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Dehydration and dehydroxylation of alumina gels prepared from tri-sec-butoxyaluminium modified with short chain aliphatic acids

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Abstract

The dehydration and dehydroxylation of alumina gels prepared from the hydrolysis of tri-sec-butoxyaluminium (ASB) at both 25 and 90°C, unmodified and modified with short chain aliphatic acids has been studied using a combination of differential thermal analysis (DTA) and thermogravimetry. The alumina phase in the gel was found to be dependent upon the temperature of hydrolysis and the modifying acid. The gels formed at 25°C from unmodified ASB contained alumina as gibbsite and at 90°C from the unmodified ASB a mixture of gibbsite and boehmite, whereas those gels formed from ASB at 25°C and modified with short chain aliphatic acids were amorphous. In DTA of the modified gels, the exotherms from the combustion of the aliphatic acid groups masked the endotherms of dehydration and dehydroxylation of the gels. Neither DTA nor thermogravimetric analysis (TGA) could determine the dehydroxylation temperature range. The application of differential thermogravimetric analysis (DTGA) enabled these temperatures to be obtained. DTGA of the gels formed from the acid modified ASB showed complex 'endograms'. Infrared spectroscopy was used to determine the molecular structures of the acetic acid modified gels.

Keywords: Dehydration; Dehydroxylation; Differential thermal analysis; Differential thermogravimetric analysis; Alumina gel; Gibbsite; Infrared emission spectroscopy; Thermogravimetric analysis; Tri-sec-butoxyaluminium

1. Introduction

Alumina gels are readily prepared by the hydrolysis of aluminium alkoxides [1,2]. Several phases of aluminium hydroxides exist according to the formula $Al(OH)_3$; gibbsite, nordstrandite and bayerite [3]. If the formula is 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 aging of the hydrolysates [4,5]. Aging 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 effect the rates of peptisation of the alumina sols. Aging of the oxo-hydroxides as gels causes structural changes in the sequence amorphous-pseudoboehmite–bayerite–gibbsite [1,2].

Chemical modifiers are used in controlling or retarding the rate of hydrolysis and condensation so that the desired material, a gel, colloidal solution or precipitate is formed [6,7]. The methodology is essential in the process of obtaining a metal sol that is suitable to be used in for example coating applica-

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tions. Acids, chlorides, alcohols, bases, and chelating agents are all substances that effectively produce a less reactive precursor [8]. These ligands undergo either one of the two reactions with the metal. Firstly, nucleophilic substitution may occur where the chemical modifier replaces an original ligand from the metal, a reaction that usually occurs if the precursor is a coordinately saturated metal [6,7],

$$\mathrm{XOH} + \mathrm{Al(OR)_3} \rightarrow \mathrm{Al(OR)}_{3-x}\mathrm{(OX)}_x + x\mathrm{ROH}$$

The second reaction is nucleophilic addition, which occurs only for unsaturated coordinated metal [6–10],

$$\mathrm{XOH} + \mathrm{Al(OR)_3} \rightarrow \mathrm{Al(OR)_3(XOH)}_{n-3}$$

The alumina sols and gels are prepared from the hydrolysis of the modified precursor with water. The tri-sec-butoxyaluminium (ASB) reacts with the modifying aliphatic acid according to the reaction:

$$\mathrm{RCOOH} + \mathrm{Al(OR)_3} \rightarrow \mathrm{Al(OOCR)}_{3-x}\mathrm{(OX)}_x + x\mathrm{ROH}$$

Sanchez et al. [11] indicated that the aluminium sec-butoxide reaction with acetic acid is an exothermic reaction. A transparent alumina gel is obtained in a faster time than in the similar reaction with a titanium alkoxide. The acetic acid:alkoxide ratio of 1:1 takes a few minutes to gel. This effect is due to the increase in condensation rate. Comparing $\mathrm{Ti(OR)_4}$ (Z=4, N=6) to $\mathrm{Al(OR)_4}$ (Z=3, N=8), the greater difference in N and Z influences the condensation rate.

Several methods are available for the study of the structure of alumina gels. One method is to use X-ray diffraction. However, if the gels contain amorphous or semi-amorphous phases where short range order prevails, then XRD is not applicable. The molecular spectroscopic techniques of infrared and Raman are suitable for the study of alumina gels [12,13]. Solid state NMR has also proved useful [12–16]. ^{27}Al SS/MAS NMR has proved useful in determining the peptisation characteristics of alumina hydrolysates. ^{27}Al NMR has proven useful for the determination of the coordination state of the aluminium [12,13]. NMR is also useful in characterising amorphous phases. The technique of thermal analysis has also been used for a long time to study alumina phases [17,18]. In this work, we have prepared alumina gels from tri-sec-butoxyaluminium modified with short chain aliphatic acids. The formation of such gels is important in aluminium production where in the Bayer process the effect of organics on alumina sols can be important. In particular, the presence of organics effects the solubility of the alumina in the caustic solutions. One means of studying the effects of acids on alumina sols is to synthesise the alumina sols in the presence of aliphatic acids. This may be achieved in two ways: (a) by peptising the unmodified ASB with the short chain acid or (b) by modifying the ASB with the acid and then peptising with the same or another acid. In order to understand the chemistry of these sols, we have converted these sols to gels to determine the structure, and in this paper, we report the thermal analysis of alumina gels formed from the hydrolysis of ASB modified with short chain aliphatic acids.

