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^{27}Al and ^{23}Na MAS NMR and Powder X-ray Diffraction Studies of Sodium Aluminate Speciation and the Mechanistics of Aluminum Hydroxide Precipitation upon Acid Hydrolysis

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Abstract: ^{27}Al and ^{23}Na MAS NMR, powder X-ray diffraction, and infrared spectroscopic investigations of freeze-dried sodium aluminates and aluminum hydroxides formed through acid hydrolysis have been undertaken, with OH/Al hydrolysis ratios between 5.3 and 2.8 being analyzed. Numerous ^{27}Al NMR resonances were observed, the intensities of which vary as a function of OH/Al ratio, and these have been assigned to four-, five-, and six-coordinate aluminum species constituting a variety of structural moieties. The dominant species at an OH/Al ratio above 4.4 appears to be a Q^0 $Na[Al(OH)_4]$ salt, as indicated by a ^{27}Al resonance at 86.6 ppm. In addition, a second, broader resonance at 71.3 ppm demonstrates the simultaneous existence of further four-coordinate aluminum species linked through oxo bonds to other four-coordinate aluminums (*e.g.*, Q^2 $[\mathit{Al}(OH)_2(OAl)_2]^{x-}$), although a range of other polyoxoanion species (*e.g.*, Q^1 $[Al_2O(OH)_6{}^{2-}]$ and Q^4 $[AlO_2{}^-]$) would almost certainly be present concurrently, also contributing to this vicinity of the ^{27}Al chemical shift range. At an OH/Al ratio between 4.4 and 4.1, a water-soluble phase forms that contains both four- and six-coordinate aluminum. At OH/Al ratios of 4.0 and below, a water-insoluble phase exists possessing four-, five-, and six-coordinate aluminum, the relative ratios of which vary with the degree of acid hydrolysis. The insoluble portion of the samples in the OH/Al $\leq$ 3.9 range exhibits ^{27}Al chemical shifts similar to those reported for transitional aluminas such as γ-, η-, and θ-Al_2O_3 and an infrared spectrum similar to pseudo-spinel gels, suggesting that a pseudo-spinel intermediate is the first phase involved in the crystallization of gibbsite. The resonance assigned to five-coordinate aluminum probably results from species involved in the transformation of the pseudo-spinel phase to pseudo-boehmite. The formation of gibbsite upon the acid hydrolysis of alkaline sodium aluminate solutions thus appears to follow the pathway pseudo-spinel → pseudo-boehmite → bayerite → gibbsite.

Introduction

The nature of the aluminum species present in aqueous solutions as a function of pH has been studied in great depth for acidic solutions.[1] However, very little is known about the structures of the aluminum species present under alkaline conditions. The importance of achieving an understanding of this is illustrated by the industrial Bayer process, which is a critical process in aluminum production that relies on the dissolution of the aluminum oxides and hydroxides present in bauxite ore in concentrated sodium hydroxide solutions. This is generally followed by initiation of the precipitation of gibbsite (γ-$Al(OH)_3$) through the addition of seed crystals.[2] The presence of impurities (organic and inorganic) can profoundly affect this industrial process,[3–5] and a complete understanding of the identity and nature of the species present at high pH could be extremely important in circumventing problems and optimizing the precipitation reaction.

In the base hydrolysis of acidic Al^{3+} aqueous solutions, the $[AlO_4Al_{12}(OH)_{24}H_2O)_{12}{}^{7+}]$ polyoxocation species (Al_{13}) is known to form below an OH/Al hydrolysis ratio (or *r* value, which refers to the number of moles of OH^- added per mole of Al) of 2.5.[6] This complex ion[7] has the form of the ϵ-Baker–Figgis[8] isomer of the Keggin[9] structure, which consists of a central tetrahedrally coordinated aluminum surrounded by 12 edge-linked octahedral aluminum sites and can be viewed as a spinel subunit.[10,11] It has been conjectured that a wide range of other polymeric species also exists, and recent evidence has suggested that discrete clusters may be formed through the coalescence of two or more Al_{13} units.[12] The mechanism of formation of the Al_{13} species through base hydrolysis has not been established, although it has been suggested that one pathway may involve the formation of a microenvironment of very high pH immediately upon the addition of each drop of base.[13,14] This microenvironment would contain $[Al(OH)_4{}^-]$ ions among other species, and it has been proposed that upon mixing, these anions are swept out and encounter the $[Al(H_2O)_{6-n}(OH)_n{}^{(3-n)+}]$ ions and other cationic species present, combining to form the Al_{13} structure.[13,14] At an OH/Al ratio of 2.5, a gel first forms, and this occurs through the coalescence of Al_{13} units and any other species present in solution.[10,11,15,16] These condensation reactions continue until an OH/Al ratio of 3.0 is reached and result in the formation of a pseudo-spinel (γ-$Al_2O_3{\cdot}xH_2O$) phase.[10,11] This intermediate quickly transforms to pseudo-boehmite (γ-$AlO(OH){\cdot}H_2O$), and then to bayerite (α-$Al(OH)_3$), and finally to gibbsite (γ-$Al(OH)_3$) if sodium ions are

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present in appropriate concentrations and the final pH is correct.[15,17-19] The pseudo-spinel phase possesses both four- and six-coordinate aluminum, whereas pseudo-boehmite and bayerite have only six-coordinate aluminum. Thus, the transformation sequence that occurs for gels formed through the base hydrolysis of acidic solutions to an OH/Al ratio of 3.0 (pH ≅ 7) is

$$\text{pseudo-spinel} \rightarrow \text{pseudo-boehmite} \rightarrow \text{bayerite} \rightarrow \text{gibbsite}$$

Above an r value of 4.0 (pH ≅ 11), aluminum hydroxides dissolve, resulting in aluminate solutions, or "liquors", the natures of which are poorly understood.[20-22] By solution ^{27}Al NMR, only one resonance has been observed for sodium aluminate solutions having OH/Al ratios in the range of 4.0 to ~20, this occurring at 80 ppm and being assigned to the $[Al(OH)_4^-]$ anion.[23,24] From potassium aluminate solutions, a $K_2[Al_2O(OH)_6]$ salt has been precipitated and the crystal structure,[25] infrared and Raman spectra,[26] and ^{27}Al MAS (magic angle spinning) NMR[27] analyses reported. The aluminum ion in this salt is a dimer that consists of two apically linked tetrahedra. Raman investigations have suggested that these $[Al_2O(OH)_6^{2-}]$ ions also exist in sodium aluminate solutions.[26] The nature of other species formed has been proposed to be governed to a large degree by a dehydration/oligomerization sequence occurring when the aluminum and/or hydroxide ion concentration is increased:[20-23]

$$\underset{CN = 6}{[Al(OH)_4(OH_2)_2^-]} \xrightarrow{-2H_2O} \underset{CN = 4}{[Al(OH)_4^-]} \xrightarrow{-H_2O}$$

$$\underset{CN = 4}{[AlO(OH)_2^-]} \xrightarrow{-H_2O} \underset{CN = 4}{[AlO_2^-]}$$

CN ≡ Al coordination number

The only reported ^{27}Al solution NMR evidence of a resonance due to six-coordinate aluminum in an alkaline aluminate was for an extremely high r value solution (OH/Al ≅ 25), and this signal was tentatively assigned to $[Al(OH)_6^{3-}]$.[24] A precipitate from highly alkaline solutions (r value not specified) was shown by ^{27}Al MAS NMR to contain some six-coordinate aluminum; however, the majority was still four-coordinate.[28] No evidence has been seen of six-coordinate aluminum in lower r value solutions, and while the existence of the last three species in the above proposed dehydration series appears feasible, the existence of the first does not. Results from a wide range of other experimental techniques such as conductivity measurements, electrometric titrations, optical properties, and X-ray scattering[22] have led to a more diverse range of oligomers being suggested.[20] One proposed series, given by the general formula $[Al_x(OH)_{4x}(OH_2)_2^{x-}]\cdot(4x + 4)H_2O$, involves only six-coordinate aluminum ions linked through hydroxo bridges. Cyclic derivatives of this series, such as $[Al_6(OH)_{24}^{6-}]\cdot 24H_2O$, have also been suggested. However, the fact that the condensed aluminate phase $NaAlO_2$ involves oxo rather than hydroxo bridges has led to the alternate proposal of an oxo-bridged series existing which involves only tetrahedrally coordinated aluminum, examples of which include the known $[Al_2O(OH)_6^{2-}]$ dimer and the proposed cyclic $[Al_6O_6(OH)_{12}^{6-}]$ ion.[20-23] If the postulated mechanism of Al_{13} formation upon base hydrolysis is indeed true, then an alternative reaction sequence which would involve analogous reactions occurring upon the acid hydrolysis of alkaline solutions may be valid. As regions of low and high pH proceed to mix, small regions of lower pH would be formed that would contain $[Al(H_2O)_{6-n}(OH)_n^{(3-n)+}]$ ions, in addition to other species. These cations would come into contact with the aluminate anions in which the aluminum is four-coordinate, conceivably resulting in the formation of complex polyoxoanions and polymers containing both four- and six-coordinate species.[29]

When solids are produced by drying these alkaline solutions, water-soluble sodium aluminates result which are generally referred to by the formula $NaAlO_2$, although it would usually be more correct to refer to them as $NaAlO_2\cdot xNaOH\cdot yH_2O$. The β- and γ-forms of $NaAlO_2$ (which are not isostructural with β- and γ-$LiAlO_2$)[30,31] are formed thermally rather than hydrolytically, and their structures have been determined through powder X-ray diffraction (XRD) studies.[32-34] β-$NaAlO_2$ is isostructural[33] with β-$NaFeO_2$[35,36] and is stable at room temperature, although exposure to moist air results in a rapid transformation to gibbsite (γ-$Al(OH)_3$) through hydrolysis.[2] The γ-$NaAlO_2$ phase is only stable above 1100 °C.[33] These β and γ polymorphs both involve condensed phases of tetrahedrally coordinated aluminum and define Q^4 frameworks (where Q^n refers to the number of oxo bridges versus terminal hydroxyl groups for a four-coordinate aluminum, *i.e.*, $[Al(OAl)_n(OH)_{4-n}]$). Numerous other sodium aluminate crystal forms exist, as evidenced by the number of reported powder diffraction patterns;[37] however, the only ^{27}Al MAS NMR studies reported to date have involved β-$NaAlO_2$,[38] precipitates from extremely alkaline aluminate solutions,[28] and the thermal decomposition of a commercial sodium aluminate of unknown initial structure.[27]

When sodium aluminate solutions are acid hydrolyzed, the formation of $Al(OH)_3$ proceeds when r decreases to a value of 4.0, and a crystallization pathway similar to that seen in the base hydrolysis of acidic solutions[10,11] (at $r = 3$) has been reported:[39]

$$\text{amorphous} \rightarrow \text{pseudo-boehmite} \rightarrow \text{bayerite} \rightarrow \text{gibbsite}$$

The nature of the water-insoluble, X-ray amorphous material preceding pseudo-boehmite formation has not been established. Solution NMR studies undertaken on $r = 4$ suspensions give only the 80 ppm resonance[40] assigned to $[Al(OH)_4^-]$, even though the final precipitate is known to contain only six-coordinate aluminum (*i.e.*, pseudo-boehmite or bayerite).[2,40] Obviously there cannot be an instantaneous transformation of all of the four-coordinate aluminum in solution to a product that contains only six-coordinate aluminum. Logically, a series of polyoxoanion complexes and polymers containing aluminum in both coordination environments must form, albeit serving as intermediate phases, and recent ^{27}Al MAS NMR evidence has suggested the existence of such proposed species.[29]

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To continue our preliminary studies[29] of the structures of the aluminum ions and polymers present in sodium aluminate solutions as a function of OH/Al ratio and solution concentration, as well as the nature of the polymers and hydroxides formed upon acid hydrolysis, ^{27}Al and (to a lesser extent) ^{23}Na MAS NMR investigations have been carried out on freeze-dried solutions. These solid-state studies were necessitated as previous solution ^{27}Al NMR studies of these alkaline solutions proved to be of limited diagnostic value, yielding only a solitary 80 ppm signal,[23,24,41] the intensity and line width of which decreased with a reduction of the OH/Al ratio.[41] Additional XRD studies of the thermal transformation of Fisher purified sodium aluminate were carried out to investigate the proposals made by Fitzgerald *et al.*[27] concerning the nature of the sodium aluminate phases formed.

