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The role of lattice water in determining the reactivity of various crystalline aluminas

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The thermal decomposition of alkali metal chlorides was studied on a series of colloidal and particulate aluminas with different crystalline phases. Decomposition was monitored by differential thermal and thermogravimetric analysis and the resulting phase development by X-ray diffraction. It was found that the presence of strongly bound lattice water in colloidal gel bohemite alumina caused significantly lower decomposition temperatures and increased reactivity towards compound formation. This has been attributed to the simultaneous loss of water via a hydrolysis reaction with the metal chloride, and subsequent phase transformation of the pseudo-bohemite into γ-alumina, forming the aluminate at a much reduced temperature.

1. Introduction

Alumina hydrates exist in many crystalline forms, the type of which depends strongly on the pH of precipitation from a salt solution, the type of alumina salt used and the subsequent ageing of the precipitate to give a crystalline phase. The precipitate resulting from a nitrate solution treated with ammonium hydroxide at pH 8–8.5, leads to the formation of a pseudo-bohemite gel on ageing with the formula $Al[(O)(OH)(H_2O)]$. This crystalline structure is distinctly different from the mineral bohemite $AlO(OH)$ with the first X-ray interference plane increased from 0.611 nm for mineral bohemite, to 0.66–0.67 nm for the gel or pseudo-bohemite, but showing identical atomic arrangement at short distances [1]. The excess water over mineral bohemite, therefore, is not to be regarded as merely adsorbed on the surface of finely divided crystallites, but situated between the elemental AlOOH structural layers, leading to an enlargement of the basal plane. Elimination of this water at $> 450\,^{\circ}C$ leads to the transformation to γ-alumina, with no excess water.

Recently, work has shown that hydrated transition metal chloride salts supported on colloidal pseudo-bohemite alumina, decompose at significantly lower temperatures than the salt alone, producing the corresponding aluminates simultaneously. This behaviour was not seen on particulate α-alumina [2]. It is thought that the lattice water in the gel bohemite is responsible in enhancing the decomposition of the chloride, and the subsequent phase transformation into γ-alumina, combined with the homogeneity of the precursor gel, is forming the aluminates at low temperatures.

However, the transition metal chlorides used in this study contain large amounts of water of crystallization, the decomposition temperature of which overlaps that of the pseudo-bohemite. It was therefore thought that for an unambiguous result, a series of high-temperature decomposing chlorides with no lattice water should be used.

In this work, we explored the decomposition of alkali metal chlorides on various colloidal and particulate aluminas of different crystalline phases. These chlorides are difficult to decompose, melting only at high temperature and without the loss of chloride, and contain no water of crystallization above 100 °C. In addition, a colloidal γ-alumina with no lattice water, supplied by Degussa, was especially chosen for comparison, to show that high homogeneity and small particle size are not a factor in the observed low-temperature decomposition reactions.

2. Experimental procedure

2.1. Sample preparation

The aluminas chosen for the present study were Condea “Disperal” colloidal pseudo-bohemite (77%–82% Al_2O_3), Degussa colloidal gamma alumina (99.9% Al_2O_3) and a standard particulate alpha alumina (99.9%). In the case of the colloidal aluminas, sols were made by dispersing the powder in water or 10^{-2} M nitric acid to a concentration of $250\,g\,l^{-1}$. Solutions of the alkali metal salts $LiCl \cdot H_2O$, NaCl and KCl (Aldrich 99.9%) were also made up to a concentration that did not upset the colloidal dispersions.

In a typical preparation, 50 ml LiCl solution was slowly added with stirring to 75 ml Condea alumina sol, to give 10% by weight of Li_2O, and the colloidal dispersion maintained, if required, by the addition of distilled water. This was then dried to a translucent water-dispersible gel at 105 °C in an air oven. A similar procedure was employed to produce 10% by weight equivalent of sodium and potassium oxides on Condea and Degussa aluminas.

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In the case of non-colloidal α-alumina, this was finely ground and water added to give a paste. The paste was dried at 105 °C and the alkali metal nitrate added by incipient wetness to give 10% by weight of oxide as before. This was again heated to 105 °C in an air oven. The oven-dried samples were then subject to thermal analysis.

