

## Aluminium-27 MAS NMR Investigations of Sodium Aluminates formed from High pH Solutions: Evidence of a Complex Polymer containing both Four- and Six-coordinate Aluminium

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Aluminium-27 MAS NMR studies of sodium aluminates and aluminium hydroxides (OH/Al = 5.3–3.9) formed through varying degrees of acid hydrolysis have revealed four-and-six coordinate aluminium species, suggesting the formation of complex polyoxoanion and/or polymeric intermediates in alkaline solution.

Investigations that have delved into the nature of the aluminium species present in aqueous solutions as a function of pH have generally pertained to acidic solutions,<sup>1,2</sup> with very little having been elucidated concerning the structures of the aluminium ions present in solution at high pH.<sup>3,4</sup> The need to obtain an understanding of this is exemplified by the Bayer process, which involve the dissolution at high pH of aluminium hydroxides. Only one resonance, at  $\delta$  80, has been

observed from <sup>27</sup>Al solution NMR studies of aluminate solutions having OH/Al hydrolysis ratios (or *r* values) greater than 4.0, and this has been assigned to the tetrahedral Al(OH)<sub>4</sub><sup>-</sup> (Q<sup>0</sup>) ion.<sup>5,6</sup> Raman investigations, however, have suggested that Al<sub>2</sub>O(OH)<sub>6</sub><sup>2-</sup> (Q<sup>1</sup>) species coexist in these high pH solutions.<sup>7</sup> The potassium salt of this structure, which consists of two apically linked tetrahedra, has been synthesized, and the crystal structure,<sup>8</sup> IR and Raman,<sup>7</sup> and <sup>27</sup>Al

**Table 1** Observed  $^{27}\text{Al}$  MAS NMR chemical shifts of the Na aluminates and aluminium hydroxides

| OH/Al ( <i>r</i> ) | $\delta$ ( $^{27}\text{Al}$ ) | OH/Al ( <i>r</i> ) | $\delta$ ( $^{27}\text{Al}$ ) |
|--------------------|-------------------------------|--------------------|-------------------------------|
| 5.5                | 86.6, 71.3                    | 4.3                | 86.6, 69.0, 8.1               |
| 5.3                | 86.6, 71.3                    | 4.2                | 70.2, 8.1                     |
| 5.1                | 86.6, 71.3                    | 4.1                | 72.5, 8.1                     |
| 4.8                | 86.6, 71.3                    | 4.0                | 71.3, 8.1                     |
| 4.6                | 86.6, 71.3                    | 3.9                | 71.3, 8.1                     |
| 4.5                | 86.6                          | 3.9 <sup>a</sup>   | 63.1, 6.9                     |
| 4.4                | 86.6, 8.1                     |                    |                               |

<sup>a</sup> Refers to water-insoluble fraction.

MAS NMR<sup>9</sup> analyses have been reported. When the hydrolysis ratio decreases to an *r* value of between 3.0 and 4.0 an aluminium hydroxide precipitate forms, with the crystallization pathway having been established as:<sup>10</sup> amorphous  $\rightarrow$  pseudo-boehmite  $\rightarrow$  bayerite  $\rightarrow$  gibbsite. The pseudo-boehmite, bayerite and gibbsite products are constituted of six-coordinate aluminium exclusively. Previous studies of the amorphous phases formed prior to pseudo-boehmite have reported only six-coordinate aluminium,<sup>11</sup> with no evidence as yet suggesting any transitional phases containing four- and six-coordinate species.

Upon the acid hydrolysis of alkaline aluminate solutions, the addition of each drop of acid would create a microenvironment of low pH containing  $\text{Al}(\text{H}_2\text{O})_{6-n}(\text{OH})_n^{(3-n)+}$  ions, amongst other cationic species. Upon stirring, these cations would encounter the  $\text{Al}(\text{OH})_4^-$  ions and other anionic species present, conceivably resulting in the formation of complex polyoxoanions and polymers made up of both four- and six-coordinate aluminium. Thus far no evidence has been reported for the existence of this type of species.

