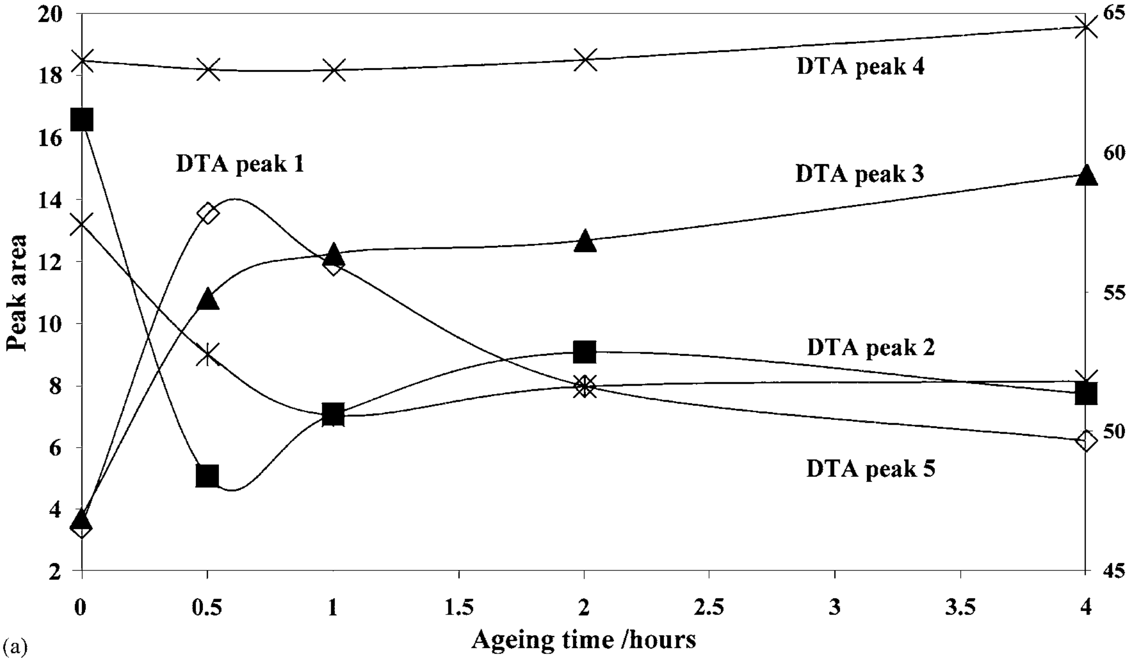
The thermal analysis of the aged hydrolysates formed at 75°C and aged for varying periods of time are reported in Table 1. Five peaks are observed in the thermal analysis patterns at around 70, 140, 238, 351 and 445°C. The first two peaks are attributed to the endotherms of adsorbed water and water chemically bound to the boehmite surface. The third endotherm is of low intensity and may correspond to the endotherm of gibbsite. The last two endotherms are attributed to the two types of hydroxyl groups in the boehmite structure. The endotherm at around 350°C is assigned to external hydroxyls and the second boehmite peak at around 445°C is ascribed to the hydroxyls, which bridge across adjacent boehmite layers.

Fig. 3a displays the variation in the relative peak areas of the five endotherms as a function of ageing time. Significant changes are observed in the areas with ageing time. The area of peak 4 remains constant and independent of the ageing time; however peak 1 shows a large increase from 0 to 0.5 h and then decreases up to 4 h of ageing. Peak 2 decreases and then plateaus after 2 h of ageing. These variations suggest that the amount of water coordinated to the boehmite surface decreases significantly upon ageing, whilst the amount of adsorbed water increases with ageing. Such conclusions are in harmony with the XRD patterns, which showed multiple *d*(0 2 0) spacings for the hydrolysate formed after 0 and 0.5 h. Here it was proposed that water was in the interlamellar space. The area of peak 5 increases and then decreases with ageing time. These results are

Table 1
Results of the thermal analysis of aged hydrolysates formed at 75°C and aged for different time intervals[a]

