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^{27}Al Magic-angle spinning nuclear magnetic resonance spectroscopic study of the conversion of basic dicarboxylate aluminium(III) complexes to alumina and aluminium nitride

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The process of conversion of hydrated basic dicarboxylate aluminium(III) complexes Al(OH)(succinate)•xH$_2$O and Al(OH)(adipate)•xH$_2$O to alumina and aluminium nitride (AlN) has been investigated by ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The powdered succinate complex was calcined under various atmospheres such as N$_2$, argon and air. The ^{27}Al MAS NMR spectra for the calcined materials at 500 °C all showed three peaks at δ 6, 33 and 63. The relative intensities of these peaks varied with increasing temperature and were also dependent on the calcination atmosphere. The ^{27}Al NMR signal of AlN at δ 114 was observed for the sample calcined in an N$_2$ atmosphere at 1150 °C whilst in all spectra of samples calcined under an N$_2$ atmosphere at >1150 °C there were no detectable signals other than those of γ-alumina and AlN. The finding that the ratio of the relative intensities of AlO$_6$ and AlO$_4$ groups in γ-alumina changes with temperature suggests that the carbothermal reduction and nitridation of alumina proceeds through intermediates with empirical formulae of the type AlO$_x$N$_y$. The degree of nitridation at each reaction temperature for the succinate complex was higher than that for the adipate complex.

High-resolution ^{27}Al magic angle spinning (MAS) NMR spectroscopy is becoming increasingly used as an aid to structural characterization of Al-containing materials in the solid state.[1,2] This has been particularly useful where powder X-ray diffraction provides little information about the aluminium distribution owing to the lack of long-range order. The chemical shift of ^{27}Al NMR is sensitive to the local coordination at the Al nucleus, *i.e.* octahedral AlO$_6$ sites resonate between δ +15 and −30, the much less common AlO$_5$ site resonates between δ +40 and +25 and tetrahedral AlO$_4$ sites resonate between δ +80 and +50.[1]

^{27}Al MAS NMR spectroscopy has been applied to characterize the Al–O–H system involving aluminas and aluminium hydroxides and to examine their transformation sequences during calcination in air or *in vacuo*.[3–7] The spectra are often not simple superpositions of lines of the constituent phases as underlying broad components are present.[3,5,6] Recently ^{27}Al MAS NMR spectroscopy has been used as a tool to determine whether solid-state intermediates of aluminium oxynitride (AlO$_x$N$_y$) are formed during the carbothermal reduction and nitridation (CRN) of α-alumina to AlN. The occurrence of intermediates was verified by comparing the NMR spectra of samples obtained by calcination of a mixture of α-alumina and carbon black under a flow of nitrogen with and without decarbonization of the residual carbon.[8]

We reported in previous papers[9,10] that AlN powder was obtained by a modified CRN method employing hydrated Al(OH)(dicarboxylate) complexes, Al(OH)(succinate) and Al(OH)(adipate), as precursors. The method is more favorable than the conventional CRN method in that it is not necessary to add any carbon source to the precursor powder. In order to elucidate the reaction steps of conversion of the aluminium(III) complexes to AlN we measured ^{27}Al MAS NMR and IR spectra and XRD patterns of samples obtained by calcining the complexes under a flow of nitrogen at various temperatures and compared them with those of calcination products in air and under a flow of argon.

Experimental

Materials

The hydrated basic dicarboxylate aluminium(III) complexes with empirical formulae Al(OH)(C$_4$H$_4$O$_4$)•xH$_2$O (AS) and Al(OH)(C$_6$H$_8$O$_4$)•xH$_2$O (AA) were prepared as described previously[9,10] and characterized by thermal analysis, IR, ^{27}Al MAS NMR and ^{13}C CP MAS NMR spectroscopy. Al$_2$(oxalate)$_3$•xH$_2$O (AO, Kanto Chemical Co.) was used as-received. Each powdered complex was calcined for 2 h without mixing with any carbon source in a crucible using the reactor described in ref. 9. The powders were calcined under an N$_2$ atmosphere in two ways: in the first, the powder was calcined in a graphite crucible by placing it into an alumina tube preheated to the reaction temperature (Q route) and in the second, the powder in an alumina crucible was placed in the tube at room temperature and then calcined at the reaction point (*i.e.* the calcination temperature; S route). In the latter route the ramp rate was 5 °C min^{-1}. In this study all calcined products for measurements of XRD patterns and IR and ^{27}Al MAS NMR spectra were used without burning off the residual carbon.