2. Experimental techniques

2.1. Synthesis of alumina sols and gels

Aluminium oxo-hydroxide hydrolysates were prepared by the reaction of tri-sec-butoxyaluminium in both cold (25°C) and hot (90°C) water. The water–alkoxide ratio was kept at 100:1. The alkoxides were introduced into the excess water with vigorous stirring. Alkoxides were modified with short chain aliphatic acids by the slow addition of the dry acid to the alkoxide using an ice bath. The modified alkoxide was then hydrolysed in water to produce the hydrolysate. 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 ~0.6 M. 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 0.1 mol of $\mathrm{HNO_3}$ 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.

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 650°C.

2.3. Infrared emission spectroscopy

FT-IR emission spectroscopy was carried out on a Digilab FTS-60A spectrometer, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere [19–21]. Approximately 0.2 mg of size fractioned alumina gel (<0.5 μm sample size) was spread as a thin layer on a 6 mm diameter platinum surface and held in an inert atmosphere within a *nitrogen purged* cell with an additional flow of argon over the sample during heating. In the normal course of events, three sets of spectra are obtained: firstly the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation is obtained at the same temperatures and thirdly the spectra from the platinum plate covered with the alumina gel sample. Normally only one set of black body and platinum radiation spectra is required.

The emittance spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum+sample, and the result ratioed to the single beam spectrum of an approximate blackbody (graphite). This spectral manipulation is carried out after all the spectral data has been collected. The spectra of a series of alumina gels may be obtained and in the spectral manipulation, the same sets of black body and platinum hot plate radiation are used for all the gel spectra. The emission spectra were collected at intervals of 25°C over the range 100–600°C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 s. Scans were monitored until thermal equilibrium was obtained; this usually required approximately 3–5 min. The spectra were acquired by coaddition of 128 scans for temperatures 100–300°C (approximate scanning time 140 s) and 64 scans for temperatures 300–600°C (approximate scanning time 45 s), with a nominal resolution of $\sim$4 cm^{-1}. Good quality spectra can be obtained provided the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands. In fact, the best quality spectra come from very thin samples of the alumina gel on the platinum plate.

The IES technique depends on the difference in temperature between the sample and the detector for its success. Thus, the greater the difference between the sample temperature and the detector, the better is the quality of the spectrum in terms of signal to noise. Hence, spectra at the lower temperatures always contain more noise. This means that the useful temperature range for the study of dehydroxylation is from 100°C and above. The difficulty of lack of signal for the low frequency region is not as pronounced. The OH stretching region is noisier because it is in the high-energy region of the spectrum. As the temperature goes up, more energy is available at higher wave numbers (Planck's law), therefore at any temperature (up to about 900°C), there is more energy at lower wave number, which gives a higher signal/noise ratio. It is for this reason that the signal gets better as the temperature is increased. Emittance values vary from 0 to 1 with a scale equivalent to an absorption spectrum. The data were linearised with respect to concentration where required, by transforming to units of $-\log 10[1-\text{emittance}(\nu)]$. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectracalc software package (Galactic Industries, Salem, NH, USA).

3. Results and discussion

3.1. Differential thermal analysis (DTA)

Fig. 1 shows the DTA of the alumina gels and the results of the analyses are reported in Table 1. The patterns are complex for all except the alumina gel formed at room temperature from the unmodified ASB. When the ASB is modified with short chain aliphatic acids, the presence of the acetate together with some residual alcohol generated during the hydrolysis results in the observation of some large exothermic peaks. The exotherms increase in size as the length of the alkyl chain increases. These peaks swamp the dehydroxylation of the alumina phases, thus preventing any assessment of which alumina phase is produced.

The alumina gel formed at 25°C shows endotherms at 85 and 288°C with a weak endotherm at 168°C. The

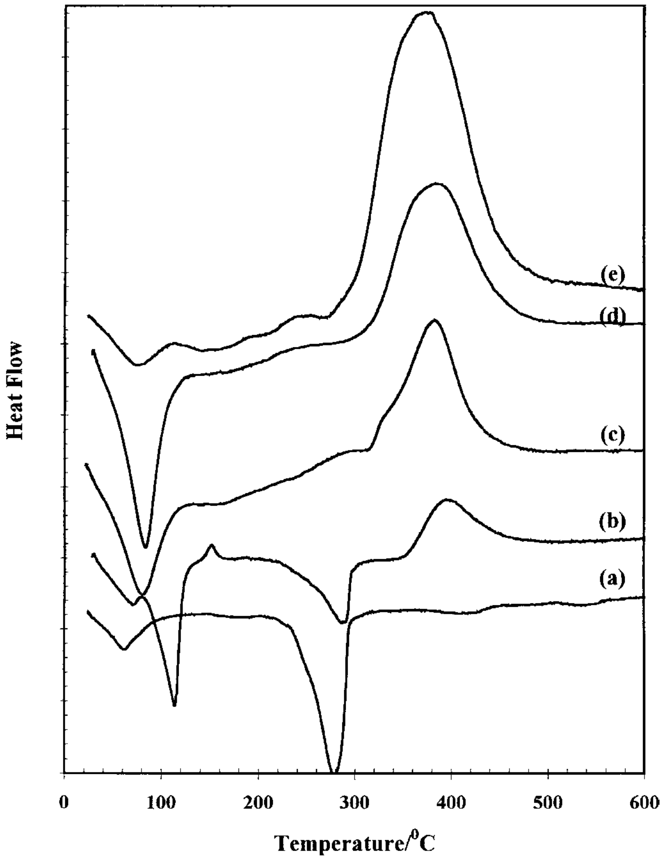

Fig. 1. DTA of alumina gels formed from tri-sec-butoxyaluminium: (a) unmodified at 25°C; (b) modified with 1 mol of acetic acid and hydrolysed at 90°C; (c) modified with 1 mol of acetic acid and hydrolysed at 25°C; (d) modified with 1 mol of propanoic acid and hydrolysed at 25°C; (e) modified with 1 mol of butanoic acid and hydrolysed at 25°C.