Peak No.	Parameter	Sample					
		0 h ageing	0.5 h ageing	1 h ageing	2 h ageing	4 h ageing	Standard boehmite
Peak 1	Peak max. (°C)	72.4	98.1	90.5	84.7	79.1	N/A
	FWHM (°C)	44.4	59.7	61.0	49.0	45.7	N/A
	Area (%)	3.41	13.6	11.9	8.0	6.2	N/A
Peak 2	Peak max. (°C)	140.9	143.2	141.4	138.5	138.0	108.7
	FWHM (°C)	80.4	63.1	68.1	65.6	68.9	66.4
	Area (%)	61.2	48.4	50.6	52.9	51.4	25.5
Peak 3	Peak max. (°C)	238.6	257.0	287.9	270.9	278.5	406.6
	FWHM (°C)	62.8	164.3	170.1	165.1	165.1	123.8
	Area (%)	3.7	10.8	12.3	12.7	14.8	27.7
Peak 4	Peak max. (°C)	351.6	400.3	409.0	405.1	407.7	467.9
	FWHM (°C)	164.9	119.6	115.3	120.0	117.0	52.5
	Area (%)	18.5	18.2	18.2	18.5	19.5	36.3
Peak 5	Peak max. (°C)	444.9	456.0	457.8	456.1	457.4	496.2
	FWHM (°C)	98.8	70.3	64.7	67.0	64.4	33.3
	Area (%)	13.2	9.0	7.0	8.0	8.1	18.0

[a] FWHM is the full width half maximum of the endotherms.



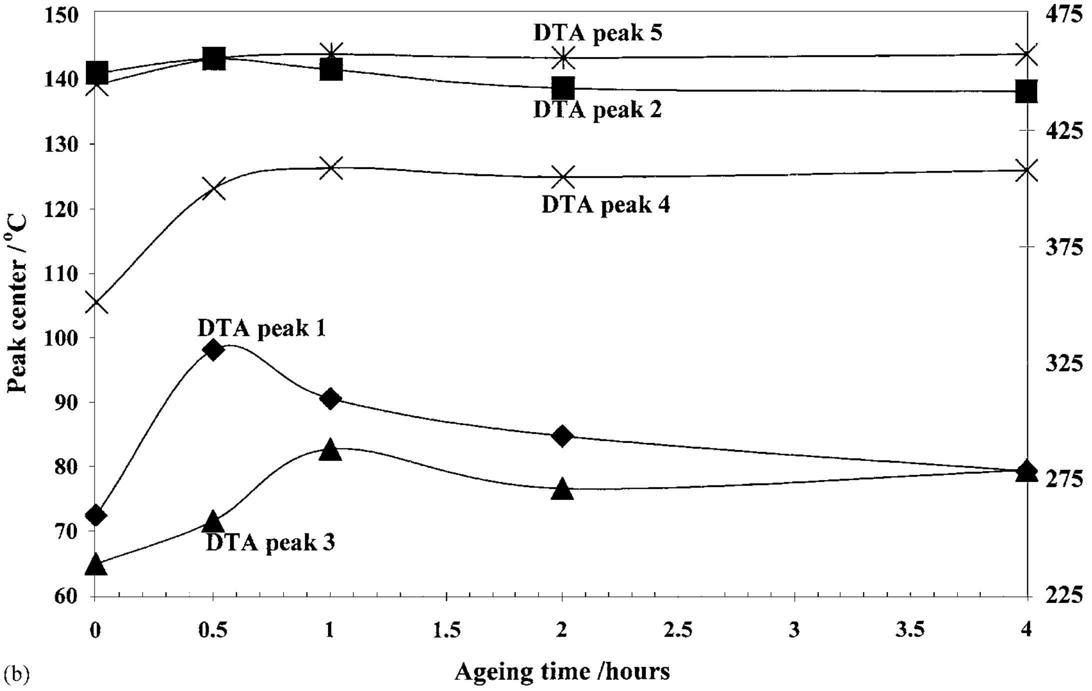


Fig. 3. (a) Variation in the relative band areas of the DTA peaks as a function of ageing time; (b) variation in the centres of the DTA peaks as a function of ageing time; (c) variation in the peak widths of the DTA peaks as a function of ageing time.

