ELSEVIER

Thermochimica Acta 359 (2000) 87–94

thermochimica acta

www.elsevier.com/locate/tca

Effect of mechanochemical activation on the thermal reactions of boehmite (γ-AlOOH) and γ-Al_2O_3

K.J.D. MacKenzie[a,*], J. Temuujin[b], M.E. Smith[c], P. Angerer[d], Y. Kameshima[e]

[a]Department of Materials, University of Oxford, Oxford OX1 3PH, UK
[b]Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 51, Mongolia
[c]Department of Physics, University of Warwick, Coventry CV4 7AL, UK
[d]Institute for Materials Research, German Aerospace Centre, 51147 Koln, Germany
[e]Department of Inorganic Materials, Tokyo Institute of Technology, Tokyo, Japan

Received 5 January 2000; received in revised form 4 April 2000; accepted 6 April 2000

Abstract

Boehmite (γ-AlOOH) and γ-Al_2O_3 were ground for 60 min and the changes in their structure and thermal reactions were monitored by X-ray powder diffraction, thermal analysis and ^{27}Al MAS NMR. Grinding does not cause the boehmite to dehydrate, but causes a decrease in the intensity of its X-ray reflections, and the formation of an amorphous phase containing tetrahedral Al and another Al site with a resonance at 36 ppm (sometimes attributed to pentacoordinated Al). The ground material thermally transforms to corundum at 940°C via γ-Al_2O_3, by contrast with the unground control, which forms corundum at 1195°C via γ and δ-Al_2O_3. Grinding γ-Al_2O_3 decreases the intensity of its X-ray reflections and induces the formation of some corundum without further heating. Complete transformation to corundum occurs at 927°C, compared with 1193°C in the unground material which transforms via δ-Al_2O_3. The relationship between the mechanochemical development of the 36 ppm ^{27}Al NMR resonance in aluminas and their hydroxyl and adsorbed water content is discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mechanochemical activation; Thermal reactions; Alumina

1. Introduction

γ-Al_2O_3 is one of several metastable alumina polymorphs which exist in the cubic system with face-centred cubic (fcc) oxygen packing. The spinel structure adopted by γ-Al_2O_3 contains 16 octahedral and 8 tetrahedral cations site per unit cell in which 62.5% of the available Al ions occupy octahedral sites and the remainder are tetrahedral [1]. To satisfy the Al_2O_3 stoichiometry, 8/3 vacancies are assumed to be distributed randomly over the tetrahedral sites [1]. When heated, γ-Al_2O_3 transforms to the stable form, hexagonal α-Al_2O_3 (corundum) via the transition aluminas δ and θ-Al_2O_3. δ-Al_2O_3 is of tetragonal or orthorhombic symmetry, having a spinel superlattice in which the cation vacancies are ordered; like its γ-phase precursor it is based on fcc oxygen packing, but with a higher degree of ordering of the interstitial cations [1]. θ-Al_2O_3 has monoclinic symmetry and is

---

[*] Corresponding author. Tel.: +44-1865-273700; fax: +44-1865-273789.
E-mail address: kenneth.mackenzie@materials.ox.ac.uk (K.J.D. MacKenzie)

PII: S0040-6031(00)00513-X

structurally isomorphous with β-Ga_2O_3 [1]. It may be formed by further ordering of the tetrahedral Al sublattice prior to the reconstructive transformation to rhombohedral corundum.

The spinel-structure transition aluminas such as γ-Al_2O_3 are known to contain residual hydroxyl groups the presence of which has been suggested to play an essential role in stabilising the defect spinel structure [2]. Opinions differ as to the concentration of residual hydroxyls necessary for stabilisation; it has been argued [1] that even one OH per unit cell is a significant number with respect to the cation vacancy concentration (2 2/3 per unit cell). In view of the role of hydration and structural water in mechanochemical reactions of oxides [3], the presence and function of the hydroxyls in γ-Al_2O_3 was expected to be an important factor in the present work.

Boehmite, γ-AlOOH, is a monohydroxide whose structure consists of layers of cubic close-packed oxygens with the aluminium located in the octahedral sites between adjacent layers. On heating it dehydroxylates to γ-Al_2O_3, which then transforms to α-Al_2O_3 via its normal route as above.