To investigate the structures of the aluminium ions and polymers present in sodium aluminates (of varying OH/Al ratio) prepared through acid hydrolysis,  $^{27}\text{Al}$  MAS NMR investigations of freeze-dried solutions were carried out. These solid-state studies were necessitated as solution NMR spectra of these alkaline solutions yield only a  $\delta$  80 signal, the intensity of which decreased with a lowering of the OH/Al ratio.<sup>12</sup> Preliminary  $^{27}\text{Al}$  MAS NMR studies of gels formed under low pH conditions compared the spectra of wet gels collected by centrifuging with those of samples that had been air-dried and freeze-dried. No differences were found, supporting the view that freeze-drying does not alter the nature of the species present.<sup>12</sup> In the case of the Na aluminates and gels formed under alkaline conditions, the kinetics of phase transformation are far more rapid than those for the low pH gels, and thus freeze-drying is necessary to allow for spectral identification of the initial phases formed upon acid hydrolysis.

A sodium aluminate solution having an OH/Al ratio of 5.5 ( $[\text{Al}] = ca. 1 \text{ mol dm}^{-3}$ ) was prepared by dissolving  $\text{Al}(\text{OH})_3$  in an appropriate amount of NaOH. Aliquot portions of this alkaline solution were then hydrolysed through the addition of *ca.*  $1 \text{ mol dm}^{-3}$  HCl, to hydrolysis ratios of 5.3 and below (Table 1) under conditions of vigorous stirring. The solutions having *r* values of 4.3 and below contained gel-like precipitates. All solutions were quickly frozen in liquid nitrogen and then freeze-dried. The samples having *r* values of 4.1 and below were well dried by this technique, whereas those of higher *r* values retained some degree of moisture. Drying using heat was avoided as it was observed that temperatures as low as 60 °C induce phase transformations in gels for which  $r \geq 4.1$ . Thus for the high *r* value samples ( $r \geq 4.2$ ) the  $^{27}\text{Al}$  MAS NMR spectra were obtained of incompletely dried gels.

The  $^{27}\text{Al}$  MAS NMR spectra were acquired on a Bruker MSL-400 spectrometer operating at the  $^{27}\text{Al}$  frequency of 104.25 MHz. Single-pulse experiments, with and without high



**Fig. 1**  $^{27}\text{Al}$  MAS NMR spectra of the sodium aluminates and aluminium hydroxides synthesized through acid hydrolysis for different values of *r*. The asterisks denote spinning side bands.

power  $^1\text{H}$  decoupling, were employed in conjunction with MAS rates of 15 kHz. At least three difference resonances are observed for the separate bulk samples (Fig. 1 and Table 1); the sharp downfield signal at  $\delta$  86.6, and the broader resonance(s) located in the range  $\delta$  72.5–69.0 have chemical shifts indicative of four-coordinate aluminium. The upfield resonance at  $\delta$  8.1 is attributed to six-coordinate aluminium. High-power  $^1\text{H}$  decoupling experiments found only the resonance at  $\delta$  86.6 to narrow. This resonance is present for all of the samples having  $r \geq 4.3$ , but its intensity varies with OH/Al ratio: it is of intermediate intensity for the *r* 5.5 sample, it is the dominant resonance for samples with *r* in the range 4.4–4.8, and then drops off sharply in intensity for the samples with lower *r* values, becoming completely unresolvable for  $r \leq 4.1$ . The observed line narrowing with high-power  $^1\text{H}$  decoupling indicates the presence of protons in close proximity to these tetrahedral aluminium sites, and this resonance is presumably due to the  $\text{Q}^0 \text{Al}(\text{OH})_4^-$  ions that are associated with the  $^{27}\text{Al}$  resonance at  $\delta$  80 in solution NMR studies.<sup>6</sup> The second resonance attributed to four-coordinate aluminium ( $\delta$  72.5–69.0) is observed for all hydrolysis ratios except the *r* = 4.5 sample. No change in linewidth is established upon high-power  $^1\text{H}$  decoupling, and therefore the tetrahedral aluminium sites responsible for these resonances are likely to be, at least to some degree, linked by bridging oxygens. The extent of second-order quadrupolar effects on