Table 1
Endotherms and exotherms of the synthesised alumina gels

Sample	Endotherm 1 *T* (°C), area (%)	Endotherm 2 *T* (°C), area (%)	Endotherm 3 *T* (°C), area (%)	Endotherm 4 *T* (°C), area (%)	Endotherm 5 *T* (°C), area (%)
Alumina gel (25°C) unmodified	85, 15.0	168, 13.5	244, 71.5		
Alumina gel (90°C) unmodified	62, 14.7	251, 23.0	277, 43.4	404, 15.4	538, 3.0
Sample	Dehydration		Dehydroxylation	Compustion	
	Endotherm 1 *T* (°C), area (%)	Endotherm 2 *T* (°C), area (%)	Endotherm 3 *T* (°C), area (%)	Exotherm 1 *T* (°C), area (%)	Exotherm 2 *T* (°C), area (%)
Alumina gel (25°C) modified with 1 mol of acetic acid	78, 45	160, 40	224, 15	346, 11	382, 89
Alumina gel (90°C) modified with 1 mol of acetic acid	71, 31	110, 43	250/285/350, 38	394, 84	424, 16
Alumina gel (25°C) modified with 1 mol of propanoic acid	81, 80	178, 20		356, 25	391, 75
Alumina gel (25°C) modified with 1 mol of butanoic acid	75, 35	147, 38	238, 30	370, 95	467, 5

areas of these endotherms are 15.0, 13.5 and 71.5%, respectively. These values simply represent the amount of thermal energy required to remove the water in the gel. Most of the energy is used to remove the water from the gel. The first two endotherms are attributed to water in the alumina gel and the third to the dehydroxylation of the alumina phase. Synthetic gibbsite shows endotherms at 261 and 284°C. Synthetic boehmite shows two dehydroxylation endotherms at 486 and 500°C [22,23]. Minor endotherms are also observed at 223 and 420°C for synthetic gibbsite [22]. It is concluded that the endotherm at 288°C in the gel formed at 25°C is due to the dehydroxylation of gibbsite. This structure was confirmed by X-ray diffraction. The gel formed at 90°C shows endotherms at 62, 251, 277, 404 and