Mechanochemical treatment (high-energy grinding) has been reported to remove the long-range order of many oxide and hydroxide compounds including the aluminas gibbsite and boehmite [4,5]. Grinding also affects the thermal behaviour of the aluminas; the temperature of corundum formation in ground gibbsite is reported [6] to be lowered by 400°C, while milling boehmite for 1.5 h is reported [7] to produce corundum *without further heat treatment.* The formation temperature of corundum from milled γ-Al_2O_3 is reported [8] to be lowered by 200°C, but the mechanochemical effect depends on parameters such as the type of mill used, the milling time, and whether the mill is cooled or uncooled [8].

The destruction of long-range order by grinding results in amorphous compounds in which the atomic configuration of the aluminium may be studied by solid state nuclear magnetic resonance spectroscopy with magic angle spinning (MAS NMR). Although this technique has been applied to studies of the thermal decomposition of a number of transition aluminas [9], the only mechanochemically activated alumina previously studied by MAS NMR is gibbsite [6], in which grinding was found to produce a phase with similar Al coordination and thermal behaviour to the X-ray amorphous ρ-Al_2O_3. The present work uses MAS NMR, X-ray powder diffraction and thermal analysis methods to study the effect of mechanochemical treatment on the structure and thermal transformations of γ-Al_2O_3 and γ-AlOOH (boehmite).

2. Experimental

The starting materials were boehmite (Dispersal, Condea Chemie, Germany) and γ-Al_2O_3, prepared by dehydroxylating this boehmite at 700°C in air for 1 h. They were ground for 60 min in a planetary mill (Fritsch Pulverisette 5) at a rotation speed of 250 rpm. The pot and milling media were of corundum, and the weight ratio of the milling media to the sample was 15:1. Thermal analysis of the ground and unground samples was carried out on 15–20 mg powder samples in flowing air (50 ml min^{-1}) up to 1300°C at a heating rate of 10°C min^{-1} using a Rigaku Thermoplus TG 8120 thermal analyzer which simultaneously determined the DTA and TG curves. On the basis of the thermal analysis data, small sub-samples were heated in air in alumina boats to various temperatures for 15 min, withdrawn from the furnace and examined by X-ray powder diffraction (Siemens D-5000 diffractometer with Cu*K*α radiation) and ^{27}Al MAS NMR at 14.1T (Chemagnetics Infinity 600 MHz spectrometer). The samples were spun at 18 kHz in a 3.2 mm probe and the spectra acquired at 156.374 MHz using a 15° pulse of 0.5 μs and a recycle time of 1 s. Spectral referencing was to the secondary standard of the AlO_6 resonance of $Y_3Al_5O_{12}$ at 0.7 ppm.

3. Results and discussion

3.1. Boehmite

The thermoanalytical curves of the ground and unground γ-Al_2O_3 and boehmite are shown in Fig. 1.

The DTA trace of unground boehmite (Fig. 1A) shows several endo-exothermic effects below 600°C, corresponding to the loss of adsorbed and structural water. The corresponding mass loss curve (Fig. 1E) indicates a total mass loss of 29.5%, of which ca. 8.5%

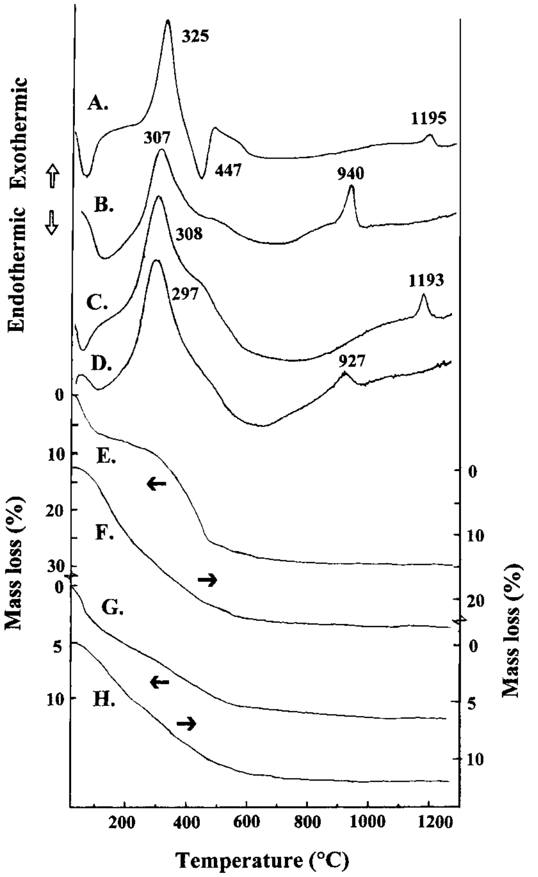

Fig. 1. (A–D) DTA curves of ground and unground aluminas; (E–H) TG curves of ground and unground aluminas; (A,E) boehmite, unground; (B,F) boehmite, ground 60 min; (C,G) γ-Al_2O_3, unground; and (D,H) γ-Al_2O_3, ground 60 min.