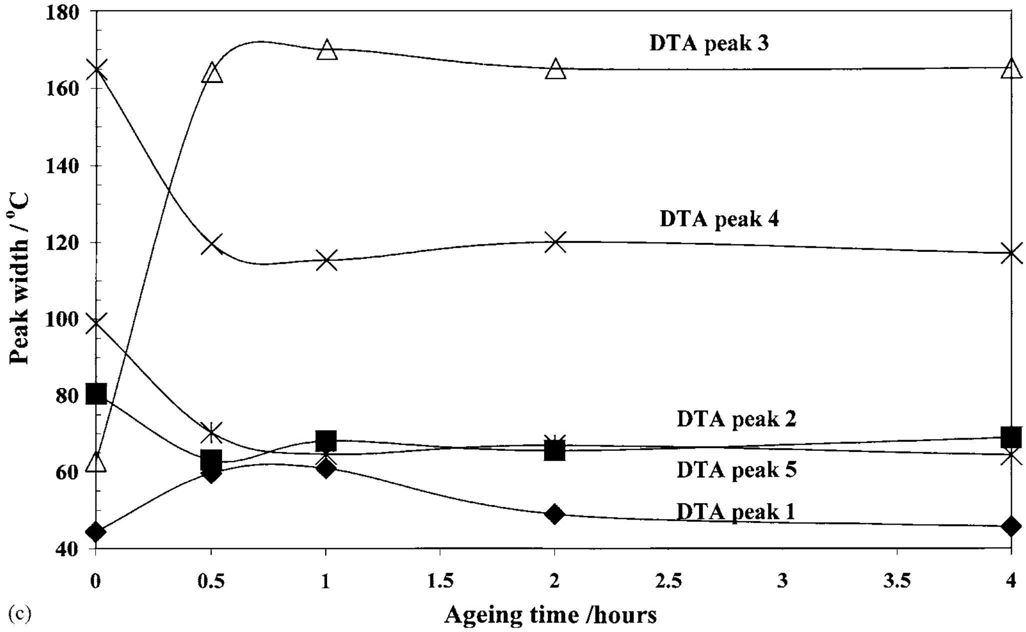


Fig. 3. (*Continued*).

important in the *interpretation of the kinetics of peptisation data*. The hydrolysates formed after 0, 0.5 and 1 h are more difficult to peptise compared with the 4 h aged hydrolysate.

Fig. 3b shows the variation in the peak centres as a function of the ageing time. Importantly the temperature of the endotherms of the two boehmite peaks increase with ageing time. Such an increase may be related to the increased crystallinity observed with the ageing process. The position of the endotherm ascribed to water coordinated to the boehmite surface is constant, whereas the temperature of the adsorbed water increases and then becomes constant. Fig. 3c shows the variation in the width of the endotherms as a function of the ageing time. Peaks 1 and 3 show an increase in peak width, whilst the remaining peaks have a decrease in width with ageing time.

4.2. Thermogravimetric analyses of the aged hydrolysates

As expected a lot of commonality is observed in the TGA and DTGA patterns of the aged hydrolysates. Table 2 reports the weight loses for the different ageing times. Three steps are distinguished. Step 1 is attributed to the weight loss of water. Whilst it is possible to distinguish between two steps in the DTA pattern for the endotherms attributed to water, in the TGA and DTGA patterns only a single step is observed. Steps 2 and 3 are attributed to the weight loss of the two boehmite hydroxyl groups. The weight loss of water appears to decrease with ageing time. Such an observation is in harmony with the results of the X-ray analysis where it was proposed that water was held in the interlayer spaces of the boehmite and this resulted in several *d*(0 2 0) spacings. A decrease in the weight loss of step 2 is observed with ageing time.

Table 2
Percent weight losses in the thermogravimetric analysis of the aged hydrolysates

Time (h)	Step 1	Step 2	Step 3
0	21	8	7
0.5	21	6	7
1	20	6	8
2	19	7	8
4	19	6.5	8.5

This result is attributed to the loss of surface hydroxyls. As the hydrolysates age, the boehmite layer stacking disorder decreases resulting in increased crystallinity of the boehmite. As the weight loss in step 2 decreases, the weight loss in step 3 increases.