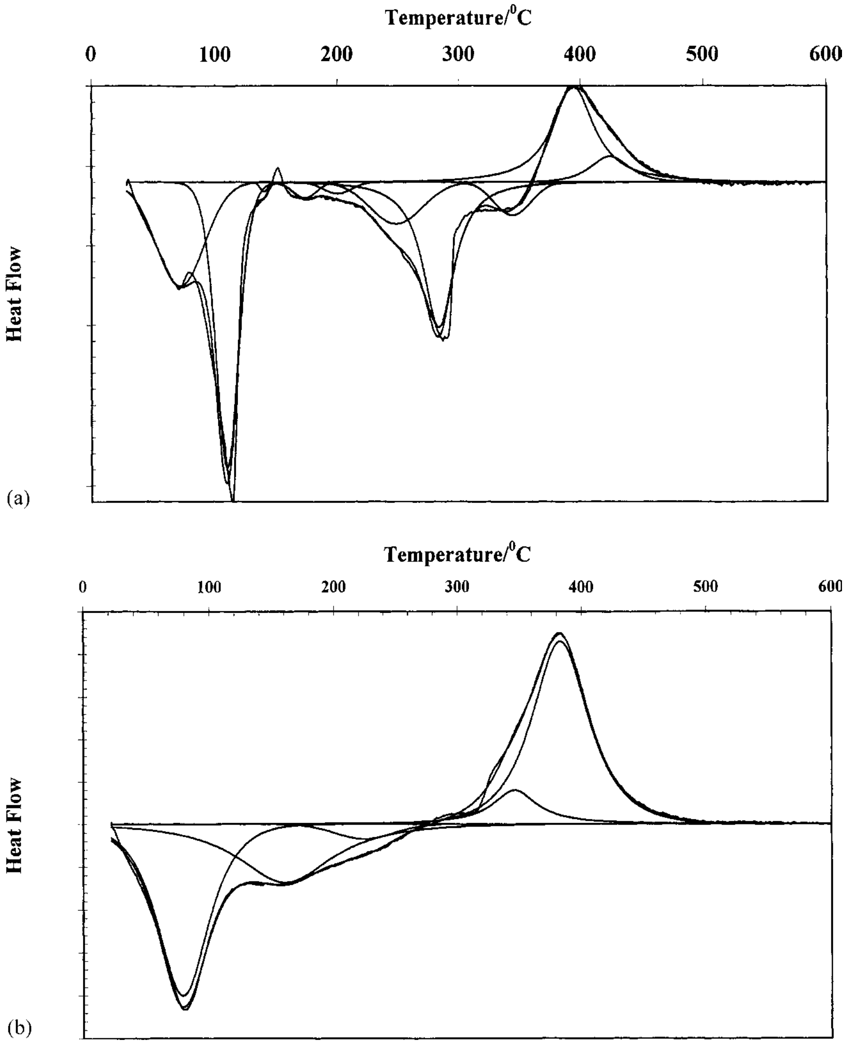

Fig. 2. (a) Component peak analysis of the endotherms of the alumina gel formed from tri-sec-butoxyaluminium modified with 1 mol of acetic acid and hydrolysed at 90°C, (b) Component peak analysis of the endotherms of the alumina gel formed from tri-sec-butoxyaluminium modified with 1 mol of acetic acid and hydrolysed at 25°C, (c) Component peak analysis of the endotherms of the alumina gel formed from tri-sec-butoxyaluminium modified with 1 mol of propanoic acid and hydrolysed at 25°C, (d) Component peak analysis of the endotherms of the alumina gel formed from tri-sec-butoxyaluminium modified with 1 mol of butanoic acid and hydrolysed at 25°C.

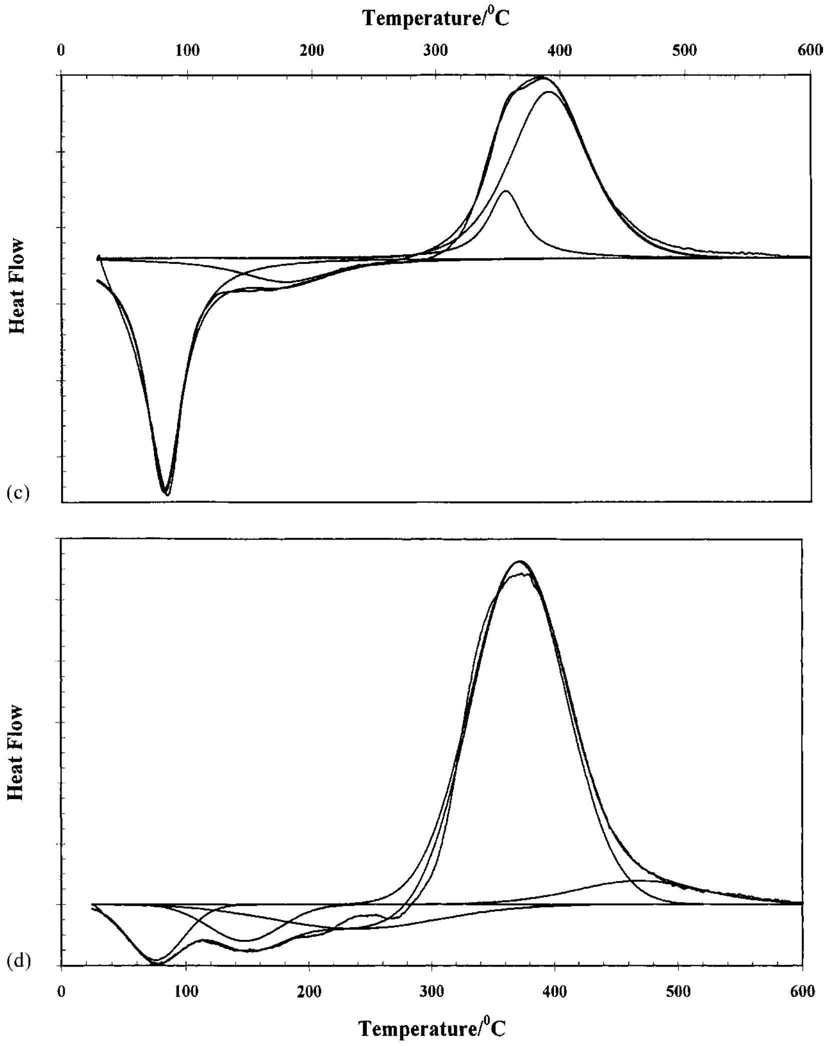

Fig. 2. (*Continued*).

538°C, which have areas of 14.7, 23.0, 43.4, 15.4 and 3%. X-ray diffraction shows that this gel contains a mixture of gibbsite and boehmite.

When the ASB is modified with 1 mol of acetic acid per mole of ASB, the DTA pattern becomes more complex. Fig. 2a shows the component analyses of the DTA pattern of an alumina gel formed from ASB modified with 1 mol of acetic acid per mole of ASB and hydrolysed at 90°C. Two endotherms are observed at 78 and 110°C with relative areas of 15.5 and 21.5%. The first endotherm is associated with water in the gel and the second which required almost 50% of the total energy for the removal of the second water. A set of three endotherms is observed at 250, 285 and 350°C. The first two endotherms are attributed to the dehydroxylation of gibbsite and the second to the dehydroxylation of boehmite. The boehmite is only a minor component in this alumina gel. Normally the hydrolysis of ASB at 90°C results in the formation of boehmite. It is apparent that the presence of the acetate suppresses the formation of boehmite. At 90°C, the sec-butanol formed upon hydrolysis is lost as it simply boils off. Therefore, the exotherm at 394°C must be due to the combustion of the acetate groups.