Theoretical Section

The full Hamiltonian, $\mathcal{H}$, describing noninteger quadrupolar nuclei such as ^{27}Al ($I = {}^5/_2$) and ^{23}Na ($I = {}^3/_2$) is written as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{CS} \qquad (1)$$

where the constituent Hamiltonians $\mathcal{H}_Z$, $\mathcal{H}_Q$, $\mathcal{H}_D$, and $\mathcal{H}_{CS}$ represent the usual Zeeman, quadrupolar, dipolar, and chemical shift interactions, respectively. Fast MAS techniques usually implement rotational frequencies (ν_r) large enough ($\nu_r \geq 12$ kHz) to average $\mathcal{H}_D$ and $\mathcal{H}_{CS}$ to zero for these nuclei, rendering the observed resonance frequency still perturbed by $\mathcal{H}_Q$. In the high-field limit, if the system is quadrupolar perturbed to first order only, then the central $(+{}^1/_2, -{}^1/_2)$ transition remains unaffected and the MAS spectrum of the satellite $[(\pm{}^1/_2, \pm{}^3/_2)$ for $I = {}^3/_2, {}^5/_2]$ and $[(\pm{}^3/_2, \pm{}^5/_2)$ for $I = {}^5/_2]$ transitions are manifested as a manifold of spinning side bands modulated by the MAS frequency (as for other inhomogeneous broadenings) over a frequency range of the order of the quadrupole frequency, $\nu_Q = 3C_Q/[2I(2I-1)]$, where $C_Q = e^2qQ/h$ is the quadrupolar coupling constant, eq is the electric field gradient (efg), and eQ is the quadrupole moment. If, however, the perturbation extends to second order, then (i) the total MAS spectrum is further broadened and (ii) the positions of the central and satellite transitions are shifted (in different directions) from the isotropic chemical shift, δ_{iso}. Thus, for such second-order broadened quadrupolar systems, the fast MAS spectrum of the central $(+{}^1/_2, -{}^1/_2)$ transition can now be described by the complex asymmetry parameter (η) and angular dependences:[42–48]

$$\omega^{(2)}_{(+^1/_2,-^1/_2)} = \omega_0\delta^{(2)}_{QS(+^1/_2,-^1/_2)} - \frac{1}{64}\frac{C_Q^{\,2}}{\omega_0}\left[\frac{I(I+1) - {}^3/_4}{I^2(2I-1)^2}\right] \times [9(3 - \eta\cos 2\phi)^2 \sin^4\theta - 12(6 + \eta^2 - 5\eta\cos 2\phi)\sin^2\theta + 4\eta^2] \qquad (2)$$

In this equation, ϕ and θ define the rotor orientation with respect to the efg tensor principal axis system, $eq = V_{zz}$ is defined as the largest component of the efg tensor, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter which describes the deviation of the local electric field gradient from cylindrical symmetry. The quadrupolar shift of the center of gravity, $\delta^{(2)}_{QS(+^1/_2,-^1/_2)}$, of the central transition away from δ_{iso} is given by:[47–51]

$$\delta^{(2)}_{QS(+^1/_2,-^1/_2)} = -\frac{3}{40}\frac{C_Q^{\,2}}{\omega_0^{\,2}}\left[\frac{I(I+1) - {}^3/_4}{I^2(2I-1)^2}\right](1 + \eta^2/3) \qquad (3)$$

Table 1. Observed ^{27}Al MAS NMR Resonances of the Sodium Aluminates and Aluminum Hydroxides as Prepared

OH/Al	δ(^{27}Al)	OH/Al	δ(^{27}Al)	OH/Al	δ(^{27}Al)
5.5	86.6,[a] 71.3	4.3	86.6,[a] 69.0, 8.1	3.7[b]	63.1, 33.9, 6.9
5.3	86.6,[a] 71.3	4.2	70.2, 8.1	3.5	65.6, 32.7, 5.8
5.1	86.6,[a] 71.3	4.1	72.5, 8.1	3.5[b]	63.1, 33.9, 6.9
4.8	86.6,[a] 71.3	4.0	71.3, 8.1	3.1	60.8, 33.9, 5.8
4.6	86.6,[a] 71.3	3.9	71.3, 8.1	3.1[b]	60.8, 33.9, 5.8
4.5	86.6[a]	3.9[b]	63.1, 6.9	2.8	58.5, 32.7, 4.6
4.4	86.6,[a] 8.1	3.7	70.2, 33.9, 8.1	2.8[b]	58.5, 33.9, 4.6

[a] Isotropic chemical shift values; all other chemical shifts remain uncorrected for second-order quadrupolar contributions. [b] Water-insoluble fraction.

Rapid sample rotation using fast MAS techniques will diminish, but not completely average to zero, the effects described in eq 2. This expression exhibits an angular behavior far more complex than the familiar $(3\cos^2\theta - 1)$ dependence encountered in the MAS averaging of other interactions. Hence, the maximum line narrowing of the second-order perturbed central $(+{}^1/_2, -{}^1/_2)$ transition achievable with fast MAS in the $\nu_r \rightarrow \infty$ limit is a factor of ~3–4, depending on the asymmetry parameter η, with the resultant line shapes exhibiting η-dependent singularities and shoulders analogous to their static powder line shape counterparts.[43,45,47,48] Equations 2 and 3 also predict that these second-order quadrupolar broadening and shift phenomena display a $1/\omega_0$ dependence, implying that the most efficient elimination of these quadrupolar effects will be achieved when fast MAS techniques are employed at the highest available magnetic field strengths.

Experimental Section

Fresh $Al(OH)_3$ was prepared by dissolving $AlCl_3{\cdot}6H_2O$ (Aldrich, analytical grade) in deionized/distilled water and then adding NaOH (Rhone-Poulenc, analytical grade) to an OH/Al mole ratio of 3. This fresh $Al(OH)_3$ precipitate was washed by centrifugation until the supernatant tested negative for chloride ions ($AgNO_3$ test). This gel was then dissolved by addition of further NaOH, yielding a sodium aluminate liquor having an OH/Al ratio of 5.5. The aluminum concentration was adjusted to 1.0 M by dilution to the required volume in a volumetric flask. These solutions were always slightly cloudy, and the undissolved aluminum hydroxide was removed by centrifuging the solution prior to acid hydrolysis. The very small amount of aluminum removed in this manner was negligible in comparison with the OH/Al ratio and Al concentrations.. Aliquots of this alkaline solution were then acid hydrolyzed through the addition of *ca.* 1 M 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. These solutions were quickly frozen in liquid nitrogen and dried by freeze-drying. The resulting sodium aluminates and aluminum hydroxides had the bulk formula $Na_2O{\cdot}Al_2O_3{\cdot}x NaOH{\cdot}y H_2O{\cdot}z NaCl$, where x, y, and z vary depending on the degree of acid hydrolysis and drying. The samples having r values <4.1 were very well dried by the freeze-drying technique, whereas those of higher r values retained some degree of moisture. Further drying using heat was avoided, as it was observed that temperatures as low as 60 °C could induce phase transformations. For higher r value samples ($r > 4.2$), the ^{27}Al MAS NMR spectra were obtained of the incompletely dried gels. To examine the effects of aluminum concentration on the species present in the various sodium aluminate solutions, a series was also prepared that had an OH/Al ratio of 4.8 and aluminum concentrations ranging from 1.25 to 0.1 M. These samples were freeze-dried in the same manner as described above after being allowed to equilibrate for several minutes.

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To examine the possible effects of freeze-drying on the nature of the species present in the alkaline solutions and gels examined, a comparison was made of drying techniques on mildly acidic aluminum systems, for which more of the chemistry has been established. Aluminum gels (OH/Al = 2.9) formed through base hydrolysis were collected in the wet form by centrifuging (hydrogels) and also in the dried form by both air-drying at room temperature (xerogels) and by freeze-drying (cryogels). The ^{27}Al MAS NMR spectra of these three samples were virtually identical,[41] supporting the assumption that freeze-drying does not alter the primary nature of the species present. To compare the effects of drying techniques on solutions rather than gels, a clear base hydrolyzed Al solution (OH/Al = 2.50) was prepared that was of appropriate pH and Al(III) concentration that little or no signal would be seen for the aluminum species by ^{27}Al solution NMR.[41,52,53] This solution was both air-dried and freeze-dried, and the MAS NMR spectra were compared with that of a crystalline Al$_{13}$ sulfate (OH/Al = 2.46). As expected, they were also extremely similar. Finally, a solution having an OH/Al value of 2.25 was prepared that contained the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ ions among other species. A comparison of the ^{27}Al solution NMR analysis of this preparation with the ^{27}Al MAS NMR spectra of the solids formed upon the air-drying and freeze-drying of this solution revealed no marked differences.[41] These checks indicate that the drying technique(s) employed bear(s) no influence on the aluminum speciation, although other physical characteristics such as surface areas and porosities will undoubtedly be affected. This is in agreement with previous studies of the effects of drying on aluminum solution and gel species.[54,55] In the case of the sodium aluminates and gels formed under alkaline conditions, the kinetics of the initial phase transformation are far more rapid than those for the low pH gels, and thus rapid freezing and freeze-drying was necessary to permit the spectral identification of the initial phases formed upon acid hydrolysis.

To examine the effect of thermally induced dehydration on these freeze-dried products, portions of each sample were subjected to temperatures of 80 °C for time periods of 1 week and 3 weeks. These effects were compared with the thermal transformation sequence of a commercial sodium aluminate (Fisher purified $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$), where samples were heated for 24 h over a range of temperatures and then characterized by ^{27}Al MAS NMR and powder X-ray diffraction. Pure β-NaAlO$_2$ was synthesized as described in the literature,[33,56] and the resulting product was stored at 180 °C to prevent hydrolysis occurring before the XRD patterns and ^{27}Al MAS NMR spectra were recorded.