4.3. Thermal analysis of the aliphatic acid modified gels

The thermal analysis patterns for the aliphatic acid modified gels are shown in Fig. 4. The results of the

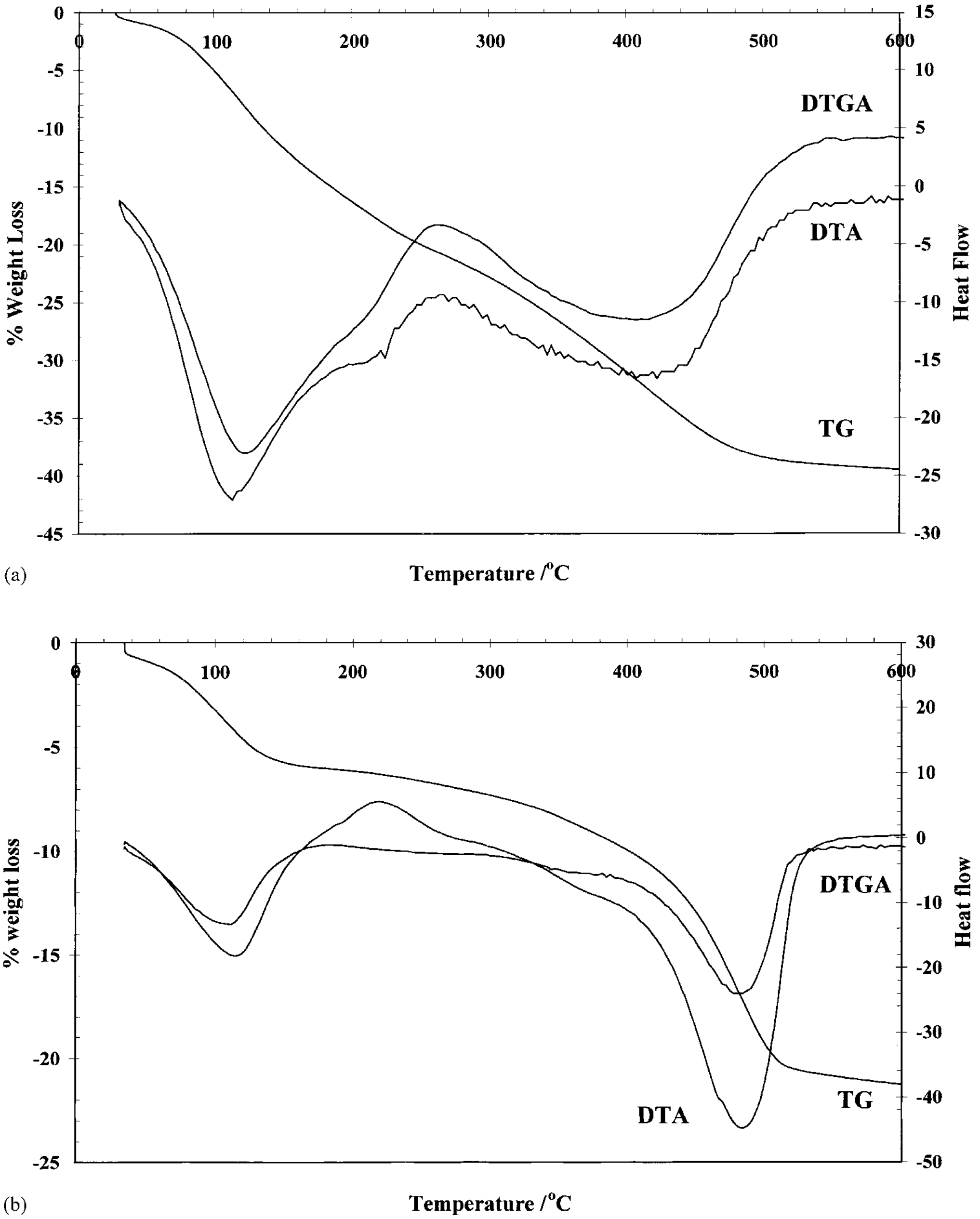


Fig. 4. DTA/TG/DTGA of (a) unmodified boehmite gel; (b) standard boehmite; (c) acetic acid modified gel; (d) propanoic acid modified gel; and (e) butanoic acid modified gel.