When the ASB is modified with 1 mol of acetic acid per mole of ASB and hydrolysed at room temperature, the DTA pattern shown in Fig. 1c results. The curve fitting is shown in Fig. 2b. Three endotherms are observed at 78, 160 and 224°C with relative areas of 22.5, 20.0 and 7.5%. The first two endotherms are attributed to the loss of water in the gel and the third to the dehydroxylation of gibbsite, which is partially masked by the large exotherm at 394°C. This large exotherm is attributed to the combustion of not only the acetate groups but also some sec-butanol which may be retained in the gel. The DTA pattern for this gel (Fig. 2b) is very different from the pattern for the gel shown in Fig. 1b. It is proposed that the gel formed contains aluminium oxyacetate and not gibbsite. X-ray diffraction shows that the gel contains an amorphous phase.

Fig. 1d and e shows the DTA patterns from the ASB modified with propanoic and butanoic acids and clearly no dehydroxylation endotherms are observed. Fig. 2c and d illustrates the component analyses of the DTA patterns. Clearly the exotherms from the combustion of retained alcohol and the aliphatic acid groups dominate these fits and in the butanoic case prevents the observation of the expected endotherms. DTA patterns showing the dehydroxylation of the alumina gels in the 250–350°C temperature range would be expected. As for the gel formed from the acetic acid modified ASB, the gels are amorphous.

The dehydration of the alumina gels formed with and without modification with short chain aliphatic acids is different. The alumina gels formed from the hydrolysis and subsequent peptisation with nitric acid show a dehydration temperature of 85°C, whereas the alumina gel hydrolysed at 90°C dehydrates at 62°C. This difference in temperature relates to the bonding mechanism of the water in the gel. It is proposed that the water in the unmodified 25°C gel is hydrogen bonded to the alumina particles, whereas in the unmodified 90°C gel, the water is simply surrounding/hydrating the alumina particles. For the 25°C acid modified gels, two dehydration endotherms are observed; firstly in the 70–80°C temperature range and secondly in the 150–170°C temperature range. For the 90°C acetic acid modified alumina gel, the second dehydration temperature is 110°C. The first dehydration temperature range is similar to that for the unmodified gels. However, the area of the endotherm is significantly larger. The thermal energy required to remove the water of hydration for the unmodified gels is ~15% of the total thermal energy. The values for the acid modified gels vary from 31 to 80%. The second dehydration endotherm is attributed to water hydrogen bonded to the acid groups adsorbed on the surface of the alumina gels.

3.2. Thermogravimetric analysis (TGA)

The thermogravimetric patterns of the alumina gels are shown in Fig. 3. Theoretically, gibbsite and boehmite should have weight losses of 34.6 and 15%. The experimental weight losses are often less than these values, and for synthesised gibbsite and boehmite, weight losses of 26.4 and 12% were obtained. The weight losses and the temperature range are reported

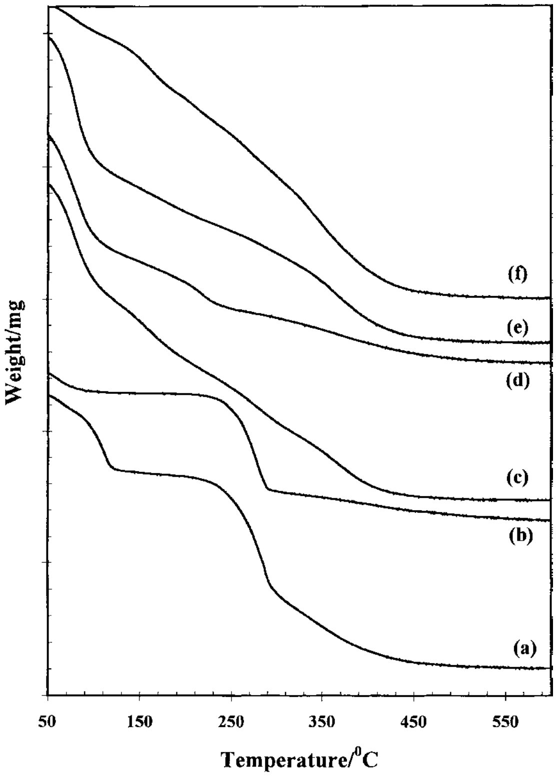

Fig. 3. TGA of alumina gels formed from tri-sec-butoxyaluminium: (a) unmodified at 25°C; (b) unmodified at 90°C; (c) modified with 1 mol of acetic acid and hydrolysed at 90°C; (d) modified with 1 mol of acetic acid and hydrolysed at 25°C; (e) modified with 1 mol of propanoic acid and hydrolysed at 25°C; (f) modified with 1 mol of butanoic acid and hydrolysed at 25°C.