The ^{27}Al and ^{23}Na MAS NMR spectra were acquired on a Bruker MSL-400 spectrometer (magnetic field strength 9.40 T) operating at ^{27}Al and ^{23}Na frequencies of 104.23 and 105.81 MHz, respectively. Single pulse experiments, with and without high-power ^{1}H decoupling, were employed in conjunction with MAS rates of 15 kHz. The quadrupolar nature of the ^{27}Al ($I = {}^5/_2$) and ^{23}Na ($I = {}^3/_2$) nuclei necessitated that flip angles satisfy the condition[51,57]

$$(I + {}^1/_2)\omega_{rf}t_p \leq \frac{\pi}{6}$$

to enable quantitative estimates to be made with an expected error of <5% in the central transition intensity. Thus, small flip angles of 10° (^{27}Al) and 15° (^{23}Na) from 0.6-μs pulses were used in conjunction with recycle delays of 1 s. ^{27}Al and ^{23}Na chemical shifts were externally referenced to 1 M AlCl$_3$ (aqueous) and 1 M NaCl (aqueous), respectively, both of which were arbitrarily set to 0.0 ppm. Chemical shifts are uncorrected for second-order quadrupolar effects and are not reported as isotropic values (δ_{iso}) unless otherwise specified. Line shape simulations of second-order broadened central ($+{}^1/_2, -{}^1/_2$) transitions and spinning side-band manifolds of satellite ($\pm{}^1/_2, \pm{}^3/_2$) transitions were performed with the POWDER and QNMR quadrupolar NMR simulation packages.

Powder X-ray diffraction (XRD) studies were carried out using a Siemens D500 diffractometer interfaced to a PC and using Sietronics SIE122D operating software. This characterization employed nickel-filtered Cu Kα radiation, 1.0° divergence slits, and 0.15° receiving slits, and continuous scans were acquired at a rate of 2° 2θ/min. All of the recorded patterns exhibit a strongly curving base line below 20° 2θ; however, this has been established to be due to an instrumental artifact rather than the presence of amorphous impurities.

Infrared spectra were run of some of the samples. These samples were in the form of KBr pellets, and spectra were acquired at 2 wavenumbers resolution on a Bomem FTIR spectrometer.

Results and Discussion

1. Acid Hydrolysis of the Sodium Aluminate Series. ^{27}Al MAS NMR studies revealed marked variations in the types of species present in the prepared samples over the approximate *r* value ranges of 5.5–4.5, 4.4–3.9, and below 3.9 (Figure 1 and Table 1). For the samples having 5.5 ≥ OH/Al ≥ 4.5, only two resonances are observed: a sharp first-order broadened signal with an isotropic chemical shift of 86.6 ppm, and an inhomogeneous second-order broadened signal with an uncorrected chemical shift of 71.3 ppm. Both of these resonances are attributable to four-coordinate aluminum. High-power ^{1}H decoupling experiments found only the ^{27}Al resonance at 86.6 ppm to narrow, indicating the close proximity of protons to these tetrahedral aluminum sites. This suggests the existence of a large homogeneous ^{1}H dipolar interaction that a fast MAS frequency of 15 kHz cannot eliminate; however, a strong ^{1}H decoupling field $\mathbf{B}_{1H}$ of 80 kHz in conjunction with this MAS frequency reduces this line width at half-height from ~360 (undecoupled) to ~120 Hz. Therefore, this resonance is assigned to the Q^0 [Al(OH)$_4^-$] anion that is associated with the 80 ppm resonance observed in ^{27}Al solution NMR studies.[24] The substantial downfield displacement of ~6.6 ppm from the observed chemical shift of the free [Al(OH)$_4^-$] anion in solution is consistent with the close proximity of a deshielding Na$^+$ ion that is fulfilling a charge balancing role. The 86.6 ppm signal is present for all of the samples having *r* > 4.2, but its intensity varies with the OH/Al ratio, being of intermediate intensity for the 5.5 sample, the dominant resonance for samples in the range 4.4–4.8, and then dropping off sharply in intensity for the lower *r* value samples, to become completely unresolvable by an OH/Al ratio of 4.1. It is the only resonance observed for *r* = 4.5, and this sample is thus assigned to a pure Na[Al(OH)$_4$] phase. The structured ^{27}Al satellite transition and ^{23}Na central transition line shapes of this "pure" Na[Al(OH)$_4$] phase (Figures 2b and c) are suggestive of a well-defined network. Although the ^{23}Na spectrum indicates a small (<10% of Na content) amount of NaCl at an isotropic chemical shift of 7.1 ppm,[27,41] it is evident from these line shapes that this small amorphous (*vide infra*) content does not induce bulk structural disorder. Such disorder would render a distribution of electric field gradients and some associated chemical shift dispersion within these quadrupolar dominated line shapes and hence introduce difficulty and/or uncertainty in their characterization. From the second rank tensorial nature of the quadrupolar interaction, perfect tetrahedral, octahedral, and icosahedral point symmetries lead to a situation where $V_{zz} = V_{xx} = V_{yy} = 0$ for the Cartesian constituents of the efg tensor, resulting in no quadrupolar contribution to line width or chemical shift. Thus, only a minor geometric distortion of the [Al(OH)$_4^-$] ion is required to induce the small, first-order ^{27}Al quadrupolar interaction within this phase that leaves the central transition unperturbed. This small quadrupolar interaction and subsequent featureless line shape of the ^{1}H decoupled ^{27}Al central ($+{}^1/_2, -{}^1/_2$) transition has necessitated the use of the MAS induced spinning side-band manifold of the satellite ($\pm{}^1/_2, \pm{}^3/_2$) transitions to facilitate the measurement of the quadrupolar parameters. The simulation of this manifold (Figure 2a) yields $C_Q = 0.62 \pm 0.05$ MHz, $\eta = 0.00 \pm 0.03$, and $\delta_{iso} = 86.6$ ppm, and these parameters can be interpreted as a minimum trigonal distortion of the [Al(OH)$_4^-$] ion point symmetry, reducing it from T_d to C_{3v}:[27,58–60]

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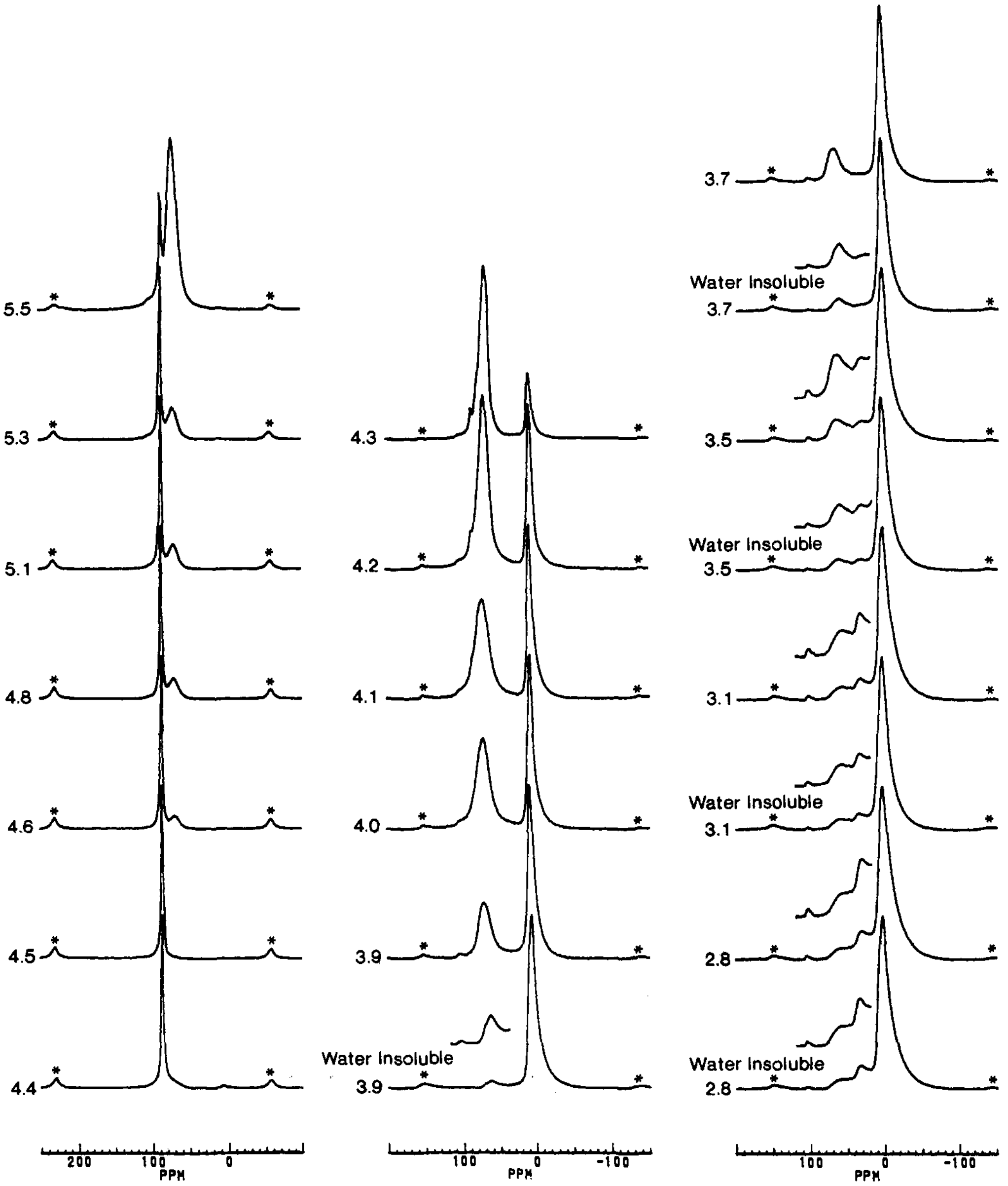
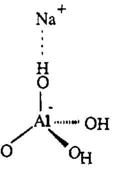


Figure 1. ^{27}Al MAS NMR spectra obtained with an MAS frequency of 15 kHz of the sodium aluminates and aluminum hydroxides formed through acid hydrolysis, as collected after freezing and freeze-drying. The spectra are of the bulk phases formed; however, for OH/Al $\leq$ 3.9, spectra are also shown of the water-insoluble fractions thereof. The OH/Al hydrolysis ratios are as indicated, and the spinning side bands within each spectrum are denoted by asterisks. The small signal at *ca.* 104 ppm visible for some of the samples is due to an aluminum impurity in the Si_3N_4 rotor material.

i.e.



Q^0 $Na[Al(OH)_4]$

Observation of the ^{23}Na MAS NMR resonance for this phase finds a distinct second-order broadened central ($+^1/_2$, $-^1/_2$) transition, as illustrated in Figure 2c, from which the quadrupolar parameters C_Q = 3.10 ± 0.05 MHz, η = 0.00 ± 0.03, and δ_{iso} = 5.9 ppm can be elucidated from the given line shape simulation. The ill-defined chemical shift ranges of different sodium coordination environments make it difficult to associate this chemical shift with a specific structural environment,[27,61] although the observations that both the ^{27}Al and ^{23}Na quadrupolar interactions exhibit axial symmetry and that stoichiometric charge balancing must be preserved invoke the view that crystallization of the Na^+ and $Al(OH)_4^-$ species occurs as discrete 1:1 ion pairs.