2.2. Sample characterization

X-ray powder diffraction (XRD) patterns for samples treated at various temperatures were recorded in the region of $2\theta = 10°–80°$ with a step scan of $0.1° \text{ min}^{-1}$ on a Philips diffractometer (Model PW1710) using CuK_α radiation.

Simultaneous differential thermal and thermogravimetric analysis (DTA–TGA) of the dried samples was carried out on a Rheometric Scientific thermal analyser (Model STA 1500) to determine weight loss and phase transformation up to 1200 °C. Flowing air was used as the sample atmosphere and the temperature was ramped at $10\,°\text{C min}^{-1}$.

3. Results and discussion

DTA–TGA results of the unsupported chlorides are shown in Fig. 1. Lithium chloride monohydrate, Fig. 1a, shows three endothermic peaks at 105, 181 and 615 °C. The low-temperature peaks correspond to the removal of structural water and any perchlorate decomposition; the weight loss of ~30% corresponds exactly to the loss of monohydrate. The endotherm, without loss of weight at 615 °C, is due to the melting of the chloride without decomposition. Sodium and potassium chlorides, Fig. 1b and c, show similar melting points at 778 and 807 °C, respectively, but without the initial decomposition, because they are anhydrous. The melting temperatures observed closely match those from the literature [3].

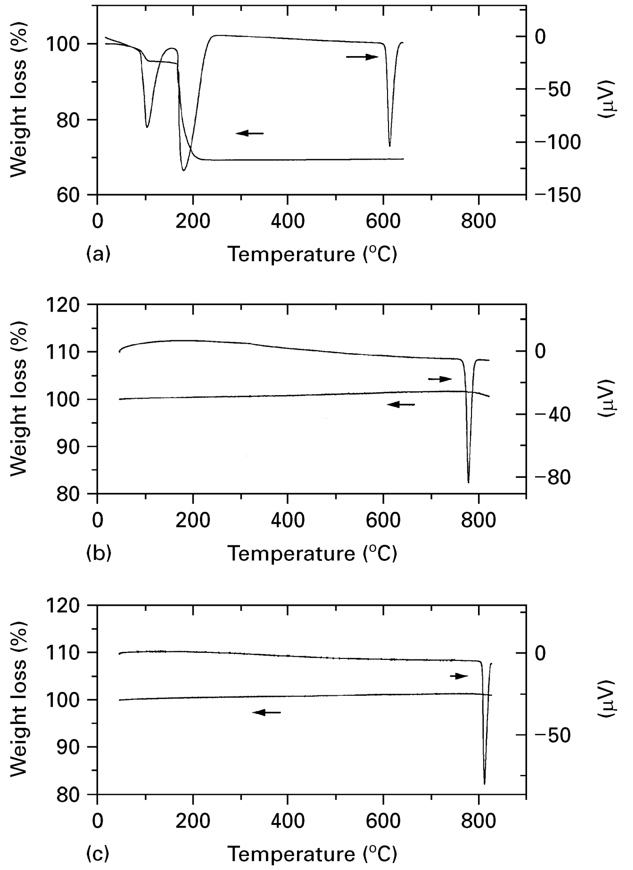

Figure 1 DTA–TGA plots of (a) $LiCl \cdot H_2O$, (b) NaCl, and (c) KCl.

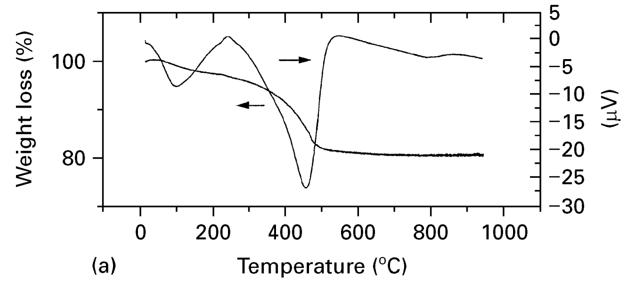

Figure 2 DTA–TGA plots of (a) Condea alumina gel, and (b) Degussa Aluminoxide C and alpha alumina.