Measurements

High-resolution ^{27}Al MAS NMR and ^{13}C CP MAS NMR spectra were recorded at ambient temperature using a Varian Unity+300 spectrometer operating at 78.2 and 75.5 MHz, respectively. The Si$_3$N$_4$ and ZrO$_2$ rotors used as a sample chamber were spun at 5 kHz (6 and 7 kHz, if necessary, to confirm spinning sidebands) during data collection. Peak positions in ^{27}Al MAS NMR and ^{13}C CP MAS NMR spectra were referenced to external 1 M aqueous AlCl$_3$ and TMS, respectively. For ^{27}Al MAS NMR spectra for the calcined materials, unless otherwise stated, typically $\pi/6$ pulses of duration 2 µs were applied to excite the (1/2, −1/2) transition, and 64 or more free induction decays were accumulated with a recycle delay of 3 s.

IR spectra of calcined materials (KBr pellets) were taken on a JASCO FT-IR 5300 spectrophotometer. Powder X-ray

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diffraction patterns were recorded using a Rigaku DMX-2500 diffractometer with Cu-Kα radiation operating at 40 kV and 50 mA.

Results and Discussion

Pyrolysis of aluminium(III) complexes under an N_2 atmosphere

The carbothermal reduction and nitridation of alumina is usually expressed by the equation

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g)$$

Therefore, if the pyrolysis of 2 mol of the basic dicarboxylate aluminium(III) complexes occurs with $\geqslant 3$ mol of carbon, they may be completely converted to AlN under an N_2 atmosphere without requiring additional carbon. It was found that the pyrolysis of 2 mol AS and AA under an N_2 atmosphere gave *ca.* 4 and 2 mol of carbon, respectively. This finding shows that the content of carbon in the aluminium(III) complexes is not proportional to those in their calcined products. The pyrolysis of AO under a flow of nitrogen gives little residual carbon.

Calcination of AS in air and under a flow of argon

The effect of calcination atmosphere on the pyrolysis of AS complexes was investigated by ^{27}Al MAS NMR spectroscopy. Fig. 1 shows ^{27}Al MAS NMR spectra of samples obtained by calcining AS complexes in air at different temperatures. For the amorphous sample calcined at 500 °C three distinct peaks are observed at δ6, 33 and 63, each of which is readily assigned to six-coordinate (AlO_6), five-coordinate (AlO_5) and four-coordinate(AlO_4) aluminium, respectively.[5,6] Several MAS NMR studies have shown the presence of the much less common AlO_5 aluminium coordination in aluminium oxides formed by calcination of various precursors such as gibbsite,[5] the sulfate salt of an Al_{13} polyoxycation dimer[11] and hydrolysis products of $Al(OBu^s)_3$.[12] AlO_5-containing species are also known to exist in barium aluminium glycolate and andalusite,[13] $Zr_{1-x}Al_xO_{2-x/2}$ materials[14] and anodically formed amorphous alumina films.[15] For the calcined product at 500 °C there is also an underlying broad component of low intensity, indicating that a small proportion of the aluminium atoms coexists in low-symmetry environments.