is lost below 170°C, a further 17.2% is lost between 170 and 500°C, with a much more gradual 3.8% loss to 1000°C. Although the two stages of mass loss below 500°C overlap somewhat, the estimated magnitude of the second step is in reasonable agreement with the theoretical mass loss of 15% for the thermal decomposition of boehmite:

$$2AlOOH \rightarrow Al_2O_3 + H_2O\uparrow \qquad (1)$$

The lower-temperature loss must therefore represent physically adsorbed water, and, by comparison with the results for γ-Al_2O_3 (below), the gradual higher-temperature loss arises from the residual hydroxyls of the γ-phase. The small exotherm at 1195°C represents the abrupt formation of corundum (α-Al_2O_3).

The DTA curve of the ground sample (Fig. 1B) retains many of the low-temperature features associated with water loss, but the disappearance of the strong endotherm at ca. 450°C suggests that the hydroxyl structure of the boehmite has been significantly disrupted by grinding. Fig. 1B also shows that the temperature of exothermic corundum formation is lowered by ca. 250°C and the thermal intensity of this event is significantly increased. The corresponding TG curve (Fig. 1F) shows that the mass losses associated with the removal of the various types of water are merged into one broad event more characteristic of the thermal decomposition of a gel, but the total loss (24.1%) is still considerably greater than for Eq. (1), suggesting that the mechanochemical treatment is not accompanied by a significant loss from the system of structural or adsorbed water.

Comparison of the XRD powder diffractograms of unground and ground boehmite (Fig. 2A and E, respectively) show that grinding essentially destroys the boehmite reflections, producing the characteristic broad features of an X-ray amorphous material on which are superimposed small residual peaks of unreacted boehmite, together with indications of incipient γ-Al_2O_3 formation and the most intense peaks of corundum (α-Al_2O_3).

Heating the unground boehmite to 300°C produces no change in the XRD powder pattern (Fig. 2A), confirming that the lower-temperature mass loss corresponds to adsorbed and not structural water. However, heating to 700°C, converts the boehmite to γ-Al_2O_3 (Fig. 2B), indicating that the second mass loss represents structural (hydroxyl) water. When the final gradual mass loss is essentially complete at 1000°C, the γ-Al_2O_3 has fully converted to the δ-form (Fig. 2C), which transforms to corundum by 1200°C (Fig. 2D).

Heating the ground boehmite to 300°C produces no change in the essentially amorphous XRD pattern (Fig. 2E), but further heat treatment to 800°C (Fig. 2F) has the effect of developing the broad peaks of γ-Al_2O_3 from the amorphous background and sharpening the corundum peaks which were initially formed by grinding. By 1000°C the sample has completely transformed to corundum (Fig. 2G).

These results suggest that the grinding process does not effect all regions of the sample equally, but produces a hydrated amorphous material containing

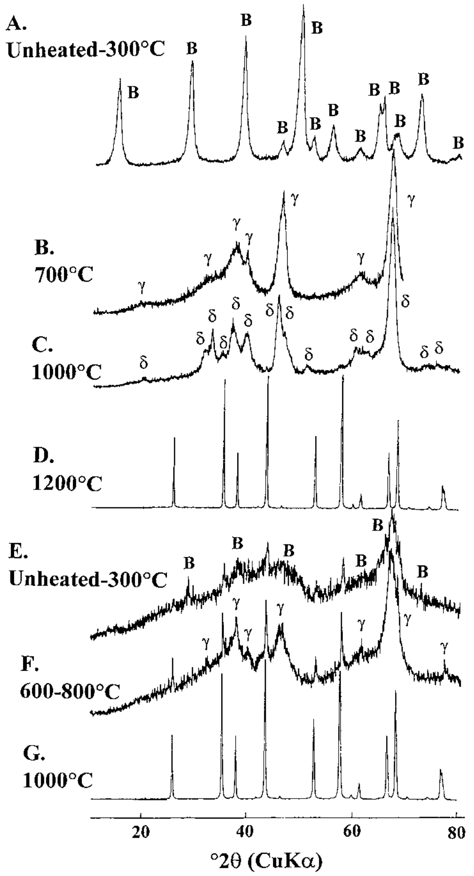

Fig. 2. Typical X-ray powder diffractograms of boehmite heated for 15 min as indicated. (A–D) Unground; (E–G) ground 60 min. Key: B, boehmite (PDF No. 21-1307); γ, γ-Al_2O_3 (PDF No. 10-425); δ, δ-Al_2O_3 (PDF No. 4-877); unmarked peaks correspond to α-Al_2O_3 (PDF No. 10-173).

