Characterization of metallurgical-grade aluminas and their precursors by ²⁷Al NMR and XRD¹

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Abstract: The structure of metallurgical- or smelter-grade aluminas (MGAs) is complex and poorly understood. Ultrahigh-field solid-state ²⁷Al NMR results on industrial as well as on laboratory-prepared aluminas are discussed in relation to XRD results. It is demonstrated that high-field NMR can effectively be used to quantify the proportion of the thermodynamically stable alpha-alumina phase in these materials. The results demonstrate that ²⁷Al NMR is a vital adjunct to XRD methods to quantify the transition alumina phases that invariably dominate the MGAs. The nature of the disorder in these materials, determined by ²⁷Al NMR, is also compared with literature data, such as XANES and EXAFS studies, on typical laboratory-prepared materials. The utility of ²⁷Al NMR studies to provide new insight into the structural complexity of metallurgical aluminas is shown.

Key words: solid-state magic-angle-spinning NMR, metallurgical-grade alumina, transition alumina, gamma-alumina, coordination number.

Résumé : La structure des alumines de qualité métallurgique (AQM) ou pour électrolyse est complexe et mal comprise. Opérant à champ élevé et à l'état solide, on a déterminé les spectres RMN du ²⁷Al d'alumines industrielles et d'autres préparées en laboratoire et on discute de ces spectres en relation avec les résultats obtenus par diffraction des rayons X (DRX). On a démontré que la RMN à champ élevé peut effectivement être utilisée pour quantifier la proportion de la phase thermodynamiquement stable d'alumine alpha qui est présente dans ces matériaux. Les résultats démontrent que la RMN du ²⁷Al est une addition absolument nécessaire aux méthodes de DRX pour quantifier les phases d'alumines de transition qui dominent invariablement les AQM. On a aussi comparé la nature du désordre dans ces matériaux, telle que déterminée par RMN du ²⁷Al, avec les résultats déjà publiés dans la littérature et obtenus par des études à l'aide de la spectroscopie d'absorption X de type XANES ou EXAFS sur des matériaux typiques préparés en laboratoire. On démontre donc l'utilité de la RMN du ²⁷Al à fournir de nouvelles indications sur la complexité structurale des alumines métallurgiques.

Mots-clés : RMN à l'état solide et à l'angle magique, alumine de qualité métallurgique, alumine de transition, alumine gamma, indice de coordination de l'aluminium.

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Introduction

Over 50 million tonnes of metallurgical-grade alumina (MGA) is produced annually, largely as a raw material for the electrolytic production of aluminum. This material is produced almost exclusively by the Bayer process to a reasonably uniform specification across the industry, in terms of specific surface area, particle size and strength, residual hydrogen or moisture as well as impurity and alpha-alumina contents. The microstructure of this material is of consider-

able interest for a number of reasons; there has, for instance, been interest in the relationship between properties and the behavior of the alumina when used in gas scrubbing systems and when fed to the reduction cell (1, 2). Furthermore, this material can also provide insights into the complex relationship within the family of the so-called "transition aluminas" produced in the calcination of gibbsite Al(OH)₃ (3).

In the Bayer process, the calcination step plays an important role in the evolution of microstructural features that can be related to the properties and the performance of the MGA

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¹This article is part of a Special Issue dedicated to Professor G. Michael Bancroft. ²Corresponding author (e-mail: j.metson@auckland.ac.nz). in the aluminum smelter. For the calcination step, production technology has progressively moved from rotary kilns to the more energy-efficient gas suspension or fluid-bedtype rapid-flash calciners, in some cases with capacity in excess of 4 000 tonnes per day (4). Due to the extended residence time, rotary kilns produce a more-homogenous and structurally ordered material. However, the literature and the understanding of the processes operating under flashcalcination conditions are lacking when compared, for example, with the typical gamma-aluminas widely used in catalysis.