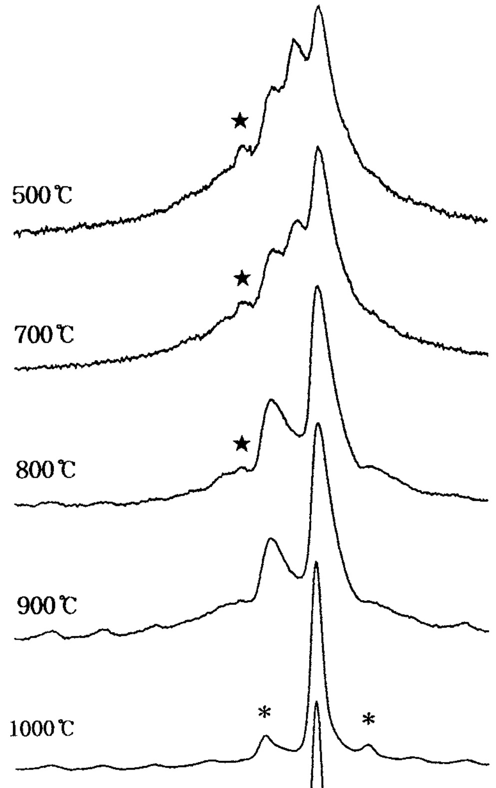

Fig. 1 ^{27}Al MAS NMR spectra of hydrated Al(OH)(succinate) calcined in air in the temperature range 500–1100 °C for 2 h. In this and the following figures, the peaks marked by stars and asterisks are signals due to Al in the Si_3N_4 rotor and the spinning sidebands, respectively.

As the calcination temperature is increased to 800 °C, aluminium atoms in AlO_5 sites gradually enter AlO_6 sites and the underlying broad peak becomes weaker. This transformation was also observed in the IR spectra. As shown in the IR spectrum of the calcined product at 900 °C (Fig. 2), a small valley occurs at the middle (*ca.* 690 cm^{-1}) of the very broad band in the 900–500 cm^{-1} region. The occurrence of the valley seems to be due to the transformation of AlO_5 into AlO_6 sites. This reasoning is based on the fact that the ^{27}Al MAS NMR spectrum of calcined $Al(OH)_3$ under a flow of nitrogen at 600 °C shows only two peaks assignable to AlO_6 and AlO_4 environments and the IR spectrum shows a small valley at *ca.* 690 cm^{-1}. The NMR spectrum for the material calcined at 800 °C is very similar to that of γ-alumina, the peaks of which are reported to appear at δ7.5 and 66,[2] and the abrupt diminution in intensity of the AlO_5-aluminium peak is likely to be associated with the burn off of carbon produced by pyrolysis of AS. Upon increasing the temperature above 800 °C the AlO_4 peak becomes weaker and subsequently vanishes at 1100 °C because of the transition from γ- through δ- and θ- to α-alumina.[16] The sample calcined at 1100 °C is identified as α-

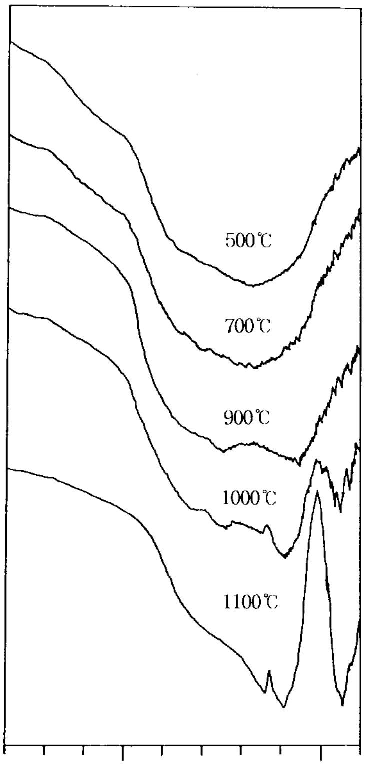

Fig. 2 IR spectra of hydrated Al(OH)(succinate) calcined in air in the temperature range 500–1100 °C for 2 h

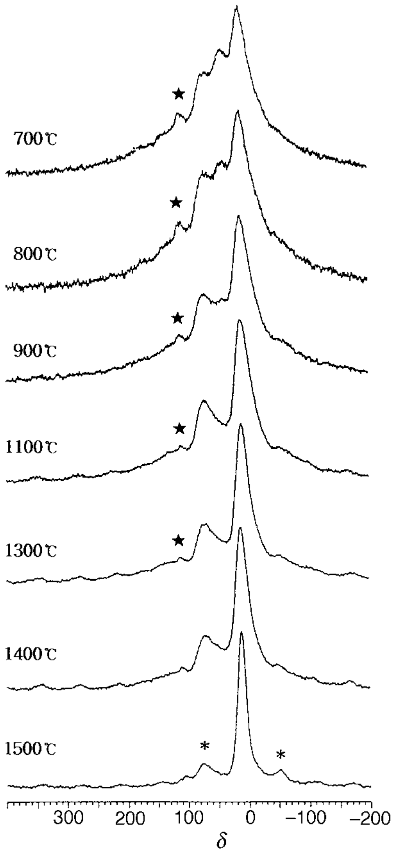

Fig. 3 ^{27}Al MAS NMR spectra of hydrated Al(OH)(succinate) calcined under a flow of argon in the temperature range 700–1500 °C for 2 h

alumina by its ^{27}Al MAS NMR and IR spectra and also from its XRD pattern.