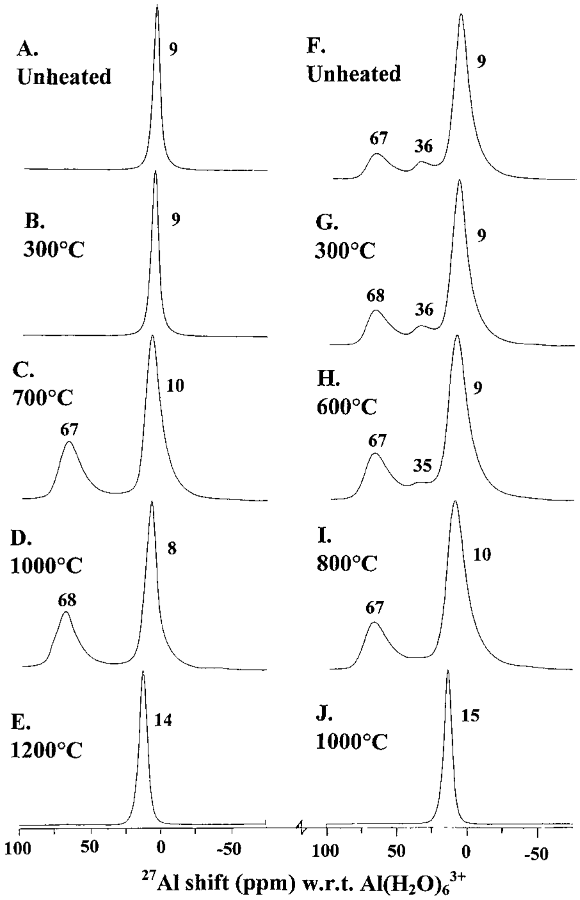

Fig. 3. Typical 14.1T ^{27}Al MAS NMR spectra of unground and ground boehmite, unheated and heated for 15 min as indicated. (A–E) Unground; (F–J) ground.

regions of variable degrees of transformation, reflected by small amounts of boehmite and fully transformed corundum. The amorphous material has some of the X-ray characteristics of γ-Al_2O_3, notably the broad reflection at ca. 67°2θ (Fig. 2E), which is significantly more intense than the small boehmite peak at this position (Fig. 2A). Loss of water from this amorphous phase leads to the evolution of the γ-Al_2O_3 structure, which abruptly transforms to corundum apparently without the formation of δ-Al_2O_3.

The ^{27}Al MAS NMR spectra of these samples are shown in Fig. 3.

The MAS NMR spectrum of unground boehmite (Fig. 3A) contains the expected single resonance at 9 ppm, characteristic of octahedral Al in one type of site. Grinding this sample produces considerable broadening of the octahedral peak (Fig. 3F) and the appearance of two small new resonances. The peak at 67 ppm arises from tetrahedral Al, while that at 36 ppm, which is commonly found in amorphous aluminates, has been ascribed to Al in either 5-fold coordination [10] or to distorted tetrahedral sites associated with the tricluster defects such as found in aluminosilicates [11]. A similar 3-peak ^{27}Al MAS NMR spectrum was previously recorded in ground gibbsite [6]. The broadness of the octahedral resonance in this spectrum would mask any evidence of the octahedral site of corundum which would appear at 14–15 ppm, and would be of low intensity.

The single octahedral site in unground boehmite survives heating to 300°C (Fig. 3B), confirming the conclusion from XRD that the water lost up to that temperature is not structural. However, by 700°C, dehydroxylation has occurred, resulting in the conversion of some octahedral Al to tetrahedral (67 ppm, Fig. 3C) and the broadening of the octahedral resonance. Pronounced tails to higher field are also seen due to the presence of a distribution of electric field gradients (EFGs) resulting from a range of distortions induced at the Al sites by dehydroxylation. Accurate simulation of such spectra requires a detailed determination of the mean interactions and their distributions [12]. However, the octahedral:tetrahedral ratio of this sample was estimated semi-quantitatively by direct spectral integration to be 1.9, in reasonable agreement with the value reported for γ-Al_2O_3 at the same field strength (2.33 [13]). The sample heated at 1000°C, which consists only of δ-Al_2O_3, shows a similar but slightly narrower spectrum (Fig. 3D) with an octahedral:tetrahedral ratio of 2.0. The transformation to corundum is marked by the abrupt loss of the tetrahedral sites and a change of the octahedral chemical shift to the characteristic corundum position (Fig. 3E).

