Alumina: Discriminative Analysis using 3D Correlation of Solid-State NMR Parameters

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Synthetic transition aluminas (χ , κ , θ , γ , δ , η , ρ) exhibit unique adsorptive and catalytic properties leading to numerous practical applications. Generated by thermal transformation of aluminium (oxy)hydroxides, structural differences between them arise from the variability of aluminium coordination numbers and degree of dehydroxylation. Unequivocal identification of these phases using X-ray diffraction has proven to be very difficult. Quadrupolar interactions of ^{27}Al nuclei, highly sensitive to each site symmetry, render advanced ^{27}Al solid-state NMR a unique spectroscopic tool to fingerprint and identify the different phases. In this paper, ^{27}Al NMR spectroscopic data on alumina reported in literature are collected in a comprehensive library. Based on this dataset, a new 3D correlative method of NMR parameters is presented, enabling fingerprinting and identification of such phases. Providing a gold standard from crystalline samples, this approach demonstrates that any sort of crystalline, ill crystallized or amorphous, mixed periodic or aperiodically ordered transition alumina can now be assessed beyond the current limitations of characterisation. Adopting the presented approach as a standard characterisation of alumina samples, will readily reveal NMR parameter – structure – property relations suitable to develop new or improved applications of alumina. Methodological guidance is provided to assist consistent implementation of this characterisation throughout the fields involved.

1. Introduction

Upon heating, aluminium (oxy)hydroxides (AlOOH or $\text{Al}(\text{OH})_3$) pass through a series of phase transitions before converting to the entirely dehydroxylated α -alumina (Al_2O_3) at high temperature.^{1–3} The structural transformation from the (oxy)hydroxides to alpha-alumina involves successive loss of water and significant densification. Thermal treatment irreversibly removes structural hydroxyl groups, successively transforming the initial (oxy)hydroxides in a sequence of more and more dense transition phases between 300 and 900 °C (Figure 1). These so-called transition alumina's are stable at ambient conditions and are distinguished by Greek letters (χ , κ , θ , γ , δ , η , ρ), according to the moment of their discovery and first description.

The transition aluminas exhibit a high-surface-area and both Brønsted and Lewis type acidity. Typically these phase are applied as dessicant, adsorbent, catalyst, catalyst support and as ceramics precursor. Abrasion and attrition resistant extrudates of transition alumina are obtained by calcination of extruded precursor aluminium hydroxide or oxyhydroxide. They are suitable sources of Al for manufacturing aluminium metal through the Bayer process. Gamma, theta and eta alumina are

popular in catalytic applications such as dehydration of alcohols, isomerisation of olefins, production of sulphur from H_2S , etc.⁴ Other important alumina-catalysed reactions include chlorination of methanol, de-hydrofluorination of organic fluorides, alkylation of phenols, de-oxygenation of bio-oils and decomposition of triglycerides. Large scale applications as catalyst support for metals include hydrosulfurization in petroleum refinery using cobalt and nickel promoted molybdenum sulfide, NO_x reduction, CO and hydrocarbon oxidation reactions on supported noble metals. Wash coated monolithic exhaust gas purification catalysts are further examples.⁴

The transformation sequences from (oxy)hydroxide up to alpha-alumina (Figure 1), are highly influenced by starting material, crystallite size, relative humidity, alkalinity, heating rate, pressure and bed depth.^{1–3,5,6}

Figure 1: Schematic representation of the thermal evolution (black arrows) of transition alumina phases in air, from the hydroxide and oxyhydroxide precursors, gibbsite, boehmite, bayerite and diaspora^{1–3,5,6}. The non-thermal transformations are shown with blue arrows.

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Clear assignment of structural models to the different phases severely was, and still is, hampered by the occurrence of complex phase assemblies along the calcination path in combination with their typical micro and nanocrystalline nature. Whereas the latter is a direct consequence of their formation by release of structural water and consequent, densification, it results in broadening of the X-ray diffraction lines, rendering PXRD patterns very difficult or impossible to analyse. (See Supplementary Information, Discussion S1) Alumina phases such as ρ or χ alumina, for example, inherently exhibit a degree of disorder too high to allow identification from x-ray diffraction.^{7,8} Comparing the structures proposed in literature revealed these phases can clearly be distinguished by three parameters only: 1) nominal water content, comprising structural hydroxyls and adsorbed water, 2) the order of the anionic sublattice, and 3) the distribution of aluminium cations therein (Figure 2). As the thermally induced transformations involve both dehydration and dehydroxylation, the atomic ratio of H versus Al is a rather insensitive parameter to globally

describe the progress of the transformation. Distinguishing

Figure 2 Three-dimensional graph correlating the ratio H/Al, the ratio of tetra-coordinated and hexa-coordinated Al and the oxygen order of α , η , δ , θ , γ , κ , ρ -alumina and bayerite (Ba), boehmite (Bo), tohndite (To), pseudoboehmite (PBo), diaspor (D), nordstrandite (Ns) and gibbsite (G). The chemical formulae are listed in the Supplementary Information, Table S1.