Fig. 3 shows ^{27}Al MAS NMR spectra of samples calcined at different temperatures under a flow of argon. The change in lineshape with increasing temperature is similar to that in air (Fig. 1), but the phase transition to α-alumina is much slower than in air (note that the spectrum for the sample at 1500 °C under a flow of argon is almost the same as that of the 1000 °C sample in air). The slowing of the transition under an argon atmosphere is caused by the presence of residual carbon in the interstices of the γ-alumina lattice. This rationale is supported by the fact that the sample obtained by calcining the AO complex at 1200 °C under a flow of nitrogen contains little residual carbon and is identified as α-alumina by its IR and ^{27}Al MAS NMR spectra, as is the calcined product of the AS complex at 1200 °C in air.

Calcination of AS and AA complexes under a flow of nitrogen

The process of conversion of AS and AA complexes to AlN under a flow of nitrogen was investigated by ^{27}Al MAS NMR spectroscopy. We reported in a previous paper[9] that AlN powder was obtained stoichiometrically by calcining the AS complex without mixing with any carbon source under a flow of nitrogen. Fig. 4–6 show ^{27}Al MAS NMR spectra for samples which were obtained by calcining the AS complex under a flow of nitrogen. In the spectrum of the AS complex (Fig. 4) the centre band occurs at δ 3, indicating six-coordinate Al^{3+}. The centre band is flanked by intense spinning sidebands, which were readily identified by varying the spinning rate. The intense sidebands reflect a broad static lineshape arising from quadrupolar broadening and chemical shift anisotropy contributions for the AS complex.[17] In the ^{13}C CP MAS NMR spectrum of the AS complex there are only two narrow peaks at δ 32.6 and 180.1 which are simply assigned to ethylenic and carboxylate carbons, respectively, indicative of only one six-coordinate Al site being present in the complex. The AS complex seems to have a polymeric structure similar to Sc(OH)(malonate)H_2O•H_2O in which the Sc^{3+} ion is approximately octahedrally coordinated, each Sc^{3+} ion being linked to the three carboxylate oxygen atoms, two hydroxyl ions and one water molecule.[18]

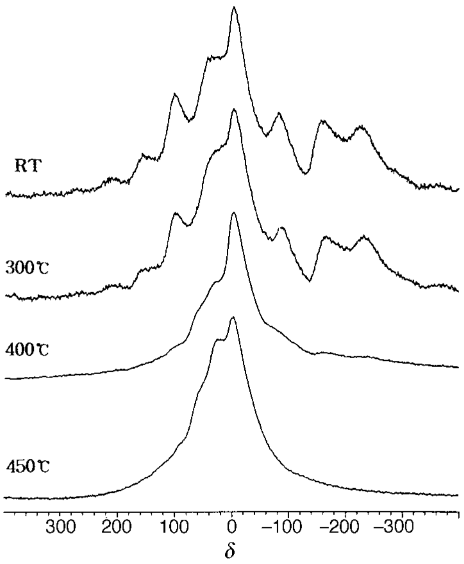

Fig. 4 ^{27}Al MAS NMR spectra of hydrated Al(OH)(succinate) calcined under a flow of nitrogen from room temperature to 450 °C for 2 h; 500 or more free induction decays were accumulated with a recycle delay of 1 s