Heating the ground boehmite to 300°C produces virtually no change in the ^{27}Al MAS NMR spectrum (Fig. 3G), but the further loss of water up to 600°C (Fig. 3H) increases the concentration of tetrahedral sites and decreases the number of 36 ppm sites, which have completely disappeared by 800°C (Fig. 3I). The 36 ppm sites therefore appear to be associated with the amorphous hydrated phase rather than the γ-Al_2O_3, since the latter with its retained hydroxyl content is the major phase at 800°C. The change in the occupation of the Al sites in the unground and ground boehmite, estimated semi-quantitatively from the ^{27}Al MAS NMR spectra, are shown as a function of temperature in Fig. 4A and B, respectively.

3.2. γ-Al_2O_3

The thermal analysis curve of the present unground γ-Al_2O_3 (Fig. 1C) shows endo-exothermic features below 600°C with an associated mass loss (Fig. 1G) of ca. 10.4%. Since the XRD trace of the samples heated

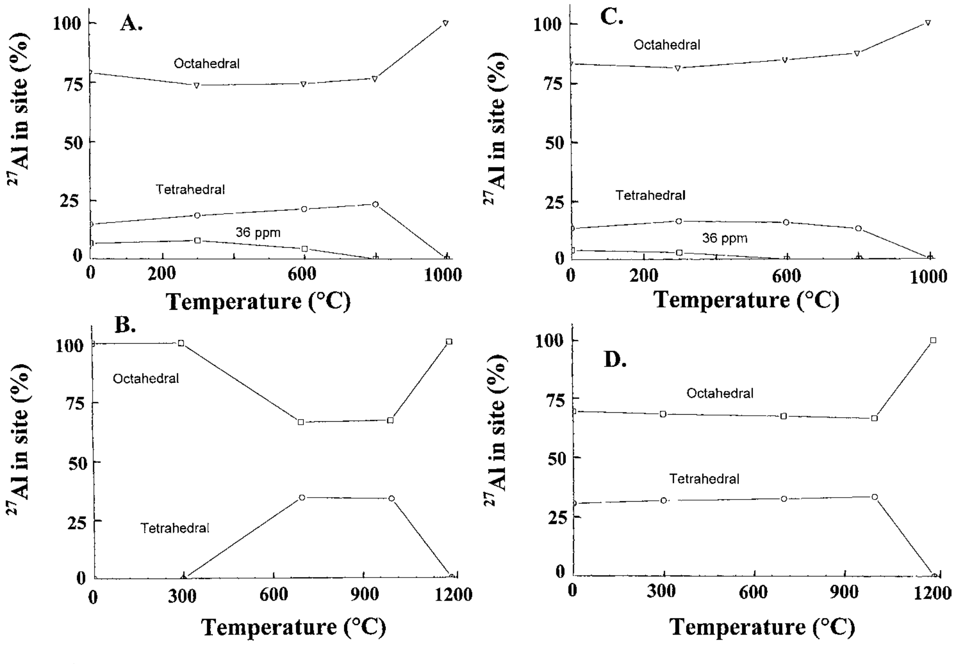

Fig. 4. Changes in the ^{27}Al site occupancies of ground and unground aluminas as a function of heating temperature. (A) Boehmite ground for 60 min; (B) boehmite, unground; (C) γ-Al_2O_3 ground 60 min; and (D) γ-Al_2O_3, unground.