The most-authoritative description of the interrelationship of the alumina phases or "forms" during calcination processes is that of Wefers and Misra (3). The speed of the modern calcination process, together with the variation of particle size, velocity, and residence time, produces a farfrom-equilibrium phase distribution both between and within individual alumina grains. MGAs can thus be viewed as granular materials comprised of aggregates of intergrown alumina crystals; generally, with a crystallite size of 10– 40 μ m. Figure 1 shows a scanning electron micrograph of a typical assembly of MGA particles. The precipitation conditions of the precursor gibbsite are selected to maximize yield in the critical size range, thus causing the dominance of heavily intergrown aggregates.

The disorder and complexity of MGA is influenced by the calcination process as well as the gibbsite precipitation stage. The calcination strategy is governed first and foremost by the need to meet a specification for a specific surface area of 70-80 m²g⁻¹, while maintaining a low residualmoisture content, necessary to limit HF generation when fed into the molten cryolite electrolyte in the reduction cell. Surface area is also critical for effective performance as a gas scrubbing medium and for optimal dissolution in the reduction cell. Surface area is maximized by controlling the transition sequence to limit maximum temperature and residence time. With increasing temperature, the phase sequence moves from the hexagonal gibbsite, Al(OH)₃, through the oxyhydroxide boehmite, AlOOH, into the cubic system represented by the spinel structured gamma-alumina (5) (Fig. 2). Neutron diffraction studies indicate that the facecentred cubic oxygen sublattice in the spinel-based transition aluminas tends to be highly ordered in these materials; however, the aluminum ions are quite disordered, leading to the broadened lines typical of their powder X-ray diffraction (XRD) patterns (6).

In gibbsite, aluminum atoms occupy two thirds of the octahedral positions, with hydroxyl groups octahedrally coordinated in double layers. This gives gibbsite a monoclinic symmetry (space group $P2_1/n$) with a hexagonal close packing of the hydroxyl groups. Upon heating, the hydroxyls are progressively lost through the structural channels formed in the gibbsite lattice by the formation of water by proton exchange between neighbouring hydroxyls (7–9). This is accompanied by the structural rearrangement of the crystal lattice, a pseudomorphic transformation (i.e., the original morphology of the parent gibbsite is retained) with little change in the external dimensions, and as a consequence, a large internal porosity develops. The long-range ordering in gibbsite or boehmite is lost, and an amorphous transitionalumina form, gamma-alumina, appears. Fig. 1. Scanning electron micrograph of "typical" metallurgicalgrade alumina particles.



Further heating results in the conversion to delta- and then to theta-alumina, which are also spinel-structured transitionalumina forms. Gamma-, delta- and theta-alumina all have a face-centred cubic packing of the oxygen anions with various amounts of aluminum cations in either the octahedral or tetrahedral interstices. The proportion of tetrahedral sites increases with temperature (10), having 25%–30% of the octahedral sites occupied for gamma-alumina and 50% for theta-alumina (11, 12), until the abrupt disappearance of tetrahedrally coordinated aluminum upon the formation of alpha-alumina (corundum), which marks the end of the transformation sequence. Alpha-alumina has a hexagonal close packing of the oxygen anions, and all of the octahedral aluminum sites are occupied (13).

The mix of "forms" and high levels of disorder in MGAs present significant challenges in understanding their structure with relation to the performance as a raw-material feed for the smelting process (14). The X-ray methods by which we might follow these phase transformations are constrained by the limited long-range order in these materials. Thus, methods, which do not rely on long-range crystallographic order, can provide new insights and improved understanding of these materials. Kato et al. have reported X-ray absorption near-edge studies (XANES) of the Al K-edge in transition aluminas (15). In the manner of NMR studies, this approach appears to provide significant insight into the occupancy of octahedral and tetrahedral sites, i.e., key to understanding the forms and transition points in the alumina samples examined. However, the XANES approach has yet to be applied to MGAs.

A new phase, described as gamma-prime-alumina (γ' -Al₂O₃) was introduced by Paglia et al., which significantly improved the fitting of diffraction data on aluminas from fluid-bed and gas-suspension calciners (16). Ashida et al. developed a model used for fitting XRD data to better accommodate the degree of structural disorder observed for MGAs





by including the contribution of theta-alumina to the background (14). However, a significant challenge is the broad and diffuse diffraction patterns of amorphous transition alumina phases, making quantitative or structural determinations difficult.