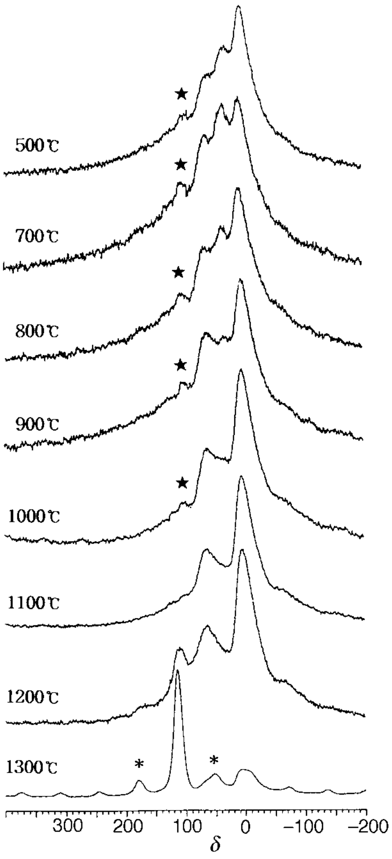

Fig. 5 ^{27}Al MAS NMR spectra of powders obtained by calcination of hydrated Al(OH)(succinate) under a flow of nitrogen in the temperature range 500–1300 °C for 2 h (Q route)

Upon increasing the temperature from room temperature to

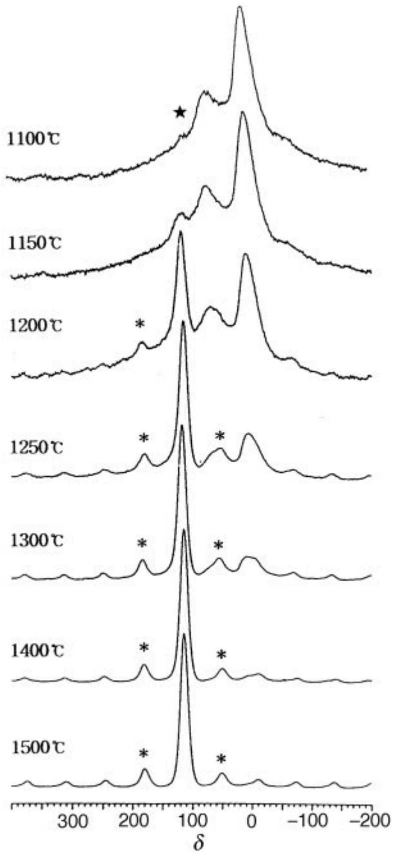

Fig. 6 ^{27}Al MAS NMR spectra of powders obtained by calcination of hydrated Al(OH)(succinate) under a flow of nitrogen in the temperature range 1100–1500 °C for 2 h (S route)

350 °C, the calcined samples changed from white to dark brown but the NMR spectra are nearly the same as that of the AS complex (Fig. 4) and no change is observed in the IR spectra. Upon increasing temperature to above the decomposition temperature (*ca.* 400 °C), the intensity of the sidebands diminishes and peaks assignable to three types of environments, AlO_4, AlO_5 and AlO_6 are observed.

Fig. 5 shows NMR spectra of samples obtained by calcining the AS complex in the temperature range 500–1300 °C (Q route). The relative intensity of the highest field peak at δ 6 decreases with increasing temperature but the ratio of intensities corresponding to AlO_4 and AlO_5 sites is nearly constant in the temperature range 500–700 °C. This indicates that with increasing temperature the stability of AlO_6 sites becomes lower than those of AlO_4 and AlO_5 sites in this temperature range. This trend in relative intensities of AlO_4, AlO_5 and AlO_6 sites is considerably different from that for samples calcined in air. It is noted that the lineshape of the sample calcined at 700 °C under a flow of nitrogen is different from those of samples calcined at 700 °C in air or under a flow of argon. Upon increasing temperature above 700 °C, the relative intensity of aluminium atoms in AlO_6 sites increases as a consequence of the gradual transformation of aluminium atoms in AlO_5 sites into AlO_6 sites. Samples calcined in the temperature range 700–1100 °C show no peaks in their XRD patterns due to their lack of crystallinity and their NMR spectra are very similar to those of samples obtained by calcination under a flow of argon (Fig. 2). The NMR spectrum of the sample calcined at 1100 °C is close to that of γ-alumina. The sample calcined at 1200 °C shows an AlN peak at δ 114,[19] and its intensity abruptly increases for the sample calcined at 1300 °C.

Fig. 6 shows NMR spectra of samples obtained by calcining the AS complex in the temperature range 1100–1500 °C using the S route. For the sample calcined at 1150 °C the formation of AlN is detected by NMR but not by XRD, indicating that the AlN powder formed is poorly crystalline. The degree of nitridation abruptly increases at 1200 °C, which is 100 °C lower than when using the Q route, suggesting that the S route is more effective than the Q route for the carbothermal reduction and nitridation of alumina. The intensity of the AlN peak increases gradually with increasing calcination temperature above 1200 °C. For the sample calcined at 1500 °C for 2 h, only the AlN peak is observed.