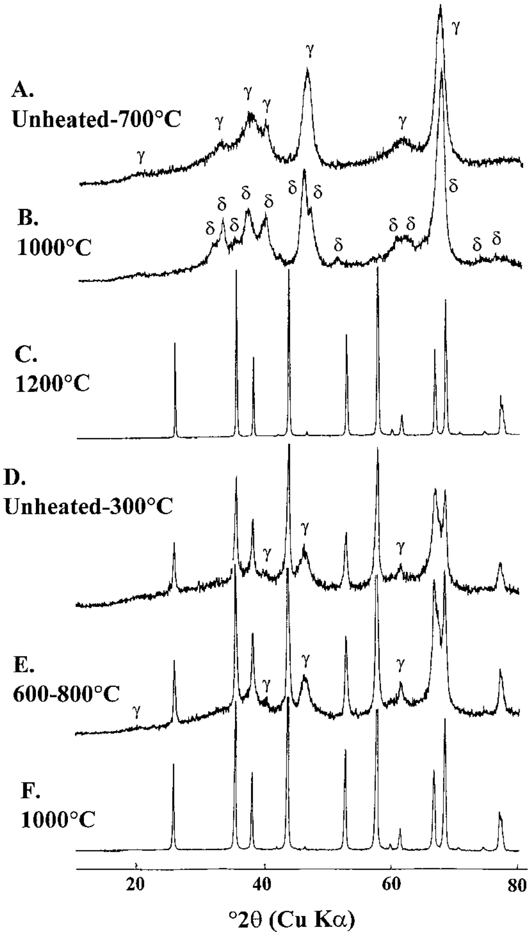

Fig. 5. Typical X-ray powder diffractograms of γ-Al_2O_3 heated for 15 min as indicated. (A–C) Unground; (D–F) ground 60 min. Key: γ, γ-Al_2O_3 (PDF No. 10-425); δ, δ-Al_2O_3 (PDF No. 4-877); unmarked peaks correspond to α-Al_2O_3 (PDF No. 10-173).

at various temperatures up to 700°C show the presence of only γ-Al_2O_3 (Fig. 5A), the mass loss up to this temperature must be due to the removal of adsorbed water, which is, however, rather firmly bound. Above ca. 600°C the mass-loss curve becomes much flatter, with a further gradual 1.2% loss up to ca. 1080°C (Fig. 1G). Thus, of the total loss of 12.3%, only the final 1.2% appears to be due to the loss of residual hydroxyl groups from the γ-Al_2O_3. This corresponds to ≈0.07 mol of OH per mole of γ-Al_2O_3. The endotherm at 1193°C is due to the transformation to corundum.

As found for boehmite, grinding the γ-Al_2O_3 has little effect on the endo-exothermic features of the DTA curve below 600°C (Fig. 1D), but the temperature of exothermic corundum crystallisation is lowered to 927°C. Little difference is observed in the shape of the mass loss curves for unground and ground γ-Al_2O_3, since in both materials the removal of water is gradual, and continues over an extended temperature range. The total water loss from both ground and unground samples is similar (12.3 and 11.6%, respectively), indicating that changes induced in the sample by grinding do not involve dehydration. Since the corundum produced by grinding should not contain structural water, the water lost from these transformed regions must remain in the system as adsorbed water.

Comparison of the XRD patterns for the unground and ground γ-Al_2O_3 (Fig. 5A and E) indicates that grinding significantly reduces the intensity of the broad γ-alumina reflections, but introduces a number of sharp new peaks corresponding to α-Al_2O_3. This result is similar to a previously-reported finding [7] that the transformation to corundum can be achieved at room temperature in boehmite by grinding; the occurrence of this transformation in the present γ-Al_2O_3 but not in the boehmite from which it was derived may be a function of the additional content of adsorbed water in the latter. Removal of the adsorbed water from the unground γ-Al_2O_3 by heating at 700°C produces no change in the XRD pattern (Fig. 5A), but the loss of the final 1% up to 1000°C results in the formation of the δ-form (Fig. 5B) which transforms to corundum by 1200°C (Fig. 5C). By contrast, in the ground sample the γ-Al_2O_3 which survived grinding is still present in the XRD pattern at 800°C (Fig. 5E), but has completely transformed to corundum by 1000°C (Fig. 5F).

The ^{27}Al MAS NMR spectra of the ground and unground γ-Al_2O_3 samples are shown in Fig. 6.

The spectrum of unground γ-Al_2O_3(Fig. 6A) shows the expected tetrahedral and octahedral resonance at 67 and 10 ppm, respectively. A semi-quantitative estimate of the relative intensities of the Al associated with these two sites, obtained by direct spectral integration, indicates the typical γ-Al_2O_3 octahedral:-tetrahedral ratio of 2.3, which decreases progressively to 2.0 on heating to 1000°C (Fig. 6D). The disappearance of the tetrahedral resonance and the

