Thermal formation of corundum from aluminium hydroxides prepared from various aluminium salts

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Abstract. Aluminium hydroxides have been precipitated from various aluminium salts and the differences in their thermal behaviour have been investigated. Pseudoboehmite derived from the nitrate, sulfate and chloride all form γ-Al_2O_3 at ~ 400°C but the formation of α-Al_2O_3 at 1200°C occurs more readily in the material derived from the sulfate. This contains a higher concentration of anionic impurities related to differences in the solubility of the original aluminium salts. The sulfate is retained in the gel to higher temperatures at which its eventual decomposition may lead to the formation of a reactive pore structure which facilitates the nucleation of α-Al_2O_3.

Keywords. Aluminium hydroxide; corundum; thermal transformation.

1. Introduction

Aluminium hydroxides exist in several modifications (gibbsite, bayerite, boehmite and diaspore). The structures of all the aluminium hydroxides consist of stacked double layers of oxygen atoms in which the aluminium cations are located in octahedral coordination in the interstices (Levin and Brandon 1998). The aluminium hydroxides are a common source of aluminium oxide (Al_2O_3), which itself exists in various metastable polymorphs (transition aluminas) in addition to the thermodynamically stable α-Al_2O_3 form (corundum). The transition aluminas (especially the γ-form) have fine particle sizes and high surface areas with enhanced catalytic surface activity of their surfaces, and find industrial applications as adsorbents, catalysts or catalysts carriers, coatings and soft abrasives (Levin and Brandon 1998). The thermal stability of the transition aluminas depends on their morphology and crystallite size (Bennet and Stevens 1998; Braun *et al* 1999). The morphology may depend on the morphology and impurity content of the aluminium hydroxide precursors, which in turn may be influenced by the aluminium salt used as the starting reagent. Since the various aluminium salts have different solubilities, the morphologies and impurity contents of the resulting aluminium hydroxides are expected to depend on the starting salt.

The aim of present work is therefore to examine possible differences in the thermal transformation to corundum of aluminium hydroxides precipitated from three different aluminium salts.

2. Experimental

The starting reagents were $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $AlCl_3 \cdot 6H_2O$ (Reachim, Russia). These were dissolved in distilled water and concentration of the stock solutions adjusted to $0 \cdot 5$ mol·l^{-1}. Aluminium hydroxide was precipitated at room temperature from these solutions by adding 1 : 1 aqueous ammonia solution at pH 9·80–9·90. The resulting precipitate was immediately washed with distilled water, filtered and dried at 60°C for 12 h. After drying it was hand-ground to pass a 0·09 μm sieve. The alumina precursor powders prepared from $Al(NO_3)_3$, $Al_2(SO_4)_3$ and $AlCl_3$, denoted AN, AS and AC respectively, were characterized by XRD (Siemens D-5000 diffractometer with CuKα radiation) and DTA-TG (Rigaku Thermoplus TG 8120). The true densities of the powders were determined using a Micrometrics Accupys 1330 instrument and their particle size distribution was measured on samples dispersed in aqueous sodium hexametaphosphate solution using a Mastersizer E instrument (Malvern Instruments Ltd. UK).

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3. Results and discussion

The XRD diffractograms of the precipitated aluminium hydroxides are shown in figure 1.

All samples are seen by XRD to contain pseudo-boehmite of low crystallinity. Sample AN contains a trace of NH_4NO_3 (PDF no. 8-452), and AC contains a significant quantity of NH_4Cl (PDF no. 7-0007), but no crystalline impurity was detected in sample AS. Since all the gels were washed with distilled water immediately after precipitation and before aging had occurred, the large amount of NH_4Cl may be due to the decreased solubility of this compound by comparison with NH_4NO_3 and $(NH_4)_2SO_4$.

Figure 2 shows the DTA-TG traces for these aluminium hydroxides, which indicate that AN and AC samples behave similarly in displaying an endotherm at about 250–270°C.

This thermal event is due to decomposition of pseudo-boehmite and, in the case of AN, the nitrate impurity (Lee and Yu 1992). All samples, but especially AS and AC, show a weak endothermic effect at about 400–410°C indicating the formation of γ-Al_2O_3 (Sunil Kumar *et al* 1997; Sathiyakumar and Gnanam 1999). At higher temperatures, small broad exotherms due to the transformation to α-Al_2O_3 occur at 1205°C, 1180°C and 1230°C in AN, AS and AC respectively. In sample AN this peak is broader than in AS and AC. The TG curves of AN and AC (figures 2D and F) indicate that all the volatile species are evolved below about 600°C. The weight loss in AN occurs in two main stages; a rapid loss of about 46% accompanies the major pseudoboehmite decomposition endotherm and is complete by about 280°C. The second, more gradual loss of about 11% is complete by about 480°C. In sample AC (figure 2F) the major endotherm is associated with a weight loss of about 27% with a further gradual loss up to 480°C.