Fig. 5 and 6 show that there are no detectable signals other than those of γ-alumina and AlN at >1100 °C and therefore AlN is considered to be formed by carbothermal reduction and nitridation of γ-alumina without γ–α alumina transformation, as found by XRD results.[9] These reaction steps are also observed in the nitridation of a mixture of aluminium polynuclear complexes, such as basic aluminium chloride, basic aluminium lactate and glucose under a flow of nitrogen.[20] We could not find any signal assignable to AlO_xN_y as reaction intermediates but this cannot rule out the possibility of their presence, since their non-detection may be due to the facts that the relative amount of each intermediate formed is very small and/or its NMR signal is broadened beyond detection by severe quadrupole broadening.[19] It was concluded from the study of the conversion of α-alumina to AlN using IR and ^{27}Al MAS NMR spectroscopy[8] that the oxidation of carbon to CO is not coupled with the reduction of α-alumina to Al vapor or volatile aluminium suboxides[21–25] but rather with the reduction of N_2 *via* AlO_xN_y to AlN in the carbothermal reduction and nitridation of α-alumina. Furthermore, this conclusion is supported by the fact that the ratio (I_4/I_6) of relative intensities of AlO_4 to AlO_6 sites in γ-alumina is not constant but tends to increase with increasing temperature for samples calcined in the temperature range 1100–1250 °C, as shown in Fig. 6. This tendency is opposite to that for samples calcined under a flow of argon in which the I_4/I_6 ratio decreases with temperature (Fig. 3). The apparent increase in the I_4/I_6 ratio (Fig. 6) was deduced from measurement of peak heights since it was impossible to deconvolute the lineshape exactly as a consequence of the deviation of the lineshape from the regular Gaussian and the occurrence of spinning sidebands. The fact that the I_4/I_6 ratio varies with temperature might be explained by the difference in reactivities between AlO_4 and AlO_6 sites rather than by reaction mechanisms involving any gaseous aluminium species. If such mechanisms were operative, the ratios would be constant.

One of the factors governing the linewidth of the AlN peak is the degree of crystallinity of the AlN powder formed, *i.e.* the linewidth becomes more narrow with increased crystallinity. As would be expected, the nitridation of γ-alumina to amorphous AlN powders occurs simultaneously with the transition of amorphous AlN into crystalline AlN powders with increasing temperature. Therefore, the linewidth of AlN peaks in the NMR spectra (Fig. 6) decreases gradually with increasing temperature up to 1500 °C.

Fig. 7 shows ^{27}Al MAS NMR spectra for samples which were obtained by calcining the AA complex under a flow of nitrogen (Q route). The spectrum of the sample calcined at 500 °C is similar to that for AS but very different from that for AO at 500 °C, which is similar to that for AA at 800 °C. Relative intensities of AlO_4, AlO_5 and AlO_6 peaks for AA as a function of temperature show the same trend in the temperature range 500–1000 °C as that for AS. For the sample calcined at 1200 °C no AlN peak is observed, in contrast with the corrresponding AS calcination product, and the degree of nitridation above 1200 °C is much lower than that for AS. This is well explained by the fact that the pyrolysis of 2 mol of AA gives 1 mol of alumina and *ca.* 2 mol of carbon, the latter being insufficient to completely reduce the alumina. It was reported previously[10] that the AA complex is completely