The powder X-ray diffraction pattern of this $Na[Al(OH)_4]$ salt (Figure 2a and Table 2) reveals a crystalline phase that was not found to match any Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file listing. Some additional broad and extremely low-intensity peaks indicate the presence of a small amount of essentially amorphous NaCl. The instability of this sample to atmospheric water vapor did not allow for a prolonged XRD scan to be obtained; however, the sample was sufficiently crystalline that the α_1 and α_2 peaks were readily resolved at high angles. The pattern could be indexed to a tetragonal unit cell, a = 7.503 and c = 5.036 Å, with systematic reflection conditions $hk0$ ($h + k = 2n$) and $0k0$ ($k = 2n$). From this analysis, two space groups, $P4/n$ (No. 85) and $P4/nmm$ (No. 129), are possible.[62] In addition, however, the only $00l$ reflection observed (002) satisfies the condition $l = 2n$, and if this is indeed a systematic reflection condition, then the space group can be assigned as $P4_2/n$ (No. 86).

The 71.3 ppm ^{27}Al resonance attributed to four-coordinate aluminum is observed for all of the samples having $r > 4.5$. Although the second-order quadrupolar parameters have not been evaluated for this resonance, the isotropic chemical shift would

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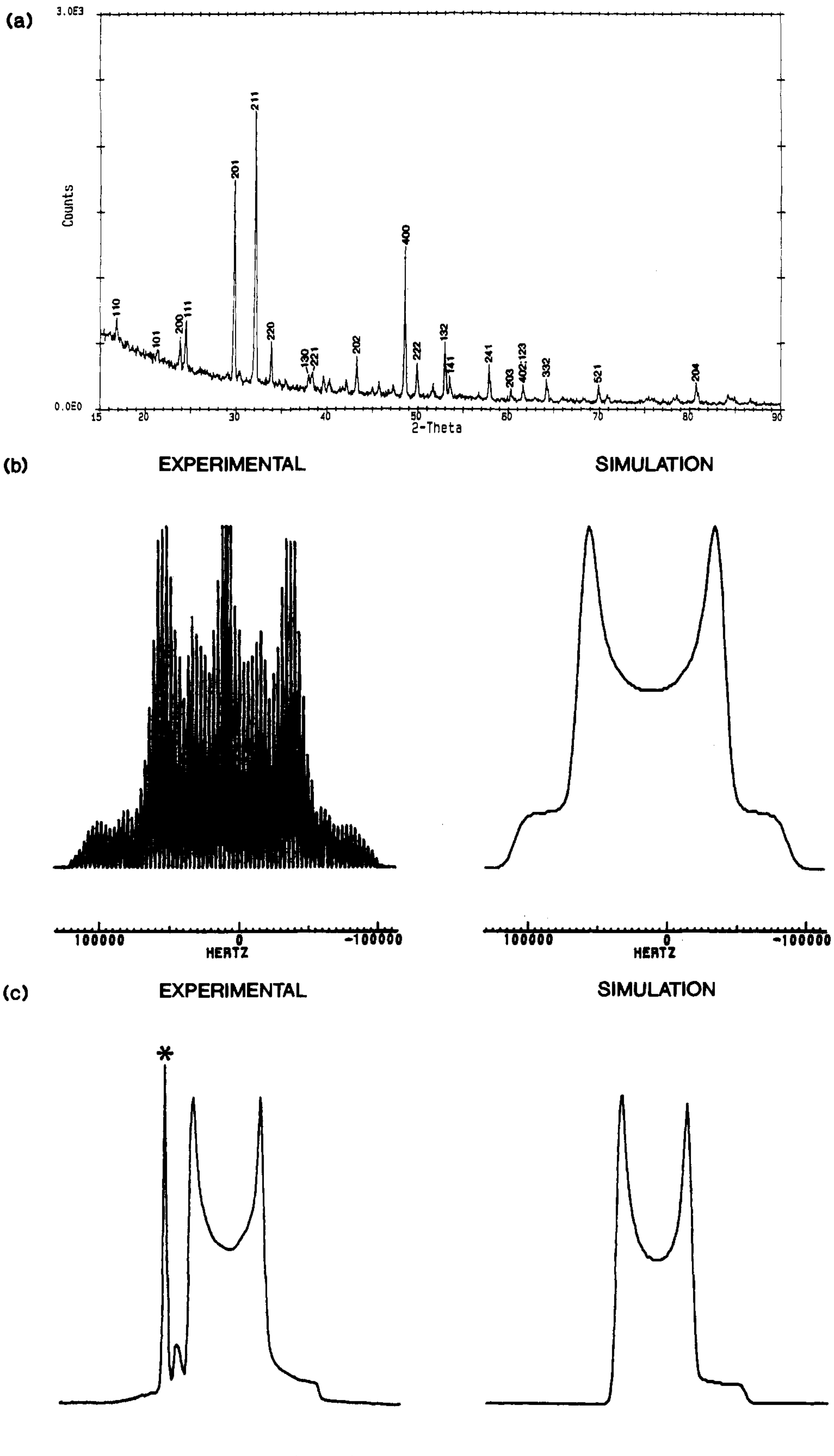

Figure 2. (a) Powder XRD pattern of Na[Al(OH)$_4$], where the marked *hkl* indexes can be indexed to a tetragonal unit cell, $a = 7.503$ and $c = 5.036$ Å (see also Table 2). The strongly curving base line at low angles is due to an instrumental artifact. (b) ^{27}Al observed and simulated satellite ($\pm^1/_2$, $\pm^3/_2$) transitions spectra for the aluminum site in Na[Al(OH)$_4$] as obtained with an MAS frequency of 3 kHz. The line shape analysis of this first-order perturbed site yields the following quadrupolar parameters: $C_Q = 0.62 \pm 0.05$ MHz, $\eta = 0.00 \pm 0.03$, and $\delta_{iso} = 86.6$ ppm. (c) ^{23}Na observed and simulated second-order broadened central ($+^1/_2$, $-^1/_2$) transition spectra for the sodium site in Na[Al(OH)$_4$] as obtained with an MAS frequency of 15 kHz. The line shape analysis of this second-order perturbed site yields the following quadrupolar parameters: $C_Q = 3.10 \pm 0.05$ MHz, $\eta = 0.00 \pm 0.03$, and $\delta_{iso} = 5.9$ ppm.

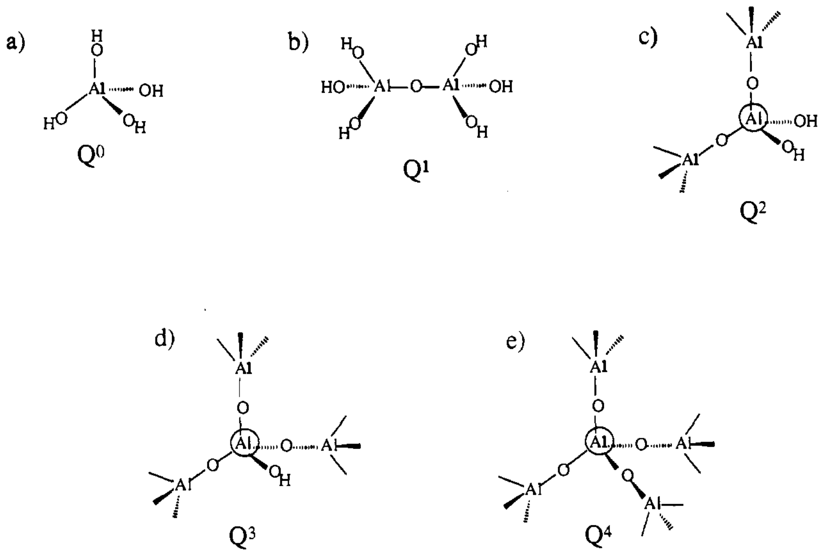

Figure 3. Examples of Q^n Al species (as circled) discussed in the text: (a) Q^0 $[Al(OH)_4^-]$, (b) Q^1 $[Al_2O(OH)_6^{2-}]$, (c) Q^2 $[\mathit{Al}(OH)_2(OAl)_2^{x-}]$, (d) Q^3 $[\mathit{Al}(OH)(OAl)_3^{y-}]$, and (e) Q^4 $[AlO_2^-]$. The Q^0 $[Al(OH)_4^-]$ species forms the crystalline $Na[Al(OH)_4]$ salt responsible for the sharp 86.6 ppm signal. The broader 71.3 ppm resonance is expected to be dominated by polymeric Q^2-type species, although contributions form Q^1, Q^3, and Q^4 species are also feasible in this ^{27}Al chemical shift region.

Table 2. Observed and Calculated Powder X-ray Diffraction Pattern for $Na[Al(OH)_4]$ (Cu Kα)

hkl	$(2\theta)_{obs}$	d_{hkl}	I_{rel}	$(2\theta)_{calc}$	$(d_{hkl})_{calc}$
110	16.72	5.296	8	16.67	5.304
101	21.23	4.179	4	21.21	4.182
200	23.68	3.743	13	23.67	3.751
111	24.36	3.636	19	24.33	3.653
201	29.64	3.008	68	29.65	3.009
211	32.00	2.790	100	32.01	2.792
220	33.73	2.648	16	33.75	2.652
002	35.56	2.528	2	35.61	2.519
130	37.84	2.371	5	37.88	2.372
221	38.28	2.344	7	38.31	2.347
112	39.61	2.275	6	39.58	2.275
301	40.20	2.237	4	40.22	2.240
311	42.10	2.145	4	42.06	2.146
202	43.27	2.090	14	43.22	2.091
122	44.97	2.016	3	44.97	2.014
231	47.24	1.924	3	47.22	1.923
400	48.48	1.877	56	48.49	1.875
222	49.92	1.827	13	49.89	1.826
302	51.46	1.769	5	51.46	1.775
132	52.94	1.731	21	52.99	1.727
141	53.47	1.714	8	53.50	1.711
241	57.86	1.594	13	57.90	1.592
203	60.30	1.536	4	60.37	1.532
402, 123	61.74	1.502	6	61.64, 61.75	1.504, 1.502
332	64.32	1.448	8	64.33	1.447
521	70.04	1.343	8	70.03	1.343
440	71.09	1.326	2	71.03	1.326
204	80.47	1.192	9	80.42	1.194

be downfield of 71.3 ppm and is thus due to condensed phases containing only four-coordinate aluminum.[38] As no line narrowing is observed upon the application of high-power ^1H decoupling, this resonance must be associated with an oxo-bridged Q^n ($1 \leq n \leq 4$) aluminum species (*i.e.*, $[\mathit{Al}(OAl)_n(OH)_{4-n}]$), examples of such being the polymeric Q^2 $[\mathit{Al}(OH)_2(OAl)_2^{x-}]$[63] and the condensed network Q^4 $[AlO_2^-]$ anions (see Figure 3). This Q^2 species has been previously characterized by ^{27}Al MAS NMR study of homogeneous commercial sodium aluminates,[27] in which the assignment was based on the observation of a distinct second-order broadened quadrupolar line shape and associated aluminum site symmetry arguments. The same second-order characteristics are not observed from this inhomogeneous, rapidly quenched system, for which only initial phases are being studied. This type of sample exhibits large degrees of structural disorder and hence a distribution of electric field gradients (and possibly some chemical shift dispersion) giving rise to the broad, featureless line shape at 71.3 ppm. It has been shown that other polyoxoanions such as the dimeric Q^1 $[Al_2O(OH)_6^{2-}]$[27] and condensed Q^4 $[AlO_2^-]$[28,38,45] species exhibit ^{27}Al chemical shifts similar to this signal; however, these are not expected to contribute significantly to these initial phases. The synthesis of the Q^1 $K_2[Al_2O(OH)_6]$ salt has only been shown to proceed under very different conditions, involving the concomitant dissolution and oxidation of aluminum metal in potassium hydroxide solution,[25,27] and is therefore not expected to coexist in this system. Similarly, the more condensed Q^3 and Q^4 species are not likely to be products of initial rapid quenching, although it will be shown (*vide infra*) that thermal transformations of such initial products do result in these types of condensed species. Thus, within this system of rapidly quenched, acid hydrolyzed sodium aluminates, this 71.3 ppm resonance is assigned predominantly to a polymeric Q^2 $[\mathit{Al}(OH)_2(OAl)_2^{x-}]$ species. The relative intensities of the 86.6 and 71.3 ppm resonances vary markedly with OH/Al ratio, with the species represented by the 71.3 ppm resonance dominating the nonhydrolyzed starting sample ($r = 5.5$) and then decreasing markedly with the initial acid hydrolysis and disappearing by an r value of 4.5, to leave only the sharp 86.6 ppm resonance. This suggests that the addition of acid serves to break up the complex polymer(s) present at $r = 5.5$, liberating increasing concentrations of $[Al(OH)_4^-]$ ions into solution, although a simple dilution effect could also be a factor contributing to this.