these chemical shifts has not been evaluated for these resonances; however the isotropic chemical shifts would all be downfield of  $\delta$  70, and are thus indicative of tetrahedral aluminium that is coordinated through oxygen to other four-coordinate aluminium sites.<sup>13</sup> These second resonance(s) likely emanate from a mixture of Q<sup>4</sup>, Q<sup>3</sup>, Q<sup>2</sup> and Q<sup>1</sup> Al species. The amorphous nature of these samples will cause the  $\delta$  72.5–69.0 linewidth to be dominated by a distribution of electric field gradients and chemical shift dispersion. The intensities in this chemical shift region vary markedly with OH/Al ratio. A dominant intensity maximum appears at  $\delta$  71.3 for the non-hydrolysed starting sample ( $r = 5.5$ ), but decreases markedly with the initial acid hydrolysis, and disappears by an  $r$  value of 4.5, leaving only the sharp  $\delta$  86.6 resonance. This suggests that the addition of acid serves to break up the complex polymer present at  $r = 5.5$  and results in Al(OH)<sub>4</sub><sup>-</sup> ions in solution, although dilution could also be a factor. A signal of very similar chemical shift to the  $\delta$  71.3 resonance ( $\delta$  69.0–72.5) begins to appear for the  $r = 4.4$  sample, and is dominant for values of  $r = 4.3$  and 4.2. Although these chemical shifts are similar, the fact that the  $\delta$  71.3 signals disappear when the OH/Al ratio decreases to 4.5 and then 'reappear' upon further acid hydrolysis indicates that different species must be responsible for these signals when  $r > 4.5$  and  $r \leq 4.4$ .

The  $\delta$  8.1 resonances attributable to six-coordinate aluminium first appear at an OH/Al ratio of 4.4, and increase rapidly in intensity as the  $r$  value decreases. Samples having  $r$  values in the range of 4.2–4.4 inclusive are all completely water-soluble, verifying that the six-coordinate resonance observed in this OH/Al range cannot be due to an aluminium hydroxide or oxyhydroxide phase such as in pseudo-boehmite or bayerite, but must be due to a polyoxoanion or polymer containing six-coordinate aluminium. The samples having  $r$  values below 4.1 are not completely water-soluble; hence the octahedral signal in these cases is at least partially (and in the  $r = 3.9$  case predominantly) due to the precipitated aluminium hydroxide. The bulk phase of the  $r = 3.9$  sample reveals two resonances at  $\delta$  71.3 and 8.1, while the resonances of the water-insoluble fraction are observed at  $\delta$  63.1 and 6.9. The signal at  $\delta$  63.1 (uncorrected for second-order quadrupolar effects) is appropriate for a tetrahedrally coordinated aluminium surrounded by octahedrally coordinated species,<sup>13</sup> and has a similar chemical shift to those reported for the transitional aluminas possessing spinel structures<sup>14,15</sup> (e.g.  $\eta$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). IR investigation of this water-insoluble fraction revealed a spectrum that was similar to that of partially aged 'pseudo-spinel' gels,<sup>16,17</sup> with poorly resolved bands appearing at ca. 730, 625 and 540 cm<sup>-1</sup>, which are very similar to those assigned as (Al–O) (*T<sub>d</sub>*), (Al–OH) (*O<sub>h</sub>*) and (Al–O) (*O<sub>h</sub>*) stretches (729, 627 and 546

cm<sup>-1</sup>) in the Al<sub>13</sub> spinel sub-unit.<sup>16,18</sup> As previously mentioned, the bulk  $r = 3.9$  sample reveals a tetrahedral signal having an <sup>27</sup>Al chemical shift at  $\delta$  71.3; thus the majority of the tetrahedral aluminium in this sample is in the form of a water-soluble polymer containing, at least predominantly, four-coordinate aluminium likely linked through oxo and hydroxo bridges to other four-coordinate aluminium sites.

These results support the view that the acid hydrolysis of aqueous aluminate solutions results in the formation of complex species containing both four- and six-coordinate aluminium in a variety of different environments that vary with the OH/Al ratio, and possibly with the Al concentration.

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