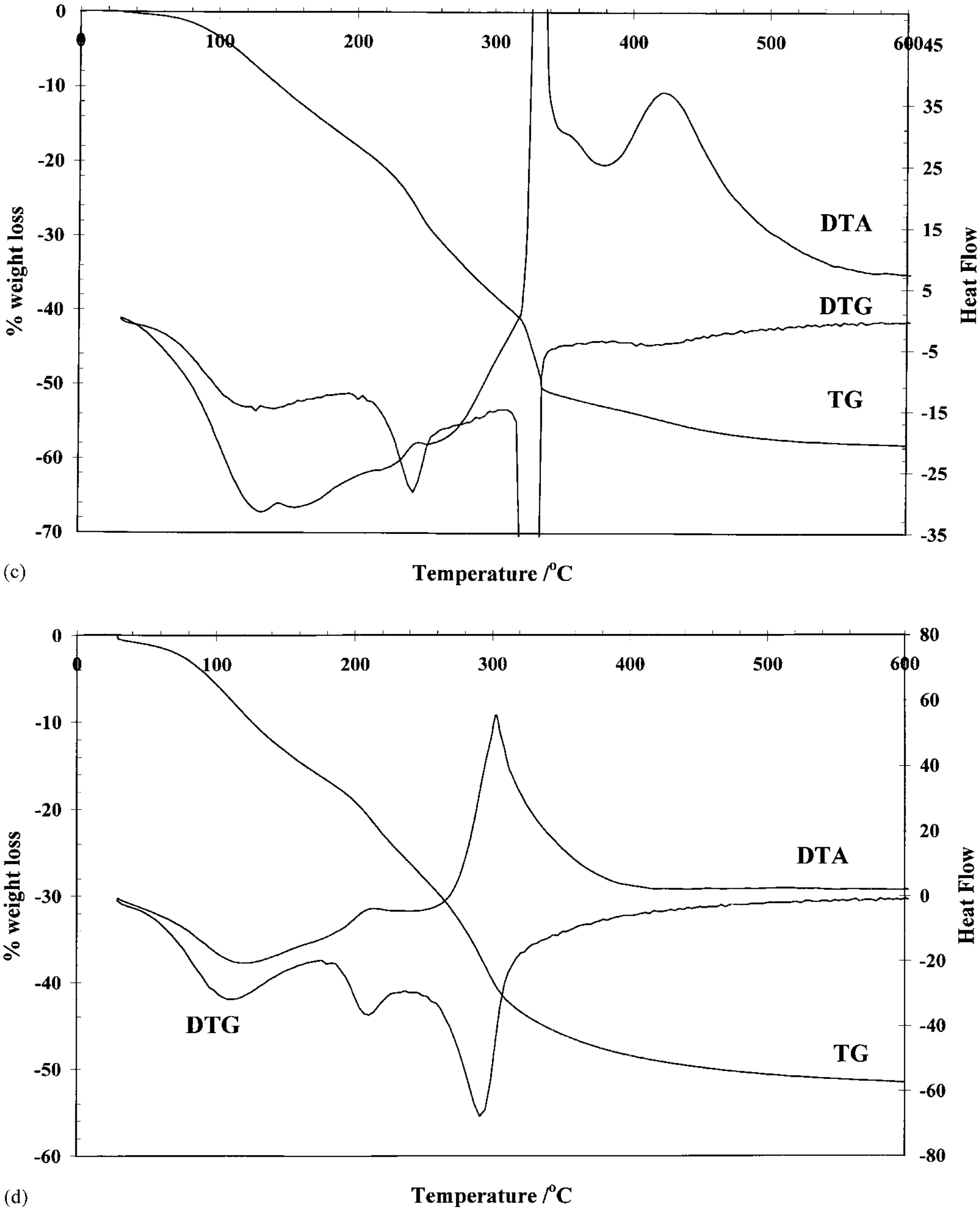


Fig. 4. (*Continued*).