The resonance at 8.1 ppm (also uncorrected for second-order effects) is assigned to six-coordinate aluminum. It initially appears at an OH/Al value of 4.4 and strongly increases in intensity with further acid hydrolysis. Samples having r values in the $4.4 \geq \mathrm{OH/Al} \geq 4.1$ range are completely water soluble, verifying that the resonance attributed to six-coordinate aluminum observed in this OH/Al range cannot be due to an insoluble aluminum hydroxide or oxyhydroxide phase such as bayerite or pseudoboehmite. This resonance displays a marked asymmetry in its MAS line shape, where the broadening appears to be more extensive on the shielded (upfield) side. For line shapes that are dominated by a second-order quadrupolar interaction, this observation has been well established through ^{27}Al MAS studies of aluminas,[64] glasses,[65-70] and clays[71] to arise from substantial structural disorder, producing a large distribution of electric field

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(63) The italic aluminum in this formula denotes Q^2 coordination, whereas the other outer-shell aluminum atoms can vary in their degrees of oxo bridging (*i.e.*, for Q^n, $1 \leq n \leq 4$), meaning that the net charge ($x-$) on this class of polyoxoanion will vary.

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gradients and varying degrees of chemical shift dispersion. As these solutions are lower in aluminum and hydroxide ion concentrations than the higher *r* value samples, it could be argued that this 8.1 ppm signal is proof of the formation of the proposed[20,21] $[Al(OH)_4(OH_2)_2^-]$ species. Dilution studies, however, found no evidence to support this view (*vide infra*), and therefore this signal must originate from a polyoxoanion or polymer containing six-coordinate aluminum. It should be noted that if dried samples having high *r* values (*e.g.*, $r > 4.4$) are allowed to sit in air at ambient temperatures, rapid hydrolysis occurs, resulting in an octahedral signal emanating from the formation of water-insoluble gibbsite. This hydrolysis may have been the source of the six-coordinate resonance reported by Müller *et al.*[28] for their sodium aluminate precipitated from highly alkaline solutions. The samples having *r* values lower than 4.1 are not completely water soluble, and therefore the octahedral signal seen in these cases is at least partially, and in some cases predominantly, due to precipitated aluminum hydroxide and/or oxyhydroxide.

When the *r* value decreases to 4.4 and below, a second broad resonance that can be assigned to four-coordinate aluminum (72.5–58.5 ppm) emerges, and this becomes the dominant signal for *r* values of 4.3 and 4.2. Although the chemical shift of this signal for the bulk samples with *r* values extending down to 3.7 (72.5–69.0 ppm) is very similar to the 71.3 ppm signal discussed for the $5.5 \geq OH/Al \geq 4.6$ range, examination of the effects of sample dehydration by heating (*vide infra*) on the ^{27}Al chemical shifts proves that these resonances must be due to different species. In addition, with increasing acid hydrolysis, this signal due to four-coordinate aluminum gradually shifts upfield and broadens, reaching a chemical shift of 58.5 ppm by an OH/Al ratio of 2.8, and the resonance due to six-coordinate aluminum simultaneously shifts from 8.1 to 4.6 ppm over the same OH/Al range. These shifts are no longer representative of condensed phases containing only four-coordinate species but rather are strongly indicative of the four-coordinate species having six-coordinate next-nearest neighbors.[38,42,72] The likely cause of formation of such complex species is that the addition of acid would create a microenvironment of low pH containing six-coordinate aluminum in cations such as $[Al(H_2O)_{6-n}(OH)_n{}^{(3-n)+}]$. The gels formed when these ions are swept out upon stirring and come into contact with the tetrahedral anions (*i.e.*, Q^0 $[Al(OH)_4^-]$, Q^2 $[\mathit{Al}(OH)_2(OAl)_2{}^{x-}]$, and possibly Q^4 $[AlO_2^-]$ and their intermediates) would likely be similar in some respects to those seen in the reverse situation, *i.e.*, the base hydrolysis of acidic solutions. In this reverse case at OH/Al ratios of *ca.* 1.0–2.5, the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}]$, or Al_{13}, spinel subunit[10,11] ion forms, and at ratios of 2.5–3.0, a gel forms that has been shown to have a pseudo-spinel structure.[10] All known alumina phases composed of both tetrahedrally and octahedrally coordinated aluminum exhibit a spinel-type structure (*e.g.*, the γ-, η-, and θ-Al_2O_3 transitional alumina phases that contain four- and six-coordinate aluminum all have defect spinel structures, as do the sodium-containing β-aluminas and the Al_{13} ion).[2,10,11] These characteristics suggest that any polyoxoanions comprised of both four- and six-coordinate aluminum that form in alkaline solutions would also have some type of defect spinel structure. The uncorrected chemical shift of 63.1 ppm observed for the water-insoluble fraction of the $r = 3.9$ sample (Figure 1) is very similar to chemical shifts reported for the γ-, η-, and θ-Al_2O_3 transitional aluminas.[10,28,41,64,73–75] An infrared investigation[41] of this water-insoluble fraction reveals no evidence of pseudo-boehmite, bayerite, or gibbsite phases; instead, poorly resolved bands are observed at *ca.* 730, 625, and 540 cm^{-1}, which resemble those observed of partially aged pseudo-spinel gels.[10,11] Previous infrared studies of the Al_{13} spinel subunit have shown the characteristic pseudo-spinel bands to occur at 729, 627, and 546 cm^{-1}, and these were assigned to $(Al–O)_{T_d}$, $(Al–OH)_{O_h}$, and $(Al–O)_{O_h}$ stretches, respectively.[10,75] These results combine to suggest that the first water-insoluble amorphous phase formed upon acid hydrolysis of the alkaline solutions is also a pseudo-spinel phase. The intensity differences between the four- and six-coordinate ^{27}Al MAS NMR resonances for the $r = 3.9$ sample and those previously reported for the spinel transitional aluminas may be due to X-ray amorphous aluminum hydroxide or oxyhydroxide phases also present that contribute to the intensity of the octahedral 8.1 ppm resonance. The major differences observed between the ^{27}Al NMR spectra of the bulk 3.9 sample and its water-insoluble portion are manifested by a much stronger relative intensity of the four-coordinate signal in the bulk sample and also their chemical shift differences (71.3 *vs* 63.1 ppm). This indicates that the majority of the tetrahedral aluminum in the bulk sample is still in the form of a water-soluble polymer. Although its ^{27}Al chemical shift (71.3 ppm) is in the range appropriate for condensed tetrahedra, we must note that this signal first occurred at an *r* value of 4.4, as did the 8.1 ppm signal assigned to six-coordinate aluminum. Hence, the water-soluble phase represented by the 71.3 ppm resonance must be comprised of polyoxoanions having predominantly four-coordinate aluminum linked through bridging oxygens to other four-coordinate aluminum sites, but with some six-coordinate aluminum also present. The relative amount of six-coordinate aluminum in these polyoxoanions would increase with decreasing *r* values, as would the degree of polymerization, and this view is supported by the gradual upfield shift of this tetrahedral signal with increasing degrees of acid hydrolysis.

When the acid hydrolysis to *r* values of 3.7 and below, an additional resonance becomes readily apparent at 32.7–33.9 ppm, and this is assigned to five-coordinate aluminum.[49,64,76–79] Close inspection of the higher *r* value samples found that this five-coordinate signal was present (although very weak) at OH/Al ratios as high as 4.3 but was not easily resolved. Neither this five-coordinate signal nor the four-coordinate signal seen for *r* values of 3.5 or below changes appreciably between the bulk and the water-insoluble phases. The possible cause of formation of a five-coordinate aluminum species will be discussed later with regard to the mechanistics of gel aging. These spectra for the low *r* value samples are similar in terms of chemical shifts to those that have been reported for thermally treated γ- and η-Al_2O_3 samples.[64,80–82]

2. Dilution Series. Upon the initial acid hydrolysis of the starting $r = 5.5$ sample to $r = 5.3$, a very marked change is seen in the intensities of the 86.6 $Na[Al(OH)_4]$ and 71.3 ppm signals, the relative amount of the species responsible for the latter (*i.e.*,

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(82) Hill, R. J.; Craig, J. R.; Gibbs, G. V. *Phys. Chem. Minerals* **1979**, *4*, 317.

[$\mathit{Al}(OH)_2(OAl)_2^{x-}$]) being observed to dramatically decrease. If the proposed dehydration/oligomerization series[20–22] involving a decrease in concentration of the complex species (*i.e.*, [AlO_2^-]) and an increase in the amount of [$Al(OH)_4^-$] upon dilution is correct, it could imply that the initial changes seen at $r \geq 4.5$ are simply due to a dilution effect rather than acid hydrolysis. To investigate this theory, and also to search for evidence of the proposed [$Al(OH)_4(OH_2)_2^-$] ions, a dilution series was examined for an $r = 4.8$ sample, with the aluminum concentration varying from 1.24 to 0.19 M. The results for all of the samples were comparable to the spectrum shown in Figure 1 for the $r = 4.8$ sample, and although minor differences were seen in relative signal intensities between the different samples, no general trend could be found, and no evidence of any type of six-coordinate species was observed in this concentration range. This result supports the view that the changes observed in the r value series examined were due to pH changes rather than dilution effects.

3. Thermal Transformations of the Synthesized Sodium Aluminates. Low-temperature (80 °C) thermal transformation sequences were carried out on the samples synthesized in section 1 to examine the products formed and to compare the identities of the species responsible for the 71.3 ($r > 4.5$) and the 72.5–69.0 ppm ($r \leq 4.4$) resonances. A previous study of thermal transformations of a commercial sodium aluminate (Fisher purified $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$) was reported by Fitzgerald *et al.*,[27] and in order to compare their results to those seen for our samples, a similar thermal dehydration study of Fisher sodium aluminate was performed using powder XRD and ^{27}Al MAS NMR to characterize the products.