Table 2
Percentage weight losses during dehydration and dehydroxylation of alumina gels

Alumina gel	Dehydration 1 (wt.% loss)	Dehydration 2 (wt.% loss)	Dehydration 3 (wt.% loss)	Dehydroxylation 1 (wt.% loss)	Dehydroxylation 2 (wt.% loss)
Temperature range	25–90°C	90–110°C	110–200°C	200–300°C	300–>400°C
Gibbsite (syn)				26.4 (34.6)	
Boehmite (syn)					12 (15)
Alumina gel (25°C) unmodified		10.3		23.0	6.7
Alumina gel (90°C) unmodified	5.0	5.7		21.3	4.3
Alumina gel (25°C) modified with 1 mol of acetic acid	23.0	14.5	14.5		14.5
Alumina gel (90°C) modified with 1 mol of acetic acid	6.0	11.5		27.8	18
Alumina gel (25°C) modified with 1 mol of propanoic acid	19.0	10.8		22.3	18.7
Alumina gel (25°C) modified with 1 mol of butanoic acid	~9	~11	~5	~12	~28

in Table 2. The thermal analysis patterns for the alumina gels prepared from ASB and not modified show the simplest weight loss with three steps. The unmodified gel formed at 90°C contains significantly less adsorbed water. The TGA curves for the alumina gels formed from ASB modified with short chain aliphatic acids show almost a continuous weight loss and the inflections in the TGA curves are difficult to define. The weight loss for both alumina gels formed from the 90°C hydrolysate and without and with 1 mol of acetic acid is ~6 wt.%. The 25°C acetic acid gels show a weight loss of ~23%. The 25°C propanoic acid gel shows a weight loss of 19.0% at 90°C and a further weight loss of 10.8% over the 110–190°C temperature range. The weight losses for the alumina gel formed from ASB modified with butanoic acid are difficult to determine with precision.

The TGA curves show a weight loss on steps even though the steps are difficult to determine. The second weight loss is in the 90–110°C range and the average weight loss is 12.5%. For the alumina gel formed with the modification of ASB with propanoic acid, it is difficult to determine the breaks in the TGA curve. Consequently, the weight loss of 29.8% is for the first two dehydration steps. For the alumina gel formed from ASB modified with 1 mol of acetic acid and hydrolysed at 25°C, a third step is observed with a weight loss of 14.5%. Thus, it would appear that the dehydroxylation of this gel is different. Acetic acid reacts with the ASB to produce sec-butanol, which in turn reacts with the acetic acid to produce the ester and liberate water. This reaction is highly exothermic. This series of reactions gives rise to the formation of $Al(OH)(CH_3COO)_2$. The TGA curves shows dehydroxylation at a higher temperature than the other gels in the range 250–280°C. It is proposed that this dehydroxylation is that of the hydroxyls from the $Al(OH)(CH_3COO)_2$. A fourth step is observed for this gel in the 325–400°C range and this is attributed to the loss of the acetates. XRD shows that the alumina in this gel is amorphous.

The weight loss for the alumina gel formed from the propanoic acid appears in three steps over the 25–110°C, 110–300°C and 350–400°C range. These steps cannot be observed in the DTA patterns, because of the exothermic peaks. It is likely that the $Al(OH)(CH_3CH_2COO)_2$ is formed in a similar manner to the $Al(OH)(CH_3COO)_2$. The weight loss in the dehydration steps is 29.8% and the weight loss in the two dehydroxylation steps is 22.3 and 18.7 wt.%. XRD shows the alumina gel to be composed of amorphous alumina. For the alumina gels prepared from the modification of ASB with butanoic acid, the TGA curve shows almost a continuous weight loss over the entire range from 25 to 425°C. Table 2 shows estimates of the weight loss over the appropriate temperature ranges.

One method of studying the dehydroxylation steps in gels, which show large exotherms in the DTA patterns, is to study the differential thermogravimetric

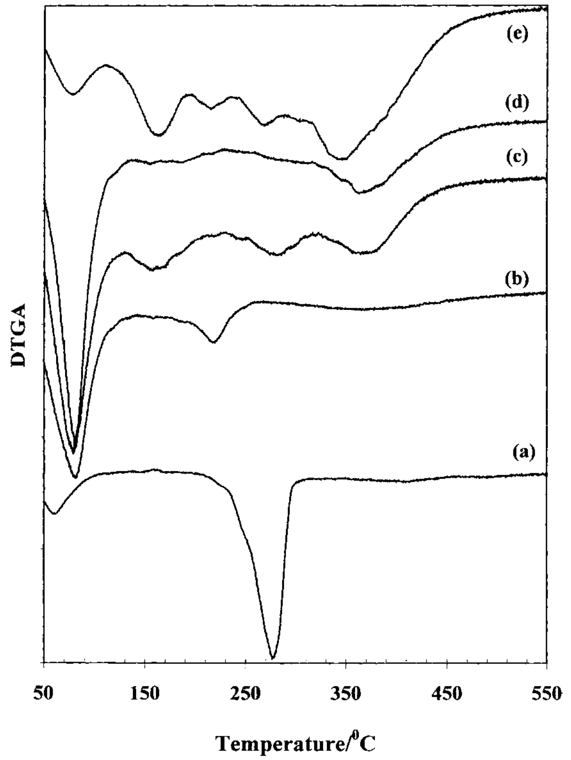

Fig. 4. DTGA of alumina gels formed from tri-sec-butoxyaluminium: (a) unmodified at 25°C; (b) unmodified at 90°C; (c) modified with 1 mol of acetic acid and hydrolysed at 90°C; (d) modified with 1 mol of acetic acid and hydrolysed at 25°C; (e) modified with 1 mol of propanoic acid and hydrolysed at 25°C; (f) modified with 1 mol of butanoic acid and hydrolysed at 25°C.

patterns. Fig. 4 shows the differential thermogravimetric patterns of the alumina gels. It should be remembered that the differential of the TGA curves determines the points of inflections in these curves. Thus, the peaks in the differential thermogravimetric analysis (DTGA) patterns represent the points of maximum weight loss and the temperature range over which this weight loss is occurring. These negative peaks do not necessarily correspond with the endotherms in the DTA curves. However, the DTGA curves eliminate the problem of the large exotherms in the DTA patterns masking the perhaps smaller endotherms.