Ingram-Jones et al. compared flash calcining with soak calcining of gibbsite in laboratory trials (17). They used XRD and ²⁷Al magic-angle spinning (MAS) NMR to examine the dehydroxylation sequence, as a function of both the calcination temperature and particle size. They suggested a cross-over of the calcination pathways shown in Fig. 2, where chi-alumina would transform into gamma-alumina for flash-calcined fine gibbsite particles ($<0.5 \mu m$) and partially for coarse (~14 µm) particles as well. The remainder of the coarse gibbsite would react via the previously discussed spinel-based (fcc) transformation sequence (i.e., boehmite – gamma – delta – theta alumina) before converting to alphaalumina. Whittington et al. proposed a similar mechanism based on quantitative X-ray analysis of laboratory aluminas (18). The authors noted that the careful control of the calcination time allows the phase distribution (although perhaps not the degree of structural disorder) of both rotary kiln and fluid-bed-calcined aluminas to be reproduced in the laboratory. Interestingly, Ingram-Jones et al. also found the chialumina originating from soak and flash-calcined gibbsites to have different short-range structures.

Solid-state MAS NMR studies can provide significant insight into the occupancy of octahedral and tetrahedral sites (the chemical shifts being characteristic of the oxide (or hydroxide) coordination $(AIO_n/AI(OH)_n))$ (19), which is key to understanding the forms of alumina in the samples tested. ²⁷Al MAS NMR chemical-shift ranges for aluminum in different coordinations with oxygen (or hydroxyls) are typically –10 to 20 ppm for octahedrally coordinated aluminum (AIO_6) , 30 to 40 ppm for pentahedrally coordinated aluminum (AIO_5) , and 50 to 80 ppm for tetrahedrally coordinated aluminum (AIO_4) (19, 20). The variation in the reported ranges for the chemical shifts reflects the range of possible Al-O bond lengths and angles, and next-nearest-neighbour species. A recently published ²⁷Al NMR study of a sol-gel manufactured theta-alumina reported the NMR parameters of its two aluminum sites (21). Several ²⁷Al studies have made use of the high sensitivity and the relatively minor contribution of particle and crystallite size effects of this technique to explore the transition aluminas (10, 11, 20–25). Furthermore, MAS NMR has also been beneficial in settling some of the ambiguity concerning the onset temperatures of the transition reactions; since XRD relies on the development of nuclei of sufficient size or long-range order for the detection of the phase, the technique does not always give reliable onset-temperature data. However, NMR has not been frequently applied to MGAs because of the low spectral resolution caused by the co-existence of different transition aluminas and the influence of the second-order quadrupolar interaction causing significant spectral broadening. With higher magnetic fields now becoming available, some of these problems may be overcome (26).

This study examines the use of multiple-field ²⁷Al MAS NMR on samples formed from the reaction of model hydroxides and MGAs, as compared to XRD data. Solid-state MAS NMR spectra of quadrupolar nuclei, such as ²⁷Al (nuclear spin I = 5/2), are broadened by the second-order quadrupolar interaction, a mechanism characterized by the quadrupolar coupling constant C_Q , in MHz (26). This second-order quadrupole interaction dominates the usually observed central transition (26) and has an angular dependence that is only partially averaged by conventional MAS. The interaction scales inversely with the applied magnetic field, so that high magnetic fields are normally advantageous, and the magnetic-field dependence can also be used to constrain the fits. In disordered solids, a distribution in bond lengths and angles for a particular site leads to a distribution in C_0 , resulting in asymmetric, rather featureless spectral lineshapes with a tail on the low frequency side. Recording the spectra from samples at multiple magnetic fields can greatly constrain the fitting even of featureless and overlapping lines. The distributions in C_Q in such materials can be simulated as a Gaussian around a central (mean) value, and the FWHM of this distribution can be used as a quantitative measure of the amount of disorder for a particular atomic site (27). In this study, three magnetic fields are applied, including 18.8 T. The aluminum-site distribution in two calcined samples and an MGA are compared using ²⁷Al MAS NMR and discussed in the context of the XRD data.