The powder X-ray diffraction pattern of Fisher Chemical purified sodium aluminate, $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ (Figure 4a), was not found to match that of any $NaAlO_2$ pattern published in the JCPDS powder diffraction file[37] and may involve more than one phase. The previous ^{27}Al and ^{23}Na MAS NMR study by Fitzgerald *et al.*[27] of the thermal transformations of this commercial sodium aluminate did not involve XRD analyses, and solely on the basis of their ^{27}Al and ^{23}Na isotropic chemical shifts, they discounted β-$NaAlO_2$ as the final product even after extensive drying at 598 °C. Their conclusions stated that the ^{27}Al δ_{iso} value of 81 ppm for this "unknown" product was not in agreement with previously reported δ_{iso} values of ~63 ppm,[72] which they inadvertently cited from an unrelated system. This was in error, as their δ_{iso} value for this product was in good agreement with an earlier δ_{iso} value of 80.1 ppm for β-$NaAlO_2$.[38] Thus, it was not surprising that our powder XRD study of the dehydration of Fisher $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ conflicted with these findings and revealed the gradual formation of β-$NaAlO_2$,[34] with no intermediate crystalline phases being formed. As depicted in Figures 4a–d, this transformation was observed to be complete by XRD after only 24 h of drying at 154 °C and is shown to be initiated by temperatures as low as 100 °C. The ^{27}Al MAS NMR spectrum of the resultant β-$NaAlO_2$ obtained from the Fisher $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ starting material is shown in Figure 5c. The first-order broadened δ_{iso} value of 79.5 ppm from this β-$NaAlO_2$ phase agrees well with both above-mentioned studies of this material. Hence, the concluding speculations of Fitzgerald *et al.*[27] that the final phase produced through the thermal treatments of Fisher $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ was comprised of isolated AlO_4^{5-} ions linked in an ionic framework by charge-balancing Na^+ ions are not supported by our study.

When the sodium aluminates and aluminum hydroxides synthesized in section 1 (r values of 3.9 and above) were heated at 80 °C for periods of 1 week and 3 weeks, some marked phase transitions occurred, as are readily observed from the ^{27}Al MAS NMR spectra shown in Figures 6 and 7 (see also Table 3). The predominant changes pertained to the transformations of the 71.3 ppm resonance for samples having OH/Al > 4.5 and the 72.5–69.0 ppm resonance for the 4.4 ≥ OH/Al ≥ 3.9 range. In the first case, heating of the higher r value samples resulted in a gradual transferal of intensity from the broad 71.3 ppm signal to a much narrower first-order broadened resonance with a δ_{iso} value of 79.5 ppm, which has been assigned to β-$NaAlO_2$ from the above study (see Figure 6). The powder diffraction patterns of these resultant mixed crystalline phases, such as that shown in Figure 5b, confirmed that β-$NaAlO_2$ (identified by the powder XRD pattern shown in Figure 5a) had indeed formed. These results are in agreement with the proposal made for samples having $r \geq 4.5$, that the observed 71.3 ppm signal emanates from

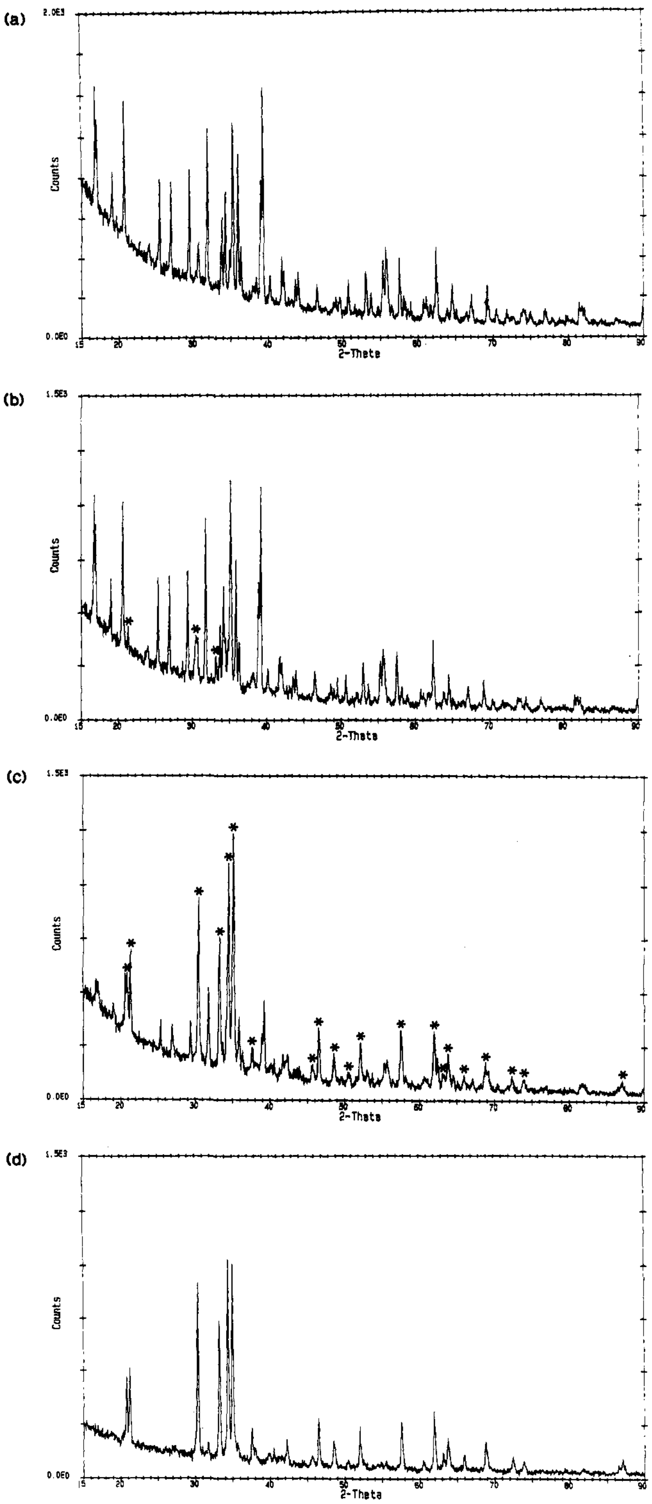


Figure 4. Powder XRD patterns of the sequential thermal transformation of Fisher purified $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ into β-$NaAlO_2$ after the sample was heated at the indicated temperatures for 24 h: (a) T = 25 °C (*i.e.*, untreated Fisher sodium aluminate); (b) T = 100 °C; (c) T = 130 °C; (d) T = 154 °C. The asterisks on the 100 and 130 °C XRD patterns indicate the emerging β-$NaAlO_2$ peaks that can be resolved from those of the starting material. The 154 °C pattern represents a complete thermal transformation to β-$NaAlO_2$.

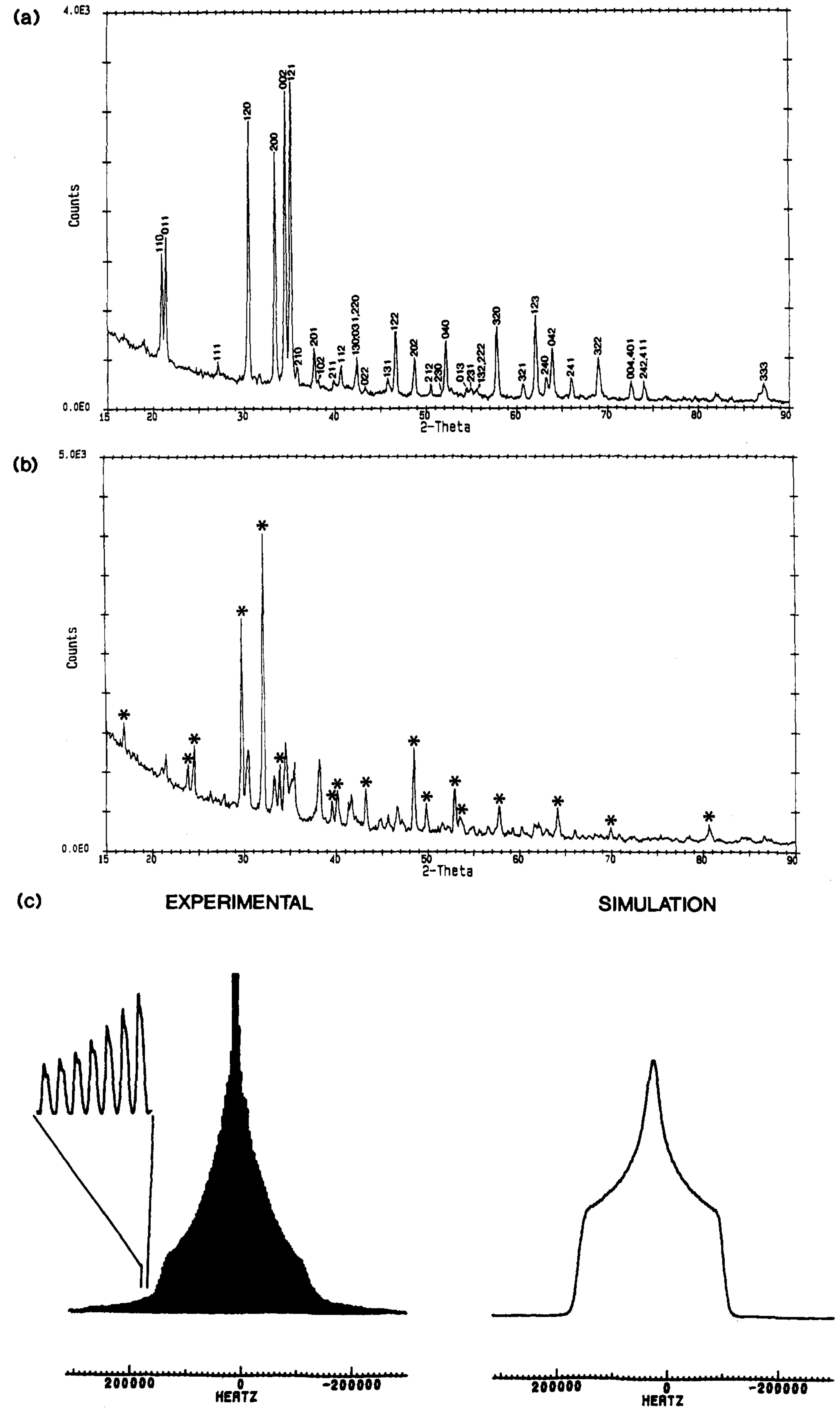


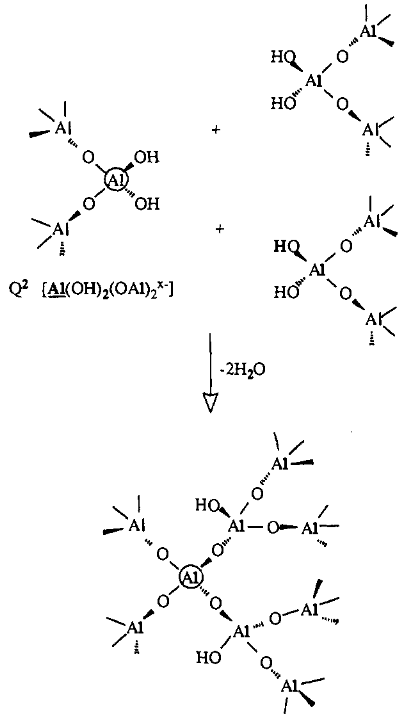
Figure 5. (a) Powder XRD pattern of synthesized β-NaAlO$_2$, with the *hkl* indices marked. (b) Powder XRD pattern of a sodium aluminate sample ($r = 5.1$) after the sample was dried for 3 weeks at 80 °C, showing a mixture of β-NaAlO$_2$ and Na[Al(OH)$_4$] phases plus a small amount of an unidentified phase. The asterisks denote those peaks identifying the Na[Al(OH)$_4$] phase. (c) ^{27}Al observed and simulated satellite ($\pm^1/_2$, $\pm^3/_2$) transitions spectra for the aluminum site in β-NaAlO$_2$ as obtained with an MAS frequency of 3 kHz. The line shape analysis of this first-order perturbed site yields the following quadrupolar parameters: $C_Q = 0.89 \pm 0.05$ MHz, $\eta = 0.91 \pm 0.03$, and $\delta_{iso} = 79.5$ ppm. Some discrepancies are observed in this comparison, as probe band width effects and resolved components of the satellite ($\pm^3/_2$, $\pm^5/_2$) transitions (see inset) are contributing to the experimental spectrum.