The thermal decomposition of boehmite may be written as

$$2AlOOH \rightarrow Al_2O_3 + H_2O\uparrow, \tag{1}$$
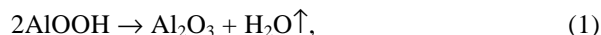
for which the theoretical weight loss is 15%. Pseudo-boehmite can contain variable amounts of additional water which must be eliminated prior to reaction (1). Sample AN loses 46% weight up to the first major inflection at 280°C; this corresponds to a pseudoboehmite composition containing 3 moles of additional water (theoretical loss 47%). Assuming the product at this stage is boehmite, and that the subsequent more gradual weight loss up to the plateau at 480°C corresponds to its dehydroxylation, the loss based on boehmite rather than pseudoboehmite is 20%. The discrepancy between this and the theoretical value for (1) may be explained in part by the nitrate impurity known to be present, and suggests that this species may display increased thermal stability in the present system and be evolved during the higher-temperature reaction. Sample AC loses 27% weight up to the first inflection at 280°C; this corresponds to ~ 1 mole of water in the pseudoboehmite (theoretical loss 23%). The loss in the second stage (14·7% based on boehmite rather than the original pseudoboehmite) is in excellent agreement with the theoretical value of 15% for (1). Thus, sample AC behaves as expected for a pure pseudoboehmite containing 1 mole H_2O.

The sulphate-derived sample AS (figure 2E) shows a much more gradual weight change, losing about 24% up to about 480°C, and a further 13% in two stages up to about 1000°C. The continuous lower-temperature loss up
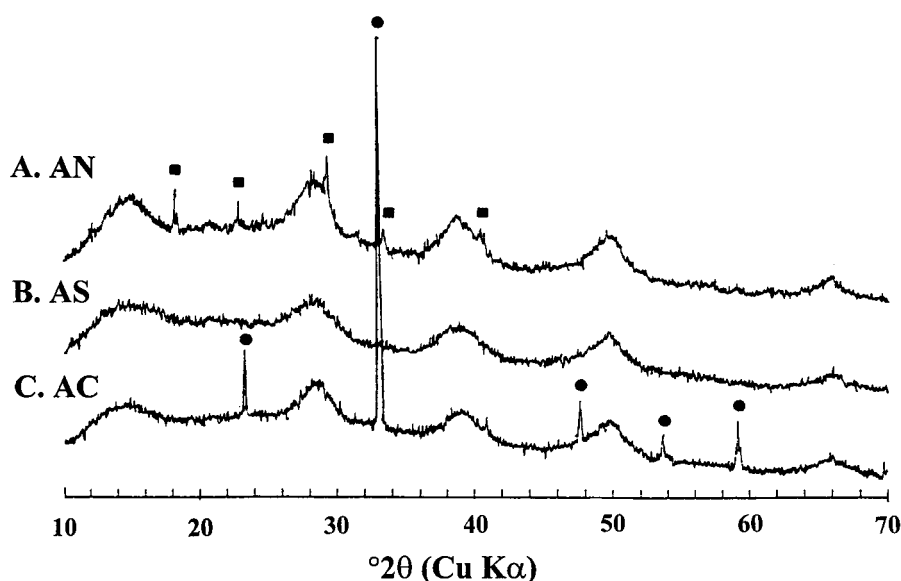

Figure 1. X-ray powder diffractograms of aluminium hydroxides precipitated from various Al salts (Key: ■ = NH_4NO_3 (PDF no. 8-452), ● = NH_4Cl (PDF no. 7-0007)).

to 480°C suggests that the dehydration reactions of the pseudoboehmite and the resulting boehmite overlap, and, if so, the pseudoboehmite must contain only a small amount of hydration water. The higher-temperature weight losses (3·3% between 480 and 700°C and about 10% between 700 and 1000°C) are most likely due to the presence of thermally stable sulfate species which decompose to sulfur oxides at about this temperature.

Pseudoboehmite and boehmite are reported to be continuous in their structure and physical properties, rendering any distinction between them arbitrary (Tottenhorst and Hofmann 1980). On heating, boehmite transforms to corundum via the sequence of transition aluminas: boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$. The final transformation from θ to α occurs above 1150°C by a process of nucleation and growth (Messing *et al* 1986).