Experimental

Materials

Two Bayer gibbsites from different refineries but with very similar specifications (in terms of particle and crystallite size, morphology, and purity) were calcined in a fluidbed-type reactor, with electrically controlled heating to ensure a uniform temperature distribution. The calcination time was 20 min, and the temperature was 1020 °C; X-ray analysis reveals that the disorder in the material is similar to that of an industrially calcined gibbsite, although the higher temperature and longer retention time than normally encountered in an industrial fluid-bed calciner produces a slightly more-crystalline material, indicated by the narrower and more-developed peaks in the X-ray diffractograms, Figs. 3– 5.

XRD

X-ray diffractometry was performed on a Bruker D8 apparatus using Cu K α X-rays, a 2 θ range of 10–80°, a stepwidth of 0.02°, and a counting time of 10 s. To obtain quantitative information about the phase composition of the samples, subsequent Rietveld refinement of the X-ray diffractograms was performed using the FullProf software (28–30).

NMR

²⁷Al experiments were carried out using Varian Chemagnetics Infinity (8.45 T), Bruker Avance II (14.1 T), and Varian Infinity Plus (18.8 T) spectrometers. All MAS NMR experiments on Varian spectrometers were performed using the Spinsight program. The spectra at 8.45 T (²⁷Al Larmor frequency 93.81 MHz) were obtained with a 3.2 mm probe at 10 kHz spinning frequency. The pulse width used was 1 µs. ²⁷Al spectra at 14.1 T (²⁷Al Larmor frequency 156.37 MHz) were obtained with a 3.2 mm probe at 15 kHz spinning frequency using the TopSpin program. The pulse width was 2 µs. ²⁷Al spectra at 18.8 T (²⁷Al Larmor frequency 208.24 MHz) were recorded with a 2.5 mm probe at 25 kHz spinning frequency. The pulse width was 1 µs. These pulse lengths meant that the tip angle was in the linearresponse regime (26). The repetition delay for all experiments was 5 s, which was sufficient to produce relaxed spectra. The spectra were referenced against YAG (Yttrium Aluminium Garnet) with the signal corresponding to the octahedrally coordinated aluminum site set to 0.7 ppm, so that chemical shifts reported are relative to the primary shift reference of 1 mol/L [Al(H₂O)₆]³⁺ at 0 ppm. The QuadFit program was used to simulate the spectra and fit the peaks (31).

Fig. 3. Rietveld refinement of XRD data for a fluid-bed calcined MGA, illustrating the wide and weak diffraction patterns stemming from the amorphous transition alumina phases present in the material.



Fig. 4. X-ray diffractogram and Rietveld refinement of XRD data for alumina A (calcined for 20 min at 1020 °C).



Results and discussion

In the last few decades, significant progress in the understanding of the complex structure and phase evolution of MGA has been made possible by advances in the fields of MAS NMR and improvements in structural modelling of diffraction data. However, quantitative measurements are still especially challenging, since the transformation reactions are continuous with several phases co-existing during the rapid heating encountered in modern calciners. Analyses of MGA show that the material is dominated by the poorly defined gamma phase(s); understanding the structure of these phases is key to understanding the properties of MGA. The relatively ill-defined and broad diffraction patterns are exemplified in Fig. 3, where the result from a Rietveld refinement on XRD data from a MGA is shown. In fact, even the structures of most transition aluminas are not fully understood (3,

Sample	Gamma-Al ₂ O ₃	Gamma-prime-Al ₂ O ₃	Total gamma-Al ₂ O ₃	Theta-Al ₂ O ₃	Alpha-Al ₂ O ₃
А	28	42	70	22	8
В	26	45	71	25	4
MGA	32	44	76	22	2

Table 1. Results from the Rietveld refinement (quantitative phase analysis (%)) of the XRD data for the laboratory-prepared aluminas, A and B, used in this study and for an industrial fluid-bed-calcined MGA sample.

Fig. 5. X-ray diffractogram and Rietveld refinement of XRD data for alumina B (calcined for 20 min at 1020 °C).



12, 32). The XRD technique is limited by the need for longrange ordering in the material. Supplementary information, as produced from ²⁷Al MAS NMR, can be very useful in better defining such systems.