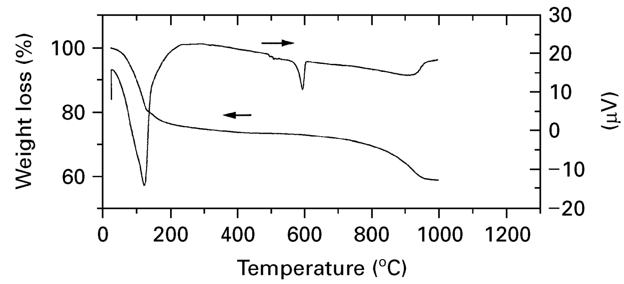

Figure 3 DTA–TGA plot of $LiCl \cdot H_2O$ supported on degussa alumina.

Fig. 2 shows the thermal characteristics of the alumina substrates used in the present investigation, without the supported chlorides. The oven-dried Condea gel (Fig. 2a) shows a low-temperature endotherm and weight loss corresponding to the loss of acid-stabilizing species (NO_3^- in this case) and a large endotherm and weight loss at 300–500 °C, which corresponds to the loss of lattice water (5%–10% by weight) and subsequent transformation of the pseudo-bohemite into γ-alumina. Fig. 2b is representative of both the particulate α-alumina and the colloidal γ-alumina treated with water and dried at 105 °C, neither losing any weight nor showing any transformation up to 1000 °C.

On heating the dried gel of LiCl supported on Degussa alumina from room temperature to 1200 °C, three distinct endotherms appear, as shown in Fig. 3. The first at 120 °C indicates loss of loosely bound water, the second at 600 °C is due to melting of the chloride without decomposition and the third at

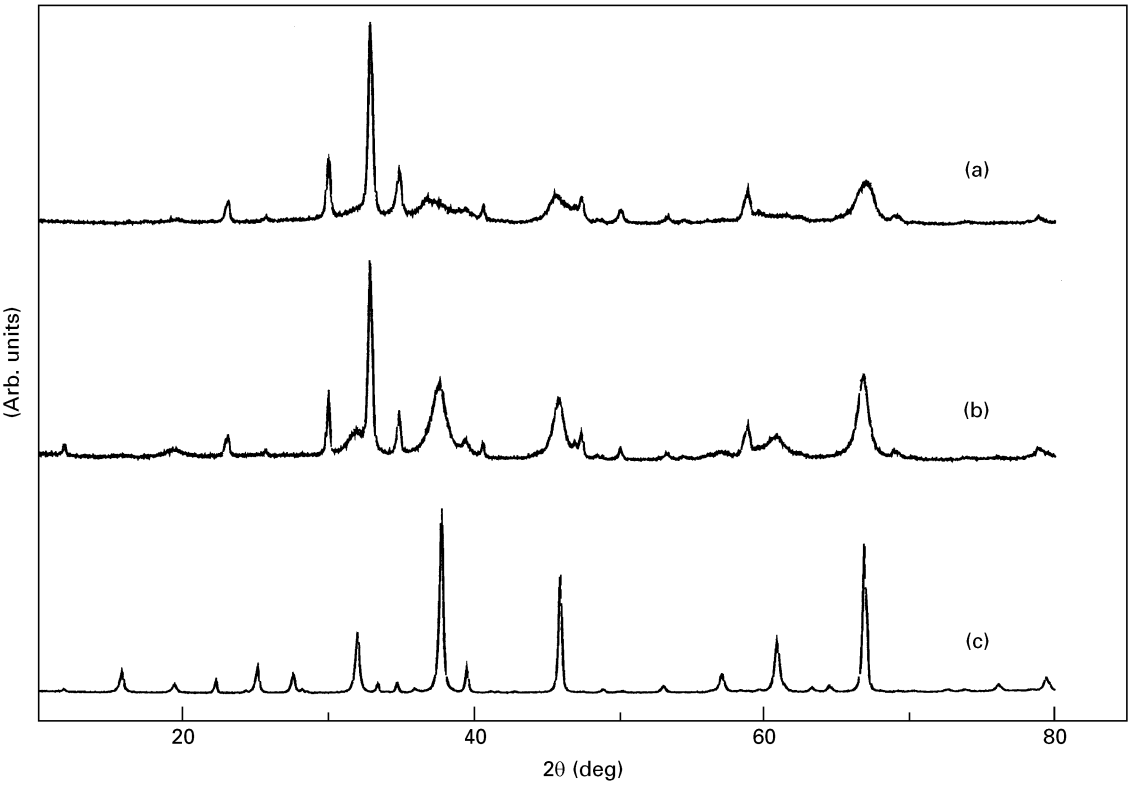

Figure 4 XRD patterns of LiCl·H_2O supported on degussa alumina heated to (a) 600 °C, (b) 800 °C, and (c) 1200 °C.