The X-ray diffractograms of the samples heated to 800°C without holding at temperature indicate that at this temperature all three gels have formed poorly crystalline $\gamm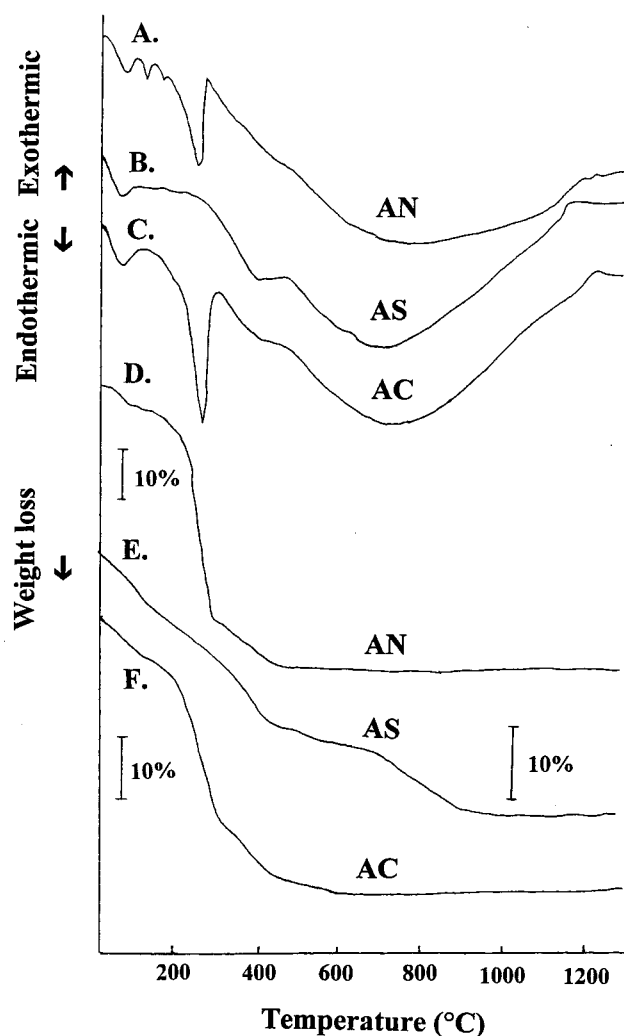a$-$Al_2O_3$ (figure 3A); the intensities of these reflections are slightly weaker in sample AS but no other differences are observed. This result is consistent with the DTA observation that the endothermic peak due to the crystallization of γ-Al_2O_3 is similar for all three samples, suggesting similar thermal behaviour up to this stage.

Heating the samples to 1000°C without holding at temperature sharpens the γ-Al_2O_3 reflections (figure 3B). The presence of δ-Al_2O_3 in these samples cannot be ruled out since they could be contained within the broad diffraction profile (figure 3B), but no evidence of θ-Al_2O_3 is present in any of the samples at this temperature. However, differences in the thermal behaviour of the three samples are

Figure 2. Thermal analysis traces of aluminium hydroxides from various Al salts (A–C, DTA curves and D–F, TG curves).
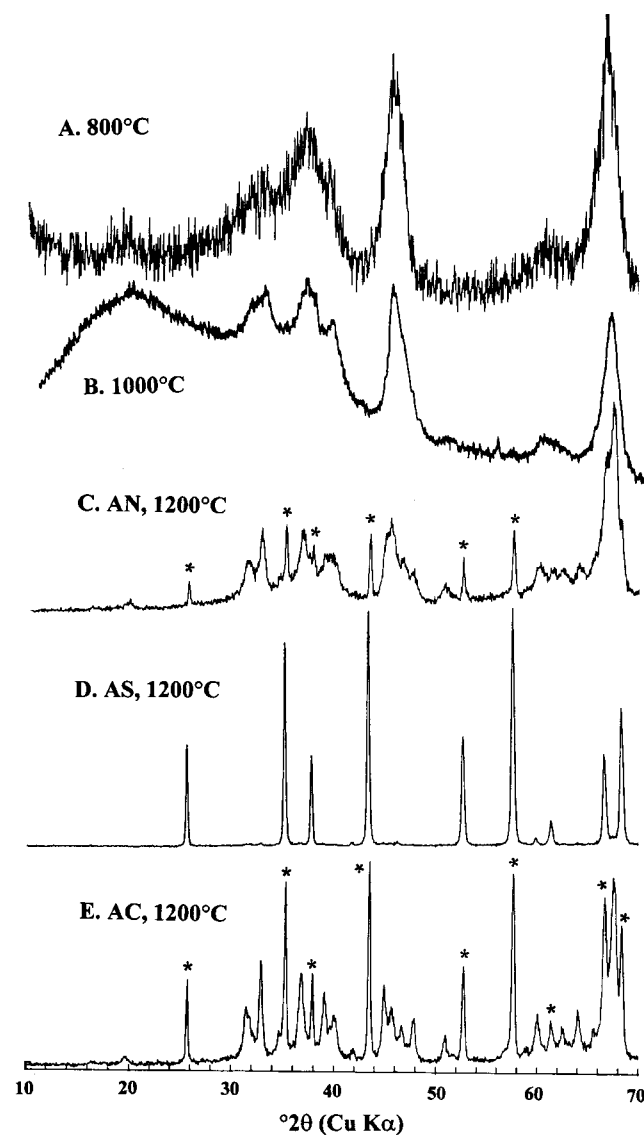