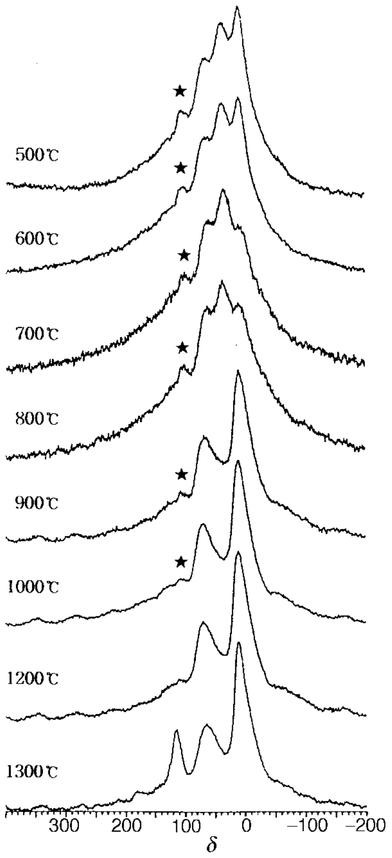

Fig. 7 ^{27}Al MAS NMR spectra of powders obtained by calcination of hydrated Al(OH)(adipate) under a flow of nitrogen in the temperature range 500–1300 °C for 2 h (Q route)

converted to AlN without residual carbon in a flow of ammonia at 1200 °C.

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References

1 G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley & Sons, Chichester, 1987.
2 M. E. Smith, *Appl. Magn. Reson.*, 1993, **4**, 1.
3 V. M. Mastikhin, O. P. Krivoruchko, B. P. Zolotovskii and R. A. Buyanov, *React. Kinet. Catal. Lett.*, 1981, **18**, 117.
4 C. S. John, N. C. M. Alma and G. R. Hays, *Appl. Catal.*, 1983, **6**, 341.
5 R. C. T. Slade, J. C. Southern and I. M. Thompson, *J. Mater. Chem.*, 1991, **1**, 563.
6 R. C. T. Slade, J. C. Southern and I. M. Thompson, *J. Mater. Chem.*, 1991, **1**, 875.
7 T. J. Bastow, J. S. Hall, M. E. Smith and S. Steuernagel, *Mater. Lett.*, 1994, **18**, 197.
8 W.-S. Jung and S.-K. Ahn, *J. Mater. Sci. Lett.*, 1997, **16**, 1573.
9 W.-S. Jung and S.-K. Ahn, *J. Mater. Chem.*, 1994, **4**, 949.
10 S.-K. Ahn, C.-W. Oh and W.-S. Jung, *J. Korean Ceram. Soc.*, 1996, **33**, 455.
11 L. F. Nazar, G. Fu and A. D. Bain, *J. Chem. Soc., Chem. Commun.*, 1992, 241.
12 D. Coster and J. J. Fripiat, *Chem. Mater.*, 1993, **5**, 1204.
13 L. B. Alemany and G. W. Kirker, *J. Am. Chem. Soc.*, 1986, **108**, 6158.
14 M. L. Balmer, H. Eckert, N. Das and F. Lange, *J. Am. Ceram. Soc.*, 1996, **79**, 321.
15 I. Farnan, R. Dupree, Z. Jeong, G. E. Thompson, G. C. Wood and A. J. Forty, *Thin Solid Films*, 1989, **173**, 209; R. Dupree, I. Farnan, A. J. Forty, S. El-Mashri and L. Bottyan, *J. Phys. (Paris) Colloq.*, 1985, **C8**, 113.
16 W. H. Gitzen, *Alumina as a Ceramic Material*, American Ceramic Society, Columbus, OH, 1970.
17 C. A. Fyfe, in *Multinuclear Magnetic Resonance in Liquids and Solids-Chemical Applications*, ed. P. Granger and R. K. Harris, Kluwer Academic Publishers, Dordrecht, 1990, p. 326.
18 E. Hanssen, *Acta Chem. Scand.*, 1973, **27**, 2841.
19 R. Dupree, M. H. Lewis and M. E. Smith, *J. Appl. Crystallogr.*, 1988, **21**, 109.
20 N. Hashimoto, Y. Sawada, T. Bando, H. Yoden and S. Deki, *J. Am. Ceram. Soc.*, 1991, **74**,1282.
21 M. Ish-Shalom, *J. Mater. Sci. Lett.*, 1982, **1**, 147.
22 P. Lefort and M. Billy, *J. Am. Ceram. Soc.*, 1993, **76**, 2295.
23 H. K. Chen, C. I. Lin and C. Lee, *J. Am. Ceram. Soc.*, 1994, **77**,1753.
24 H. K. Chen and C. I. Lin, *J. Mater. Sci.*, 1994, **29**,1352.
25 L. Kepinski and M. Zawadzki, *J. Mater. Chem.*, 1995, **5**, 2013.

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