950 °C is attributed to the decomposition of the chloride and subsequent phase transformation of the alumina. A similar thermal response is observed for both NaCl and KCl supported on the colloidal γ-Al_2O_3 showing that neither the single water of crystallization of the lithium chloride nor the nanosized particles of the Degussa alumina, have any effect on chloride decomposition below the normal decomposition temperature.

The phase development of the lithium chloride decomposition described above is shown in Fig. 4. At 600 °C, only LiCl and γ-Al_2O_3 are present. At 800 °C, LiCl is still present as indicated in the DTA–TGA trace, but some of the alumina has transformed into δ-Al_2O_3. Finally, at 1200 °C, with loss of chloride, the lithium oxide reacts with the alumina which is now transforming to α-Al_2O_3, to give a mixture of $LiAlO_2$ and $LiAl_5O_8$. The pattern is repeated for NaCl and KCl with compound formation at the $\delta \rightarrow \alpha$ transition to give β-$NaAl_{11}O_{17}$ and β-KAl_5O_8.

The water-treated α-alumina dried to constant weight at 105 °C and impregnated with alkali metal chloride, showed no difference in the decomposition behaviour from that of the colloidal γ-alumina; however, as expected, the $\delta \rightarrow \alpha$ transition endotherm was absent.

The thermal behaviour of alkali metal chlorides on the pseudo-bohemite, however, was completely different. A typical DTA–TGA trace for the decomposition of NaCl is shown in Fig. 5. Here a steady weight loss is observed up to 550 °C, where it stabilizes with no further loss. A series of endotherms additional to the bohemite to γ-alumina transformation and water loss seen earlier, indicates an additional decomposition over the bohemite alone. Chloride analysis of this sample at 600 °C shows no residual traces at this temperature, thus indicating a loss of chloride coinciding with the loss of water from the pseudo-bohemite. The small exotherm at 600 °C suggests the formation of a compound.

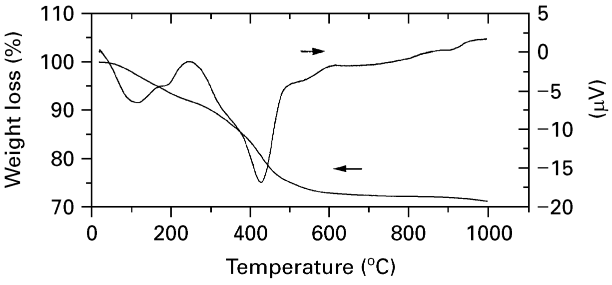

Figure 5 DTA–TGA of NaCl supported on Condea pseudo-bohemite alumina.

X-ray diffraction of the products of this decomposition are shown in Fig. 6. This clearly shows the absence of NaCl as a phase, and that even at a temperature as low as 600 °C, formation of the aluminate has started, corresponding to the observed exotherm. The excess alumina remains as a γ-phase to at least 1000 °C. This thermal behaviour is characteristic of all the chlorides studied on the pseudo-bohemite.

The fact that all the alkali chlorides decomposed at the same temperature regardless of their different stabilities, and that this decomposition coincides with water loss from the pseudo-bohemite, suggests some form of hydrolysis reaction is taking place.