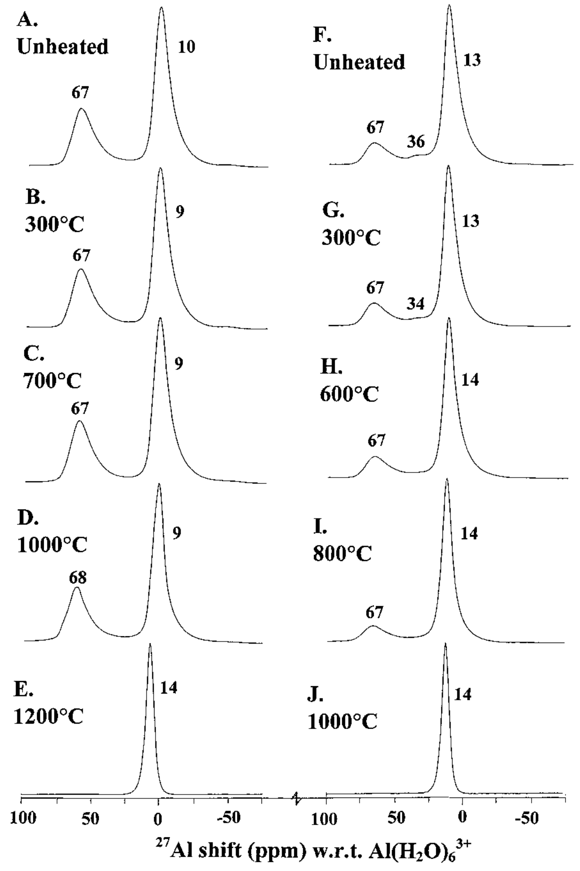

Fig. 6. Typical 14.1T ^{27}Al MAS NMR spectra of unground and ground γ-Al_2O_3 unheated and heated for 15 min as indicated. (A–E) Unground; (F–J) ground.

shift of the octahedral peak to the characteristic value for corundum occurs abruptly below 1200°C (Fig. 6E).

Grinding causes a marked decrease in the intensity of the ^{27}Al tetrahedral resonance of the γ-Al_2O_3 spectrum, and the appearance of a small amount of the resonance at ca. 36 ppm (Fig. 6F). This survives heating at 300°C (Fig. 6G), but has virtually disappeared by the time most of the adsorbed water has been removed at 600°C (Fig. 6H). The changes in Al site occupancy of unground and ground γ-Al_2O_3 with heating temperature are shown in Fig. 4B. The preponderance of corundum in all these ground samples is reflected by the position of the octahedral resonance, which ranges from 13 ppm in the unheated sample to 14 ppm at 800°C.

3.3. Implications for the origin of the 36 ppm NMR resonance

Taken together with the previously published data for ground gibbsite [6], the present results can be used to explore possible relationships between the structural and hydration water content of the aluminas and the mechanochemical evolution of the various NMR signals. The structural (hydroxyl) water contents of gibbsite and boehmite (with respect to Al_2O_3) are 34.6 and 15.0 wt.%, respectively, while the corresponding value for the present γ-Al_2O_3 deduced from the TG results (above) is 1.2 wt.%. It has been suggested [13] that the relative intensities of the various ^{27}Al MAS NMR signals obtained by direct spectral integration of the centre bands, particularly that at 36 ppm, may be affected by the magnetic field strength and spinning speed. To provide a valid comparison of the MAS NMR results for these three aluminas, the results of experiments made at 11.7T and 12 kHz on samples ground under identical conditions for 60 min were therefore used. The integrated intensities of all three Al sites in the ground aluminas were plotted as a function of the hydroxyl water, adsorbed water and total water contents. Of these, the only systematic relationships observed were between the 36 ppm resonance intensity and the water contents of the three aluminas (Fig. 7).

Neither the tetrahedral or octahedral resonances exhibit such a relationship, which suggests that all

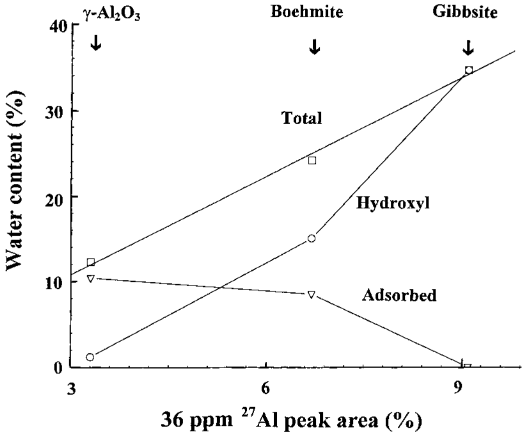

Fig. 7. Integrated area of the 36 ppm ^{27}Al MAS NMR peak area of aluminas as a function of their water contents. The gibbsite data are from Ref. [6].