In Figs. 3–5, the results from the XRD measurements and the Rietveld refinements for the MGA sample and alumina A and B are displayed. The numerical data from the quantitative phase analysis (using the Rietveld method) are listed in Table 1.

The ²⁷Al MAS NMR spectra obtained from alumina A at three fields are shown in Fig. 6, along with the individual simulated peaks for each aluminum environment. The NMR parameters and relative intensities of each site for both aluminas A and B are shown in Table 2. The ²⁷Al MAS NMR spectrum of the MGA sample is shown in Fig. 7. Integration of the various lineshapes revealed that this sample consists of a much-higher fraction of the gamma-alumina phase (see Table 3). The key to the robustness and uniqueness of these fits, despite significant spectral overlap, is that the same parameters are used to fit the spectra at all three fields. The ability to fit all three fields accurately with spurious parameters would be highly coincidental and is hence unlikely. Also, the positions (and parameters) of several peaks are not arbitrary, as they are largely determined by the known phases that are present in this sample (i.e., gamma-, theta-, and alpha-alumina).

This assignment of the peaks was made by comparison to the chemical-shift positions and NMR parameters previously reported for a sol–gel theta alumina and corundum (21). The chemical shifts and C_Q values for the theta phase are in good agreement with the published data, although the presence of

a distribution in C_Q in the theta form present here suggests it is more disordered than the sol–gel formed sample (21, 26). This disorder appears to be present in the corundum phase too, which could explain why the C_Q value is slightly larger here than the commonly accepted value of 2.38 MHz (33).

The peaks at 71 and 16 ppm have much larger ΔC_0 , corresponding to a broader distribution of aluminum environments, as would be expected from a more disordered alumina phase. Hence, these peaks probably belong to the more-disordered gamma-alumina. Wefers et al. considered theta-alumina to be an intermediate between the lowtemperature transition aluminas and the energetically favored alpha-alumina (3). Levin et al. showed that a disordering of the gamma phase is required to obtain the lattice parameters for theta-alumina (34). Furthermore, numerous XRD studies show that theta-alumina has narrower and more-developed peaks than gamma-alumina, also indicating a more-crystalline, or ordered structure (e.g., Stumpf et al. (35)). It is therefore assumed that gamma-alumina is more disordered than theta-alumina, and consequently that gamma-alumina has more asymmetric peaks (i.e., a broader distribution of $C_{\rm O}$) and larger mean $C_{\rm O}$.

The peak centred at a chemical shift of approximately 38 ppm indicates the presence of pentahedrally coordinated aluminum (AlO₅) in accordance with previously reported values for the chemical shift (20, 23, 36). The presence of penta-coordinated aluminum is consistent with the disordered nature of the MGAs and is thought to originate from more highly distorted (disordered) sites (components) in an X-ray amorphous part. More disordered or even amorphous aluminas, if present in significant quantities, limit the accuracy of XRD methods for quantitative phase measurements of MGAs. In gamma-alumina, penta-coordinated aluminum has also been speculated be present and would originate from aluminum at the external surface and be associated with the Lewis acidity and catalytic activity of the materials (24).

The only remaining question is the small peak at 23 ppm where ΔC_Q is only 4 MHz. This could be associated with a more "ordered" site within the disordered gamma or a small amount of penta-coordinated aluminum perhaps within the theta phase.

The distribution of aluminum cations between octahedral and tetrahedral positions for the transition aluminas has been investigated in several studies. Considering the ideal spinel structure as a basis for the gamma-alumina structure, the fraction of octahedral to tetrahedral aluminum is 0.67. The deformed spinel structures (usually represented as $Al_8^{\Box}O_{12}$, where \Box represents a vacant Al), either with octahedral or tetrahedral cation vacancies, gives a theoretical fraction of octahedral aluminum of 0.63 and 0.75, for octahedral or tetrahedral vacancies, respectively. Based on the results in this

Fig. 6. Fitted ²⁷Al MAS NMR spectra of alumina A (calcined for 20 min at 1020 °C). The black line is the experimental spectrum, and the red line is the sum of the individual fitted curves.