It is known that lattice water exists in thorium nitrate, and that on heating at 490 °C, hydrolysis and

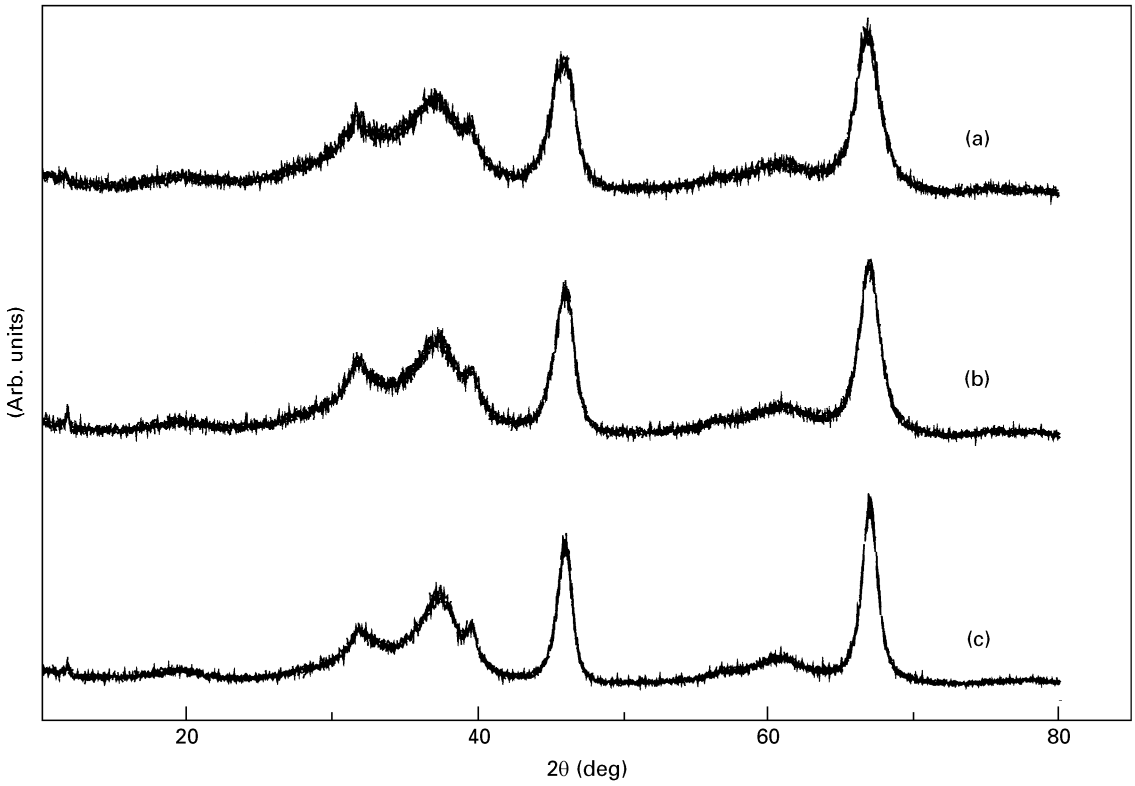

Figure 6 XRD patterns of NaCl supported on Condea pseudo-bohemite alumina heated to (a) 600 °C, (b) 800 °C, and (c) 1200 °C.

polymerization of the salt occurs [4], producing a water dispersible colloid according to the following reaction

$$MX_n + yH_2O \rightarrow n[M(OH)_yX_{n-y}] + yHX \quad (1)$$

It is therefore probable that the lattice water between the elemental layers of the pseudo-bohemite is hydrolysing the alkali metal chloride as the transformation to γ-alumina is taking place, producing a volatile acid species and a polymeric aluminate precursor which readily crystallizes at low temperature. The colloidal nature of the Condea alumina support also ensures a high dispersion of reactants and therefore a homogeneous product, but does not aid the hydrolysis reaction which appears to be a direct result of the presence of lattice water.

4. Conclusion

It has been demonstrated that the presence of lattice water within a colloidal support can significantly reduce the decomposition characteristics of the supported salt. In doing so, and in the case of the alkali metal chlorides highlighted here, it opens a new route to the disposal of high melting salts and to the stoichiometric low-temperature synthesis of alkali metal aluminates without volatilization at high temperatures. More detailed work using proton CP-MAS NMR is being carried out on this hydrous alumina and its analogous counterpart γ-FeOOH, to understand the nature of this lattice water, and its role in the stabilization of inorganic sol dispersions.

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