peak component analysis of the DTA patterns are shown in Table 3. The DTA pattern for the unmodified gel (Fig. 4a) is similar to that of the aged hydrolysates but differs from the pattern for the boehmite (Fig. 4b). The DTA patterns for the aliphatic acid modified gels are very different from that of the unmodified gels and from the standard boehmite (Fig. 4c–e). The DTA pattern for the unmodified gel shows endotherms at

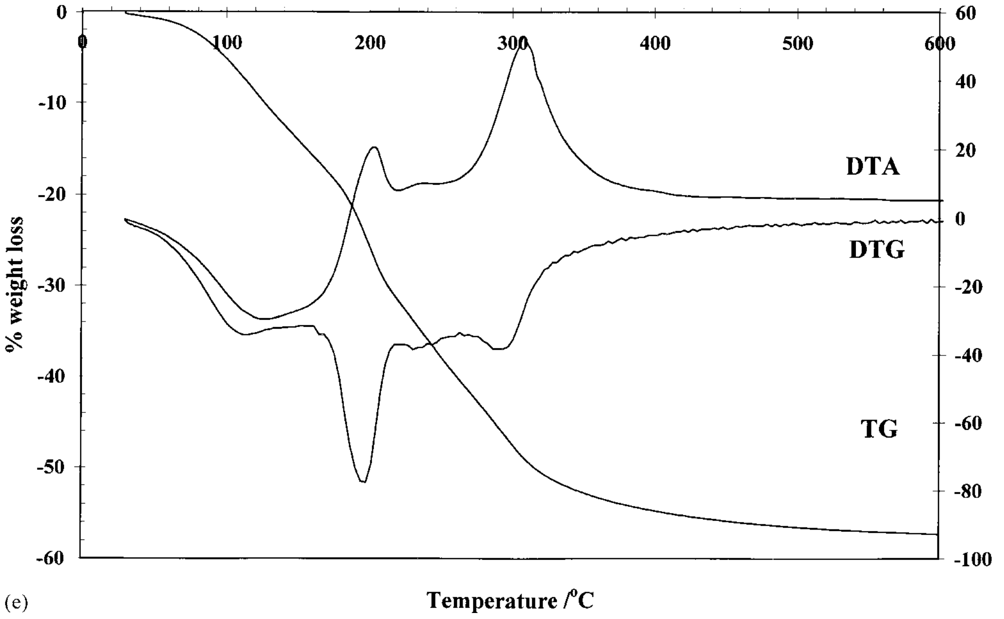


Fig. 4. (*Continued*).

69, 116, 186, 365 and 443°C. The areas of these endotherms are 1.7, 27.5, 24.1 33.6 and 13.1%, respectively. The DTA pattern for boehmite shows peaks at 109, 407, 468 and 496°C (refer Table 1). The areas of these peaks are 25.5, 27.7, 36.3 and 18.0%. The difference between the two patterns rests with the widths of the endotherms for the unmodified gel. Otherwise the peak areas and temperatures of the endotherms are similar. The first two endotherms are assigned to water loss. The peak observed at 186°C may be attributed to low amounts of gibbsite-like structures in the gel, even though X-ray diffraction is unable to detect gibbsite. The two endotherms observed at 365 and 443°C are assigned to the loss of boehmite hydroxyls.

The DTA patterns for the aliphatic acid modified gels show very different behaviour. The DTA pattern of gel formed from acetic acid modified ASB is dominated by the exotherms observed at 333, 350 and 420°C. Endotherms are observed at 123, 172, 220 and around 467°C. The endotherm for the loss of boehmite hydroxyls appears to be hidden by the large exotherms at 333 and 420°C. It is not understood why there are three exotherms. The sharp exotherm at 333°C may be attributed to the combustion of the acetic acid. The DTA patterns for the gels formed from the ASB modified with propanoic and butanoic acids are similar. Three endotherms are observed at 119, 177 and 242°C for the propanoic acid modified gel. These endotherms are attributed to the loss of water from the gels. The first endotherm is ascribed to the loss of water from the gel and the second to the loss of water hydrogen bonded to the boehmite surfaces.