the water, both structural and adsorbed, is implicated in the formation of the 36 ppm peak, but that the presence of hydroxyl water is a necessary and sufficient condition. Previous observations of this NMR resonance in γ-Al_2O_3 heated to 600°C [9] have been attributed to pentacoordinated Al atoms at the surface of the particles. This species is suggested [9] to stabilise the defect spinel structure of γ-Al_2O_3 in a similar manner to Na^+ (and H^+). If the 36 ppm resonance is thus assumed to be associated with defect formation, the relationships of Fig. 7 suggest that the defects produced by mechanochemical activation of the aluminas may occur preferentially at the hydroxyl sites. However, since the water is not lost from the system during grinding, it is not immediately clear why the vacancies in the resulting structure are not stabilised by protons rather than pentacoordinated Al. In view of the gel-like nature of the mechanochemical product, an alternative explanation may be the stabilisation of the 36 ppm Al species by protons or water. This possibility is also consistent with the progressive loss of the 36 ppm resonance during the removal of the water by subsequent heat treatment (Fig. 6).

4. Conclusions

Grinding boehmite (γ-AlOOH) for 60 min destroys a significant proportion of the boehmite X-ray peak intensities and produces an X-ray amorphous component which retains its original water content. On heating, this water is progressively removed over an extended temperature range, by contrast with the well-defined thermal dehydroxylation of unground boehmite. The ground material forms a mixture of γ-Al_2O_3 and corundum (α-Al_2O_3) at 600–800°C, and is fully transformed to corundum in an exothermic reaction at 940°C. This transformation temperature is ca. 260°C lower than in unground boehmite, in which the intermediate formation of δ-Al_2O_3 is observed at ca. 1000°C.

When this boehmite is thermally converted to γ-Al_2O_3 prior to mechanochemical treatment, the grinding is sufficient to transform a significant proportion to corundum without the loss of water from the system. Subsequent heating at 900–1000°C completes the transformation to corundum, without the formation of intermediate transition phases. Without grinding, this γ-Al_2O_3 thermally transforms to corundum at 1193°C, via δ-Al_2O_3.

The amorphous phase formed from boehmite by grinding contains, in addition to the original octahedral Al sites, newly formed tetrahedral sites and other sites characterised by an Al NMR resonance at ca. 36 ppm. A similar 36 ppm Al resonance is detected in ground γ-Al_2O_3. The intensity of this peak appears to be linearly related to the original content of structural and adsorbed water in the sample, and progressively decays to zero as the water is thermally removed. Although this resonance has previously been attributed to a pentacoordinated Al species which stabilises the defect spinel structures of the transition aluminas [9], the present results suggest that it may arise from Al sites associated with and possibly stabilised by protons or structural water.

Acknowledgements

K.J.D.M is indebted to the Royal Society of New Zealand for a James Cook Research Fellowship under which part of this research was carried out. MES thanks HEFCE and EPSRC for funding NMR instruments at Warwick through JREI awards.

References

[1] I. Levin, D. Brandon, J. Am. Ceram. Soc. 81 (1998) 1995.

[2] S. Soled, J. Catal. 81 (1983) 252.

[3] E.G. Avvakumov, E.T. Devyatkina, N.V. Kosova, J. Solid State Chem. 113 (1994) 379.

[4] Y. Arai, T. Yasue, I. Yamaguchi, Nippon Kagaku Kaishi 8 (1972) 1395.

[5] T. Tsuchida, N. Ichikawa, React. Solids 7 (1989) 207.

[6] K.J.D. MacKenzie, J. Temuujin, K. Okada, Thermochim. Acta 327 (1999) 103.

[7] A. Tonejc, A.M. Tonejc, D. Bagovic, C. Kosanovic, Mater. Sci. Eng. A181-2 (1994) 1227.

[8] O.A. Kirichenko, V.A. Ushakov, O.A. Andryushkova, S.V. Ivchenko, V.A. Poluboyarov, Inorg. Mater. 35 (1999) 333.

[9] C. Pecharromán, I. Sobrados, J.E. Iglesias, T. González-Carreño, J. Sanz, J. Phys. Chem. B 103 (1999) 6160.

[10] M.E. Smith, Appl. Magn. Reson. 4 (1993) 1.

[11] M. Schmucker, H. Schneider, Ber. Bunsenges Phys. Chem. 100 (1996) 1550.

[12] G. Kunath-Fandrei, T.J. Bastow, J.S. Hall, C. Jager, M.E. Smith, J. Phys. Chem. 100 (1996) 15138.

[13] R.H. Meinhold, R.C.T. Slade, R.H. Newman, Appl. Magn. Reson. 4 (1993) 121.