study (Table 3), it cannot be unambiguously deduced whether octahedral or tetrahedral vacancies are favored. It is generally considered, and also experimentally supported, that aluminum would favor octahedral coordination in gamma-alumina under normal conditions (usually meaning

that no hydrogen is included in the structure), leaving tetrahedral vacancies in the spinel-based framework (6, 24). A recent study, however, suggests a preferential distribution of aluminum over tetrahedral sites for gamma-alumina (37). In another study, conducted by Lee et al., the distribution of octahedral and tetrahedral aluminum in gamma and alpha alumina was examined using MAS NMR as well as quantum mechanical calculations; this reported a fraction of $0.7 \pm$ 0.02 (11). It should be noted that in some of the earlier work, the lower magnetic-field strengths and lower MAS frequencies employed result in significant interference of the octahedral spinning sidebands with the peaks stemming from tetrahedrally and pentahedrally coordinated aluminum. This makes accurate quantification of the spectra very difficult. Another possible reason for the significant variation in the observed distribution of aluminum between different sites is the influence of different preparation techniques and precursor materials in the various studies.

Zhou et al. examined eta-, gamma-, and theta-aluminas using profile refinement of neutron diffraction data (6). They suggested that, in gamma-alumina, a fraction of the aluminum cations would also occupy non-spinel sites, aptly labelled as quasi-octahedral, as they lie so close to the octahedral aluminum sites; the distance being only 0.373 Å. They ascribe these sites mainly on the surface of the gamma-alumina where they also would contribute to the catalytic activity of the material. The occupation of non-spinel sites in gamma-alumina is supported in the study by Wolverton et al., who propose that not only surface sites would show this abnormal coordination but also atoms in the bulk (12). One possible explanation of the small 23 ppm peak observed here is that it is the quasi-octahedral aluminum resulting from a distorted gamma-alumina framework resulting from the incomplete transformation or complexphase composition, which puts further stress on the structure. If the peak at 23 ppm is a quasi-octahedral site belonging to the gamma-alumina, this would correspond to 11% and 8% of the "octahedrally" coordinated aluminum atoms in alumina A and B, respectively. However, the deformed spinel-based crystal structure for gamma-alumina derived by Zhou et al. suggests that 25% of the aluminum atoms would be in quasi-octahedral coordination.

Theoretical and computational studies strongly indicate that cation vacancies in octahedral sites would be energetically favorable in gamma-alumina (12, 38). Krokidis et al. propose an equilibrium structure for gamma- alumina with 69%-75% of the aluminum ions in octahedral positions. The fractions of octahedrally coordinated aluminum (Table 3) show some agreement with this structure. However, the short heating times and the presence of theta- and alpha-alumina could distort the gamma-alumina structure, resulting in an incomplete lattice framework, and perhaps accounts for the AlO₅ observed. Data obtained on crystallographically pure, single phase systems cannot be directly compared to the data obtained for the structurally disordered systems represented by the samples used in this study. Nevertheless, important information on the coordination environment can be deduced from the results.

For the theta-alumina, the ideal structure would give a 50:50 distribution for aluminum over tetrahedral and octahedral sites (12). The experimental results for aluminas A, B,

Table 2. Peak parameters used in the curve fitting of the NMR data, collected at 18.8 T, for alumina A (calcined for 20 min at 1020 °C) and the resulting peak intensities. The relative abundances are approximate, since the spinning sideband intensities were not included in the integration.

²⁷ Al NMR Peak	Chemical Shift (±2 ppm)	Mean C _Q (±1 MHz)	$\begin{array}{l} \Delta C_{\rm Q} \\ (\pm 1 \text{ MHz}) \end{array}$	Alumina A Intensity (%)	Alumina B Intensity (%)	Alumina Phase
Tet 1	77	5.5	3	15	20	Theta
Tet 2	71	8	6	15	12	Gamma
Pent 1	38	8	7	2	2	b
Oct ^a	23	5	4	4	3	Gamma
Oct 1	16	7	9.5	33	37	Gamma
Oct 2	14	3.5	3	8	5	Alpha
Oct 3	10	3	3.5	23	22	Theta

^aPossibly a quasi-octahedral peak (see discussion).