Exotherms are observed at 301 and 329°C. These gels, which are formed from the boehmite-like hydrolysates have a very high surface area. Thus the gels may retain some of the dibutyl ether (b.p. = 141°C), butanoic acid (b.p. = 163.5°C) and/or sec-butanol (b.p. = 99.5°C). Thus the exotherm observed at around 220°C may be attributed to the loss of these adsorbed species. The major exotherm observed at 301°C is attributed to the combustion of propanoic acid. A similar set of results exist for the butanoic acid modified gel. Two endotherms are observed at 123 and 165°C and are attributed to the water in the gel and water hydrogen bonded to the boehmite in the gel. Three exotherms are observed at 200, 238 and 308°C. The large exotherms observed at 308 is attributed to the combustion of the surface-adsorbed butanoic acid.

Table 3
Results of the thermal analysis of aliphatic acid modified alumina gels aged for different time intervals

Peak No.	Parameter	Non-modified diluted	Acetic acid modified	Propanoic acid modified	Butanoic acid modified
Peak 1	Peak max. (°C)	69.1			
	FWHM (°C)	36.9			
	Area (%)	1.7			
Peak 2	Peak max. (°C)	116.2	123.1	118.7	123.3
	FWHM (°C)	70.3	74.3	80.3	76.2
	Area (%)	27.5	−772.5	−1740.6	−461.22
Peak 3	Peak max. (°C)	185.9	172	176.7	165.1
	FWHM (°C)	92	52.6	45.6	35.7
	Area (%)	24.1	−167.8	−394.2	−92.7
Peak 4	Peak max. (°C)		220.2	242	200.1
	FWHM (°C)		147	73.8	23.2
	Area (%)		−1617.7	−428.4	83.99
Peak 5	Peak max. (°C)		272.8	301.2	237.8
	FWHM (°C)		26.5	26.2	23.8
	Area (%)		−39.6	1208.8	19.31
Peak 6	Peak max. (°C)	364.6	333.1	329.5	308.2
	FWHM (°C)	140.5	4.5	57.3	44.5
	Area (%)	33.6	470	1315.9	550.6
Peak 7	Peak max. (°C)		350.7		
	FWHM (°C)		40.5		
	Area (%)		448		
Peak 8	Peak max. (°C)	442.7	420.2		
	FWHM (°C)	83.5	80.9		
	Area (%)	13.1	1163.4		
Peak 9	Peak max. (°C)		496.3		
	FWHM (°C)		86.2		
	Area (%)		416.1		

4.4. Thermogravimetric analyses of the aliphatic acid modified gels

Table 4 reports the weight losses for the unmodified and aliphatic acid modified gels. For the unmodified gel, three weight loss steps are observed as for the TGA patterns of the aged hydrolysates. Steps 1 and 2 are attributed to the weight loss of bulk water in the gel and to the water hydrogen bonded to the boehmite surface. Step 3 is assigned to the loss of the boehmite hydroxyl groups. Steps 4 and 5 are attributed to the weight loss of the aliphatic acids caused by their

Table 4
Percent weight losses in the thermogravimetric analysis of the aliphatic acid modified gels

Modification type	Step 1	Step 2	Step 3	Step 4	Step 5
Non-modified diluted gels	12.75	7.05	19.41	N/A	N/A
Acetic acid modified gels	20.87	8.23	13.54	7.96	7.30
Propanoic acid modified gels	20.24	8.80	14.80	6.90	7.10
Butanoic acid modified gels	19.54	11.15	11.7	7.89	6.57

Table 5
Band component analyses of the DTG curves for the unmodified and modified alumina gels