The TGA for the alumina gel formed without modification of the ASB and hydrolysed at 90°C are observed at 60 and 275°C. These values correspond to the DTA endotherms in Fig. 1a. For the alumina gel formed from the modification of ASB with 1 mol of acetic acid and hydrolysed at 90°C, two endograms are observed at 90 and 225°C with a very broad continuum over the 300–450°C temperature range. The endotherms in the DTA patterns were observed at 110 and 290°C. For the alumina gels formed from the modification of ASB with 1 mol of acetic acid and hydrolysed at 25°C, four weight changes are observed at 90, 175, 280 and 390°C. The first weight loss corresponds well with the endotherm in Fig. 1c. However, no other endotherms could be observed in the DTA pattern. This example clearly demonstrates the usefulness of the technique of differential thermogravimetry. Neither DTA nor TGA could identify the dehydroxylation temperatures. For this particular gel, four weight losses were observed.

The DTGA pattern for the alumina gel formed from the modification of ASB with 1 mol of propanoic acid shows an intense endogram at 95°C with two small peaks at 165 and 205°C and a broad endogram at 390°C. The pattern resembles that of the acetic acid produced gel. X-ray diffraction shows that this gel contains amorphous alumina that on aging transforms to pseudoboehmite. The DTGA pattern for the alumina gel formed from the modification of the ASB with butanoic acid is complex with endotherms observed at 90, 170, 220, 275 and 390°C. The first endogram corresponds to the loss of water from the gel. This gel must contain several chemical species that dehydroxylate or debutanate at these endograms. Nevertheless the DTGA pattern shows weight losses occurring over specific temperature ranges which could not be observed with either DTA or TGA.

3.3. Infrared spectroscopy

Acetic acid in butyl ether shows two peaks at 1720 and 1761 cm^{-1} which are attributed to the symmetric and antisymmetric C=O stretching of the undissociated acetic acid (Fig. 5) [24]. Upon reacting the dry acetic acid with ASB in the ratio of 1:1 in butyl ether at a concentration of 0.06 M, these bands shift to 1603 and 1645 cm^{-1}. These bands are attributed to the monodentate bonding of the acetate group to the aluminium in ASB [24]. In the alumina gels formed from the modification of ASB with 1 mol of acetic

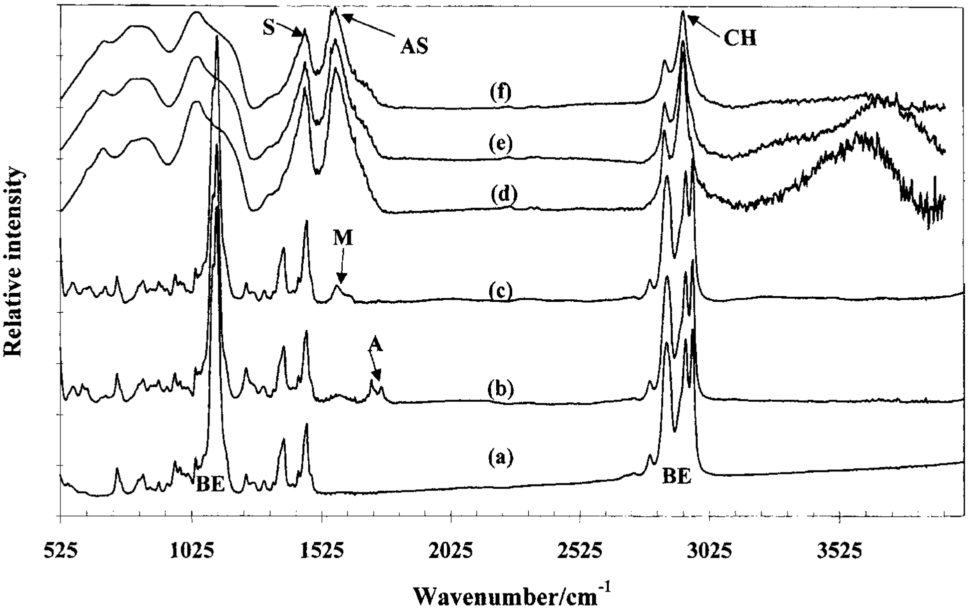

Fig. 5. Infrared spectra of: (a) butyl ether; (b) 0.6 M acetic acid in butyl ether; (c) ASB/acetic acid 1:1 as 0.6 M in butyl ether; (d) acetic acid modified alumina gel at 250°C; (e) 300°C; (f) 350°C (M represents the monodentate C=O antisymmetric stretch, A the free acetate, S the monodentate C=O symmetric stretch, AS the antisymmetric stretch, BE is butyl ether and CH the CH stretching vibrations of acetic acid).