^bSmall quantity of AlO₅ from some amorphous component of gamma- or other transition alumina (such as the X-ray amorphous chi- or rho-alumina).

Table 3. Total intensities and fraction of octahedrally coordinated aluminum for the various transition alumina phases, for aluminas A and B and the MGA sample.

Sample	Total gamma-Al ₂ O ₃ (±2%)	Total theta- Al_2O_3 (±2%)	Total alpha- Al_2O_3 (±2%)	Fraction of octahedral Al in gamma-Al ₂ O ₃	Fraction of octahedral Al in theta-Al ₂ O ₃
A	50	38	8	0.71	0.61
В	51	42	5	0.67	0.52
MGA	66	28	3	0.82	0.61

Note: The quasi-octahedral peak (at a chemical shift of 23 ppm) is included in the gamma-alumina.



Fig. 7. The ²⁷Al MAS NMR spectrum of MGA obtained at 18.8 T, with simulated peaks (same colors as Fig. 6).

and the MGA show some agreement with the ideal structure. The theta-alumina in alumina B appears to be very close to the ideal structure. In alumina A and the MGA, the complex-phase mixture and severe disorder in the material results in the lineshapes of the associated resonances showing much more disorder than in a crystalline alumina. The "theta" phase present in these two samples may actually be closer to the more-disordered delta-alumina phase, which would explain the lower tetrahedral to octahedral ratio.

Recently, a number of authors report on the use of various synchrotron radiation sources to investigate the transition

aluminas and their transformation reactions (15, 39–42) as well as some aluminum-containing minerals and zeolites (43, 44). It seems that by examining the Al K-edge XANES or NEXAFS features, information on the coordination environment can be obtained. The methods clearly show some promise for analyzing disordered systems, such as MGAs. Quantification is made in a similar manner as with the NMR results in this study; i.e., by curve fitting of the obtained spectrum. The results generally give a distribution of octahedral and tetrahedral aluminum closer to unity regardless of the calcination temperature (15, 40), which does not agree well with NMR data nor has there been any report of pentahedrally coordinated aluminum for which there is strong experimental evidence in this and other studies.

It is clear that there still exists considerable ambiguity over several issues relating to the transition aluminas, the variations in structure that occur, and the accurate characterization of these structures. The true structure and the distribution of aluminum cations and vacancies for some of the transition aluminas remain yet to be discovered (3, 32). Another outstanding question is the location of the residual hydroxyl groups, initially thought to be located on the exterior of the alumina structure and at grain boundaries. In gassuspension or fluid-bed calcined MGAs, the very high heating rates are expected to result in a far more random distribution. Computational studies indicate that for the formation of cubic spinel-based transition alumina forms, protons may have a stabilizing effect on the structure (45), but contradictory results are obtained in neutron diffraction studies (6, 12). It has also been suggested that hydrogen would be present as water from the decomposition reactions of gibbsite and boehmite and located within the amorphous structure (3, 46).

The MGAs must be viewed as a kinetically "frozen" material in which the different phases exist not in a simple binary mixture, but in a continuum of evolving and disappearing phases. Local variations between particles and even within particles further contribute to difficulties and uncertainties with interpreting the data. The structural domains transcend both short-range nanostructures and longer-range ordering; a combination of techniques such as MAS NMR and XAS with XRD will be necessary for a more-complete understanding of these important materials.

Conclusions

It has been shown that ²⁷Al MAS NMR spectroscopy can be used to quantify the distribution of aluminum between different sites in the component phases of MGAs. The use of multiple applied magnetic fields, and especially the availability of higher magnetic fields, is crucial to constrain the simulations. The results also clearly demonstrate that the complementary information obtainable by XRD significantly aids quantification. Amorphous aluminas, if present in significant quantities, can however limit the accuracy of XRD methods for quantitative phase measurements of MGAs. An NMR peak at 23 ppm was detected and could be due to aluminum in a quasi-octahedral coordination, relating to a distorted gamma-alumina form. In conclusion, ²⁷Al MAS NMR has been shown to be an extremely useful part of experimental methodologies to examine the commercially significant and structurally interesting transition aluminas and their precursors.

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