Table 3. Observed ^{27}Al MAS NMR Resonances of the Sodium Aluminates and Aluminum Hydroxides after the Samples were Heated for 1 and 3 Weeks at 80 °C

OH/Al	$\delta(^{27}\mathrm{Al})$	OH/Al	$\delta(^{27}\mathrm{Al})$
5.5	86.6,^{a} 79.5,^{a} 73.7	4.4	86.6,^{a} 8.1
5.3	86.6,^{a} 79.5,^{a} 73.7	4.3	86.6,^{a} 67.8, 38.6, 8.1
5.1	86.6,^{a} 79.5^a	4.2	86.6,^{a} 67.8, 36.2, 8.1
4.8	86.6,^{a} 79.5^a	4.1	86.6,^{a} 71.3, 8.1
4.6	86.6,^{a} 76.4	4.0	86.6,^{a} 71.3, 8.1
4.5	86.6^a	3.9	67.8, 8.1

[a] Isotropic chemical shift values; all other chemical shifts remain uncorrected for second-order quadrupolar contributions.

predominantly Q^2 [Al(OH)$_2$(OAl)$_2^{x-}$] four-coordinate aluminum species. Upon dehydration, the polymers appear to progressively condense, ultimately resulting in the ordered β-NaAlO$_2$ species in which all aluminum has Q^4 coordination, and this can be readily envisaged for condensation of the above Q^2-type species:



This thermally induced ordering alleviates the chemical shift dispersion and distribution of electric field gradients that dominate the 71.3 ppm resonance to produce the narrow first-order broadened signal with δ_{iso} = 79.5 ppm. Although the line width at half height (~320 Hz) of this 79.5 ppm signal is comparable to that reported for Na[Al(OH)$_4$] (86.6 ppm, ~360 Hz, undecoupled), the line width of this β-NaAlO$_2$ resonance is insensitive to the application of high-power ^{1}H decoupling with no further line narrowing being achieved after the implementation of fast MAS. This observation is consistent with a condensed framework of tetrahedra linked by oxo bridges, where any intrinsic ^{1}H dipolar broadening invoked by the presence of terminal hydroxyl groups (*i.e.*, at crystal edges and defects) would be a negligible portion of the total signal and would be potentially eliminated by the fast MAS rate of 15 kHz. Analysis of the spinning side-band manifold of the ($\pm^1/_2$, $\pm^3/_2$) satellite transitions modulated by an MAS frequency of 3 kHz (see Figure 5c) yields the quadrupolar parameters C_Q = 0.89 ± 0.05 MHz and η = 0.91 ± 0.03. Some deviation from the simulated line shape is observed as probe band width effects and resolved contributions from the satellite ($\pm^3/_2$, $\pm^5/_2$) transitions (see inset on Figure 5c) reduce the accuracy of the simulation in the outer chemical shift regions. This value of C_Q is somewhat smaller than the previously reported values of ~1.9 MHz[27] and 1.4 MHz (η = 0.5),[38] which may reflect a variation in the true Na crystalline order of the samples analyzed; however, the methods of C_Q measurement employed in these earlier ^{27}Al MAS NMR studies of β-NaAlO$_2$ are not clear.

Interestingly, the ^{27}Al MAS NMR spectra revealed no change after heating of the Na[Al(OH)$_4$] (r = 4.5 sample), indicating this phase to be extremely stable to dehydration under these temperature conditions. When the samples within the 4.4 ≥ OH/Al ≥ 4.0 range were heated under identical conditions, however, the broad tetrahedral signal (72.5–69.0 ppm) decreased in intensity, with a concomitant increase in the intensity of the narrow 86.6 ppm resonance, implying an immediate transformation to Na[Al(OH)$_4$] (see Figure 7). This observation was also confirmed by powder XRD. In addition, for the r = 4.2 and 4.3 samples, a signal at *ca.* 33 ppm due to five-coordinate aluminum became readily apparent. These thermal transformation results thus prove the earlier hypothesis that the tetrahedral signals of similar chemical shift for $r > 4.5$ and $r \leq 4.4$ *must* be due to different species. The identity of the species responsible for the broad tetrahedral signal for $r \leq 4.4$ is not easily ascertained. If the resonance due to octahedral aluminum were partially due to an [Al(OH)$_4$(OH$_2$)$_2^-$] species, then the sequential removal of water could readily result in a five-coordinate species being formed, followed by Na[Al(OH)$_4$]:

$$\underset{\mathrm{CN}=6}{[\mathrm{Al(OH)_4(OH_2)_2^-}]} \xrightarrow{-\mathrm{H_2O}} \underset{\mathrm{CN}=5}{[\mathrm{Al(OH)_4(OH_2)^-}]} \xrightarrow{-\mathrm{H_2O}} \underset{\mathrm{CN}=4}{[\mathrm{Al(OH)_4^-}]}$$

Although this is the simplest explanation, it could not have been the predominant route of formation of the Na[Al(OH)$_4$] phase, as the broad tetrahedral signal is observed to preferentially decrease with respect to its octahedral counterpart. In addition, the dilution experiments previously discussed for an r = 4.8 series revealed no evidence of the monomeric [Al(OH)$_4$(OH$_2$)$_2^-$] species existing, and it would be even less likely to exist at this lower r value range in which polymers rather than monomers predominate. The degree to which the Na[Al(OH)$_4$] forms upon sample dehydration appears to follow the approximate r value order 4.0, 4.1 > 4.2, 4.3, indicating that there is a significant change in what the tetrahedral resonance represents between the samples having r values of 4.1 and 4.2. Similarly, the MAS NMR spectra of the bulk r = 3.9 and 4.0 samples differed only marginally in the tetrahedral/octahedral signal ratio. However, dehydration had no apparent effect on the 3.9 sample, whereas the 4.0 sample exhibited a marked transformation to the Na[Al(OH)$_4$] phase. The signal assigned to a defect spinel-type phase in the r = 3.9 sample was also unaffected by heating at 80 °C. These results indicate that a gradual structural transformation occurs between r = 4.5 and 3.9 and that a range of different species must contribute to the broad tetrahedral resonance observed. As previously discussed, this is postulated to represent an increase in the degree of polymerization as well as the incorporation of increasing amounts of six-coordinate aluminum into the water-soluble polymer. This trend accentuates the difficulty involved in assigning the 72.5–69.0 ppm signal to any particular species, and the reason that such polymeric species would transform to produce Na[Al(OH)$_4$] upon dehydration is not obvious.

4. Postulated Mechanistics of Phase Transformations. These studies of the solid phases formed by acid hydrolyzing and freeze-drying sodium aluminate liquors have suggested that in the highly alkaline solutions ($r > 4.5$) the predominant species present are Q^0 [Al(OH)$_4^-$] ions as well as polyoxoanions consisting of four-coordinate aluminum, of which the predominant amount is in Q^2 coordination, as well as minor amounts being in other Q^n coordinations (*i.e.*, the Q^4 end-member [AlO$_2^-$] framework anion). Results seen for samples acid hydrolyzed to OH/Al values of below 4.5 support the view that complex species containing four-, six-, and sometimes five-coordinate aluminum are formed in a variety of different environments that vary with the OH/Al ratio. Once the hydrolysis ratio has decreased to 3.9, the chemical shift of the tetrahedral resonance of the water-insoluble portion of the sample is appropriate for assignment to an aluminum spinel phase.

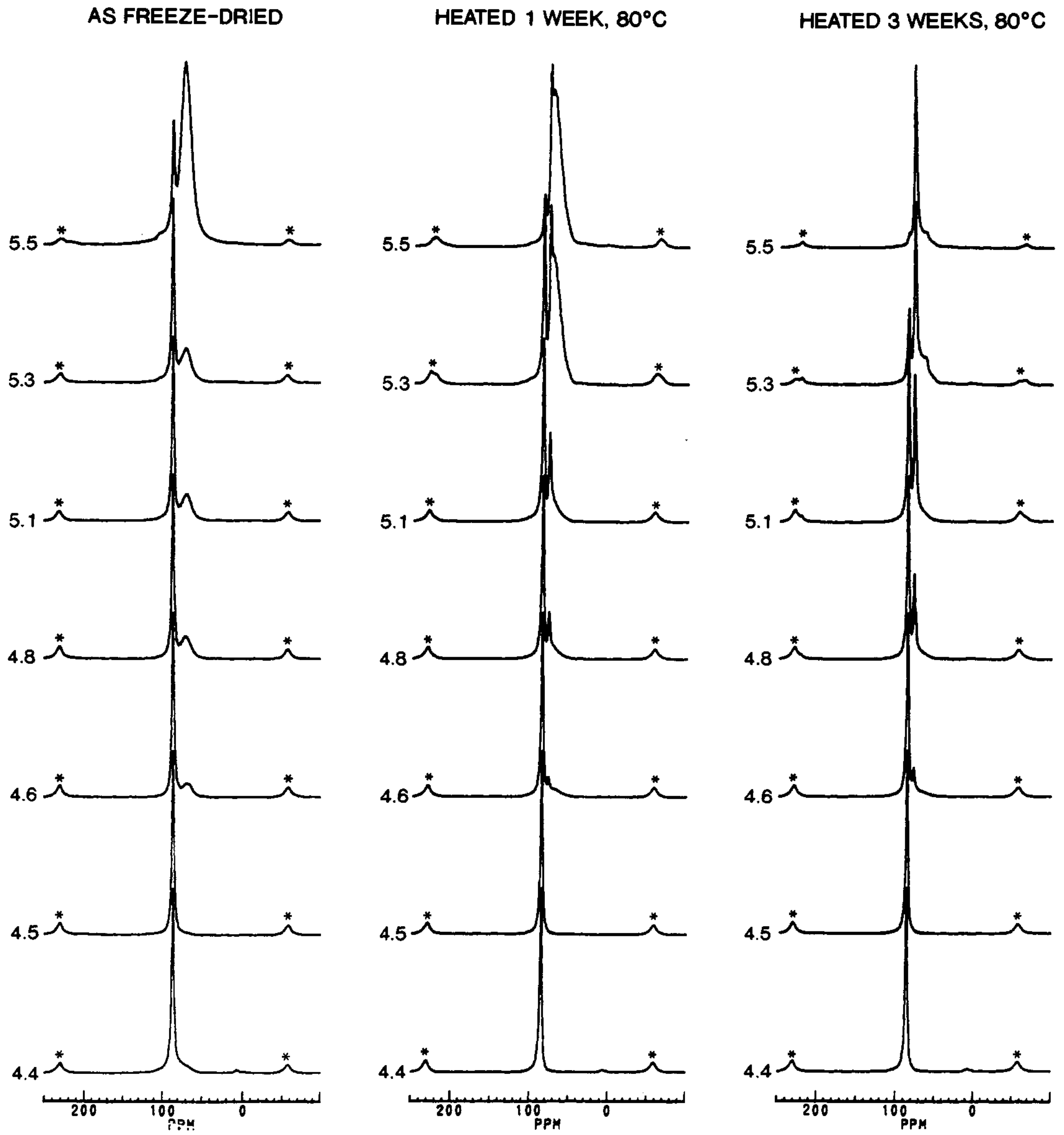


Figure 6. ^{27}Al MAS NMR spectra of the sodium aluminates and aluminum hydroxides for the $5.5 \geq \mathrm{OH/Al} \geq 4.4$ range, as collected after freezing and freeze-drying and further drying through heating for periods of 1 week and 3 weeks at 80 °C. The OH/Al ratios are as indicated, and the spinning side bands within each spectrum are denoted by asterisks.