Figure 3. X-ray powder diffractograms of alumina samples precipitated from various Al salts. A. Typical pattern for all samples heated to 800°C and immediately cooled. B. Typical pattern for all samples heated to 1000°C and immediately cooled. C–E. Samples heated to 1200°C and immediately cooled. In traces C and E the asterisks denote α-alumina (PDF no. 10-173), unmarked peaks correspond to θ-alumina (PDF no. 23-1009). In trace D, all the peaks correspond to α-alumina.

revealed on heating to 1200°C without holding at temperature (figures 3C–E). The samples derived from precursors AN and AC contain the diffraction lines of θ-Al_2O_3 (PDF no. 23-1009) and α-Al_2O_3 (PDF no. 10-0173). The intensity of the α-Al_2O_3 pattern is greater in the sample from AC than in the sample from AN. This result, and the broader DTA exotherm of sample AN suggests that the nucleation of α-Al_2O_3 occurs more heterogeneously in this material. By contrast with AN and AC, sample AS is converted completely to corundum at this temperature, consistent with the DTA result. These findings indicate that unlike AN and AC, AS transforms either without passing through the θ-phase, or that the lifetime of this phase in AS is comparatively brief. Although it is possible for fine-grained γ-Al_2O_3 to transform directly to corundum, the present difference in thermal behaviour does not appear to be related to the grain size of the initial gel particles since their particle size distributions and median particle sizes d_{50} are essentially identical ($d_{50} = 16\cdot71$ μm, $17\cdot57$ μm and $16\cdot28$ μm for AN, AS and AC, respectively).

The true density values of the unheated gel powders derived from AN, AS and AC are $2\cdot25$ g·cm^{-3}, $2\cdot46$ g·cm^{-3} and $2\cdot18$ g·cm^{-3}, respectively. The higher density of as-prepared AS reflects the high proportion of basic sulfate impurities retained in the gel at this stage. The reported solubility of aluminium sulfate is less than that of the nitrate and chloride (Okada *et al* 1991). Thus, under identical conditions of precipitation and aging, the hydroxide derived from aluminium sulfate contains a higher concentration of basic salts than the precipitate obtained from aluminium nitrate because of the smaller solubility of the sulfates (Dzisko 1979). This high concentration of basic aluminium salts must occur in sample AS as amorphous sulphate species which rupture the intramicellic bonds in the aluminium hydroxide (Trawczynski 1993).

By contrast with the as-prepared densities, the densities of AN, AS and AC heated at 800°C are $3\cdot23$ g·cm^{-3}, $3\cdot01$ g·cm^{-3} and $3\cdot24$ g·cm^{-3}, respectively, suggesting that samples AN and AC contain relatively more γ-Al_2O_3 (density $3\cdot67$ g·cm^{-3}) than AS. This result is also consistent with the XRD results at 800°C. However, although the presence of sulfate impurities in gel AS appears to slightly inhibit its transformation to γ-alumina below 800°C, the thermal decomposition of these impurities at 1000–1200°C apparently facilitates the higher-temperature transformation to corundum. The high temperature decomposition of amorphous basic sulphate species may lead to the formation of an active vermicular-like pore microstructure characterized by coexisting contiguous solid phases and pores from which α-Al_2O_3 might readily nucleate.

4. Conclusions

The high-temperature thermal behaviour of alumina precursors synthesized under identical conditions changes when different aluminium salts are used as the starting reagents. In particular, aluminium hydroxide prepared by precipitation from aluminium sulfate transforms more readily to corundum at 1100–1200°C than hydroxides prepared from the nitrate or the chloride, even though the thermal reactions of all three compounds below 1000°C are similar. The difference in high-temperature behaviour is probably related to the presence of basic sulphate species carried over in the precipitated pseudoboehmite. These species are thermally stable at temperatures > 600°C, but eventually decompose with the formation of a pore structure which facilitates the nucleation of α-Al_2O_3.

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