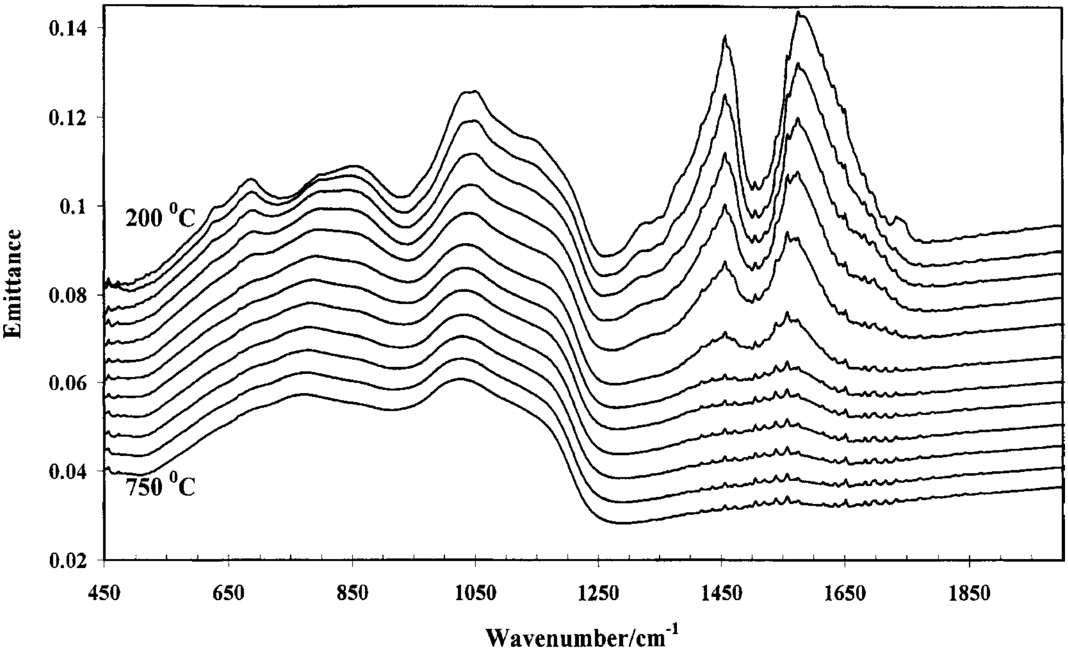

Fig. 6. Infrared emission spectra of alumina gel formed from the 25°C hydrolysis of ASB with acetic acid over the temperature range 200–750°C.

acid the antisymmetric stretching band is observed at 1587 cm^{-1}. The symmetric stretching mode is observed at 1464 cm^{-1}. However, this is the overlap of this band with the 1430 cm^{-1} HCH bending mode. What the spectra clearly show is that the alumina gels contain acetate groups bonded to the aluminium in a monodentate coordination.

Spectra d to f also show the loss of hydroxyls from the gel. In the 250°C spectrum two bands are observed at 3642 and 3475 cm^{-1} using curve fitting techniques. The higher frequency mode is attributed to the OH stretching vibration of aluminium hydroxyls. The lower frequency vibration may be due to the hydroxyl groups in the gel, which are hydrogen bonded to acetate groups. Alternatively, the 3475 cm^{-1} band may be due to hydroxyls attributed to water in the gel. The hydrogen bond causes the frequency to be shifted to lower values. These bands are observed at 3707 and 3142 cm^{-1} in the 300°C spectrum. As thermal degradation of the gel is occurring, these hydrogen bonds are being removed and the frequency of the hydroxyl stretch is then observed at 3700 cm^{-1}. It is proposed that a phase change is occurring between 250 and 300°C, which involves the loss of acetate groups. The difference between the two spectra at 250 and 300°C in the hydroxyl-stretching region is observed in the relative intensities of the two bands at 3642 and 3475 cm^{-1}. The intensities are in the ratio of 1.7–1.5 in the 250°C spectrum and are 1.7–0.7 in the 300°C spectrum. The intensity of the band at ~3475 cm^{-1} has decreased by more than 50% in this temperature range. The loss of acetate groups may be observed by the decrease in intensity of the CH stretching vibrations at ~2927 and 2861 cm^{-1}. The intensity of these bands is approaching zero as the dehydroxylation occurs. In the 350°C spectrum, two weak bands are observed at 3397 and 3632 cm^{-1}. The infrared emission spectra show that some acetate groups are retained up to ~450°C. Such observations fit well with the DTGA pattern where an endogram is observed in the range 325–375°C (Fig. 4c). Also a weak band is observed at 1335 in the 250°C spectrum which shifts to 1320 in the 350°C spectrum and is lost by 400°C (Fig. 6). This band is attributed to the Al–O–C bond. Importantly, XRD showed the gel to be amorphous, the infrared emission spectra shows some rearrangement of the molecular structures upon thermal degradation.

4. Conclusion

The alumina gel formed from the nitric acid peptisation of the hydrolysate formed from the reaction of tri-sec-butoxyaluminium with water is shown to be gibbsite. Peptisation at 90°C resulted additionally in the formation of some pseudo-boehmite as determined by X-ray diffraction and infrared spectroscopy. When the alumina gels are formed from the modification of the ASB with acetic acid and peptised at 25°C, complex gels involving $Al(OH)(CH_3COO)_2$were produced. The calcination of this gel to 600°C produced amorphous alumina. When the dehydroxylation endotherms are masked by the exotherms due to the combustion of the aliphatic acid and the alcohol in the DTA patterns, the differential thermogravimetric curves were used to determine these phase changes. Neither DTA nor TGA could be used to determine the complex patterns.

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