These points suggest that any polymers that form in alkaline solutions containing both four- and six-coordinate aluminum may exhibit a defect spinel-type structure. Aluminum spinels have a very strong tendency to form "normal" rather than "inverse" structures, meaning that there is a preference for having a larger divalent cation rather than aluminum in the tetrahedral position,[82] and defect transitional alumina spinels have the vacancies situated in the tetrahedral rather than octahedral sites. These polymers can thus be represented by the formula $\gamma\text{-}\mathrm{Al_2O_3}\cdot x\mathrm{H_2O}$,[10] although this is undoubtedly an oversimplification, as there would still be hydroxyl groups present, and the relative amounts of these would vary with the OH/Al ratio and degree of aging. Due to the disproportionately higher number of tetrahedrally than octahedrally coordinated aluminum atoms present in alkaline solutions, the lattice aluminum vacancies would be forced to be concentrated in the six-rather than the four-coordinate sites. As this is the reverse of the trend seen for aluminum spinels, it would likely result in the formation of an extremely unstable phase.

Hence, these results have shown that the formation of gibbsite in dilute aqueous solution follows the same crystallization pathway regardless of whether the neutral pH range is reached from initial acidic or alkaline pH regimes:

pseudo-spinel → pseudo-boehmite → bayerite → gibbsite

The major difference seen between the two cases, however, is the much faster kinetics of transformation of the pseudo-spinel to the pseudo-boehmite phase in the case of the acid hydrolysis of the alkaline solutions. The aging of the pseudo-spinel phase formed in this way would likely follow an analogous path to that occurring for the gels formed through base hydrolysis.[10] This has been proposed to occur through cleavage of the Al–O–Al (and Al–O(H)–Al) bonds between adjacent sheets parallel to the pseudo-spinel 111 planes:[10,11]

$$\begin{array}{c} -(\mathrm{Al{-}O{-}Al})- \\ -(\mathrm{Al{-}O{-}Al})- \\ \gamma\text{-}\mathrm{Al_2O_3}\cdot x\mathrm{H_2O} \end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{c} -(\mathrm{Al{-}O{-}Al})- \\ -(\mathrm{Al{-}OH} + \mathrm{HO{-}Al})- \\ \gamma\text{-}\mathrm{AlO(OH)}\cdot y\mathrm{H_2O} \end{array} \xrightarrow{\mathrm{H_2O}}$$

$$\begin{array}{c} -(\mathrm{Al{-}OH} + \mathrm{HO{-}Al})- \\ -(\mathrm{Al{-}OH} + \mathrm{HO{-}Al})- \\ \mathrm{Al(OH)_3}\ \text{sheets} \end{array}$$

These cleavages would initially yield an oxyhydroxide intermediate containing some five-coordinate aluminum, and this is a likely origin of the ^{27}Al MAS NMR resonances that have been assigned to five-coordinate aluminum in the low *r* value samples. Pseudo-boehmite would result when cleavage had progressed further, and eventually a sheet hydroxide structure (bayerite) would result. Under the appropriate conditions, this could readily rearrange to form gibbsite. As alluded to above, the key to the different kinetics of phase transformations in both of these scenarios lies in the

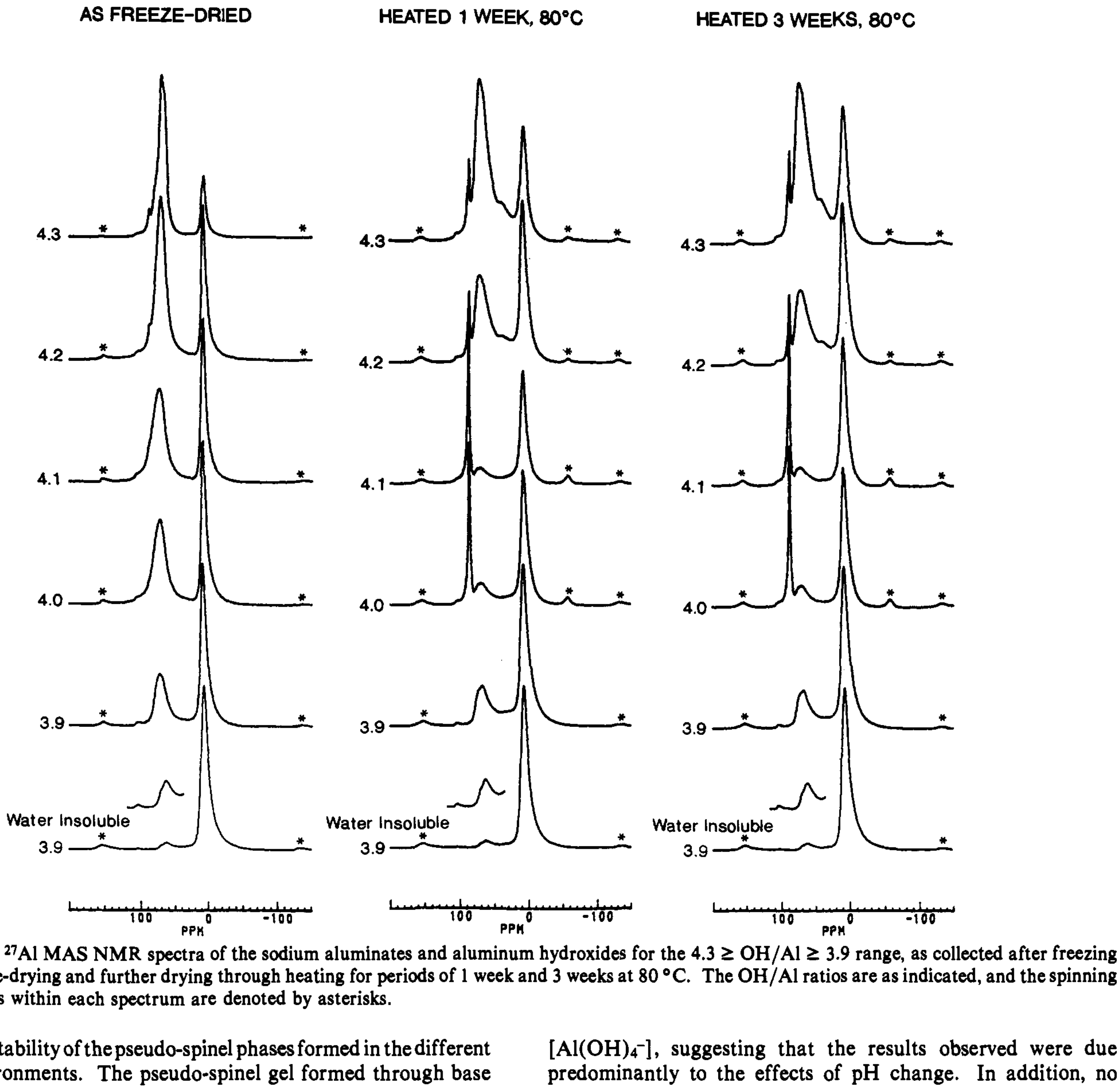


Figure 7. ^{27}Al MAS NMR spectra of the sodium aluminates and aluminum hydroxides for the $4.3 \geq OH/Al \geq 3.9$ range, as collected after freezing and freeze-drying and further drying through heating for periods of 1 week and 3 weeks at 80 °C. The OH/Al ratios are as indicated, and the spinning side bands within each spectrum are denoted by asterisks.

relative stability of the pseudo-spinel phases formed in the different pH environments. The pseudo-spinel gel formed through base hydrolysis (OH/Al = 3.0) results from the coalescence of Al_{13} tridecamers, and MAS NMR results have shown the gel to have the vacancies situated in the four- rather than the six-coordinate sites,[10] which is the preferred case for Al spinels. In the case of its counterpart formed through acid hydrolysis of an aluminate solution, however, the reverse scenario would have to be true, the vacancies being forced into the octahedral positions. Such an unstable structure would likely undergo a prompt transformation to a more stable structure, which would account for the more rapid kinetics of formation of pseudo-boehmite in the acid hydrolysis of alkaline solutions to $r = 4$ than in the base hydrolysis of acidic aluminum solutions to $r = 3$.[41]

Summary

These NMR spectroscopic and X-ray diffraction analyses of the solid phases formed by acid hydrolyzing and freeze-drying sodium aluminate liquors have implied that in the highly alkaline solutions ($r > 4.5$), the predominant species present are Q^0 $[Al(OH)_4^-]$ ions as well as polyoxoanions that contain a large degree of four-coordinate Q^2 aluminum ($[Al(OH)_2(OAl)_2^{x-}]$) and possible small amounts of other Q^n ($1 \leq n \leq 4$) species (*i.e.*, $[Al(OAl)_n(OH)_{4-n}]$). The ^{27}Al MAS NMR chemical shifts at 9.40 T of the above assigned species are 86.6 (Q^0 $Na[Al(OH)_4]$) and 71.3 ppm (Q^2 $[Al(OH)_2(OAl)_2^{x-}]$). Simple dilution was not observed to cause the Q^2 anions to dissociate, thereby forming $[Al(OH)_4^-]$, suggesting that the results observed were due predominantly to the effects of pH change. In addition, no evidence was seen in these diluted, highly alkaline ($r > 4.5$) solutions for the $[Al(OH)_4(OH_2)_2^-]$ ion that has been proposed to form in very dilute solutions.[20,23]

The samples acid hydrolyzed to OH/Al values of below 4.5 revealed that species containing both four- and six-coordinate and in some cases also five-coordinate aluminum are formed, the precise aluminum environment varying with the OH/Al ratio. Upon being acid hydrolyzed to r values of 3.9 and below, a large portion of the sample is water insoluble. The chemical shift of the tetrahedral resonance in these cases is appropriate for assignment to an aluminum spinel phase. Due to the much higher number of four-coordinate than six-coordinate aluminum atoms present in such gels, they are likely to be quite unstable and to rapidly undergo a phase transformation. Such a transformation would likely parallel that seen for gels formed through base hydrolysis (to $r = 3$)[10] and would first yield an intermediate amorphous phase containing four-, five-, and six-coordinate aluminum. Pseudo-boehmite would be the next phase formed, followed by bayerite, and, under the correct counterion conditions, gibbsite would be the final product.

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