Weight loss step	Fitted parameter	Boehmite	Non-modified diluted	Acetic acid modified	Propanoic acid modified	Butanoic acid modified
Step 1	Centre (°C)	69.2	107.2	128.5	114.9	119.5
	FWHM (°C)	32.8	70.4	80.3	31.1	78.4
	Area (%)	1.8	25.6	16.1	25.1	24.5
Step 2	Centre (°C)	106.6	188.5	239.4	207.6	195.0
	FWHM (°C)	52.0	118.8	17.3	20.9	33.2
	Area (%)	23.5	29.1	3.0	14.6	34.9
Step 3	Centre (°C)	257.5	304.6	257.1	273.7	239.8
	FWHM (°C)	80.2	62.7	134.2	49.0	34.6
	Area (%)	3.0	3.4	50.8	49.5	6.2
Step 4	Centre (°C)	394.0	376.6	326.7	291.1	286.9
	FWHM (°C)	128.8	138.2	8.1	9.6	67.9
	Area (%)	23.3	33.6	30.0	10.8	34.5
Step 5	Centre (°C)	463	444.6			
	FWHM (°C)	52.6	70.1			
	Area (%)	30.6	8.3			
Step 6	Centre (°C)	490.9				
	FWHM (°C)	33.1				
	Area (%)	17.9				

combustion. Glaubitt et al. [13] suggested that the propionate groups are lost in the 150–250°C range for spinnable modified alkoxide sols. The alkoxide retained in the spun fibre was lost in the 250–360°C range.

The DTG curves are shown in Fig. 4. Table 5 reports the band component analyses of these DTG curves. The DTG curves for the unmodified alumina gel and the standard boehmite closely match the DTA curves. The first DTG peak for the unmodified gel is observed at 107°C and is ascribed to the loss of water in the gel. The corresponding DTA peak was observed at 116°C. The second weight loss step is observed at 189°C and may be attributed to water, which is coordinated to the boehmite-like surface in the gels. Three further weight loss steps are observed at 305, 377 and 445°C. These weight losses correspond with the loss of hydroxyls from the boehmite. The first and third weight losses are minor.

The advantage of using DTGA patterns is that the difficulty of overlapping endotherms and exotherms are avoided, and the minima in the DTGA patterns better represent the thermal changes in the modified alumina gels. The DTG curves in Fig. 4c–e clearly demonstrate the temperatures of the weight loss in the thermal analysis of the aliphatic acid modified gels. Four steps in the weight losses are identified. The first weight loss occurs in the 115–129°C range. The second weight loss step is observed at 239, 208 and 195°C for the acetic, propanoic, butyric acid modified gels. The temperature of this weight loss step decreases with aliphatic acid chain length. The percentage weight loss increases substantially with the acid size for this step. The third weight loss step occurs at 257, 274 and 240°C for the three acids. The third weight loss for the butyric acid modified gel is small. The fourth weight loss step occurs at 327, 291 and 287°C for the acetic acid, propanoic and butanoic acid modified gels. This step for the unmodified gel occurred at 327°C and is in harmony with the decrease in the temperature for this weight loss with chain length.

5. Conclusions

Alumina oxy(hydroxide) hydrolysates were formed from the hydrolysis of (s-BuO)$_3$Al dissolved in anhydrous dibutyl ether. These hydrolysates were aged for times up to 4 h. X-ray diffraction showed that the alumina oxy(hydroxide) was boehmite. The *d*-spacings of the hydrolysates varied with the time for ageing due to the incorporation of water in the interlayer spaces. The (s-BuO)$_3$Al was modified with equimolar amounts of anhydrous aliphatic acids dissolved in dibutyl ether and the gels from the hydrolysates were formed. The X-ray diffraction patterns of these gels showed large *d*-spacings for the (0 2 0) reflection than for boehmite. This increased *d*-spacing is attributed to the incorporation of water in the interlamellar spaces.

The thermal analysis of the aged hydrolysates showed five DTA peaks at 70, 140, 238, 351 and 445°C. These peaks are attributed to the dehydration of the gel and the dehydroxylation of boehmite. The effect of ageing causes the decrease in the water adsorbed on the hydrolysate surface to decrease significantly. Ageing effects the kinetics of peptisation and aged hydrolysates are more readily peptised. Thermal analysis of the aliphatic acid modified gels displayed significantly different patterns from either boehmite and the unmodified gel. The aliphatic acid chain length caused a decrease in the temperature of dehydroxylation of the boehmite-like gel.

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