Figure 3 ABC stacking sequence with octahedra and tetrahedra sharing edges

phases with a similar degree of hydration requires additional parameters.^{9,10} As the condensation of hydrogen-bonded oxygen layers implies successive re-ordering of the oxygen sublattice, this order can serve as second parameter for phase identification. Indeed, all phases under consideration, with the exception of the fully amorphous alumina gels and maybe the extremely disordered ρ alumina, can be described as dense packings of oxygen planes, with aluminium cations occupying the vacancies in between the planes. In dense stacking sequences, the ratio of tetrahedral and octahedral vacancies is always 2:1.

Within a layer, octahedra share edges with neighbouring octahedra and faces with tetrahedra, and opposite. In stacking sequence ABA, octahedra share faces with octahedra in the upper and lower layers, whereas in the ABC sequence, they only share edges between layers (Figure 3). As charge distribution forbids occupation of tetrahedra sharing a face with either octahedra or tetrahedra, the stacking sequence of the anion sublattice limits the possibilities to distribute cations over the vacancies. Furthermore, early transition aluminas systematically show disorder in their cation occupation. With increasing temperature order in cation as well as oxygen sublattice is increasing. Hence, as criterion for phase identification the layer sequence of the anionic sublattice and the ratio of occupied tetrahedra versus octahedra can serve to fully identify a transition alumina and an aluminium (oxy)hydroxide. However, direct identification of some alumina phases (eg., ρ or χ alumina) from x-ray diffraction alone is not possible owing to the degree of disorder in the systems.

Solid-state NMR is a powerful characterization technique for materials.^{11–13} ^{27}Al NMR spectroscopy is very often used, as aluminium is omnipresent in materials necessary for science and technology. The parameters defining the structure of the transition alumina phases have direct or indirect influence on the local environment of the ^{27}Al nucleus, and should be reflected in its chemical shift and quadrupole parameters. As will be demonstrated below, ^{27}Al MQMAS is the ideal tool to measure these parameters, providing a straightforward spectroscopic identification of any transition alumina by a single experiment. Although very important ^1H and ^{17}O NMR experiments have been carried out to investigate the structure of transition aluminas,^{14–17} ^{27}Al is definitely the most suitable NMR probe for these phases. Solid-state ^{27}Al NMR is able to give highly resolved NMR signatures even for those phases which cannot be identified by x-ray diffraction.

1.1. ^{27}Al NMR spectroscopy in materials science

The NMR properties of ^{27}Al (see Table 1) provide a good NMR receptivity, at frequencies accessible by common NMR probe-heads. Consequently, ^{27}Al NMR is an obvious choice to assist structure elucidation of aluminium containing materials.^{18–21} The nuclear spin 5/2 of ^{27}Al results in a nuclear quadrupole moment interacting with local electric field gradients (EFG). Although this interaction can severely broaden the spectra, it provides an extremely sensitive probe to the local chemical environment of a quadrupolar nucleus in solids.

Table 1. NMR properties of aluminium (^{27}Al nucleus)

Properties	Magnitude	Unit
Spin number (I)	5/2	
Nuclear magnetic moment (μ)	4.30869	μ_{N}
Gyromagnetic ratio (γ)	6.976×10^7	$\text{rad T}^{-1} \text{s}^{-1}$
Resonance frequency (at 11.4 T)	130.284	MHz
Quadrupole moment (Q)	146.6	mb
Relaxation times (T_1)	<10	s
Natural abundance (%)	100	%
Receptivity (relative to ^1H)	0.207	
Receptivity (relative to ^{13}C)	1220	
Isotropic chemical shift (δ_{iso}) range (for non-metallics)	$-25 > < +110$	ppm
Quadrupole coupling constant (C_Q)	$1 > < 20$	MHz

In case of ^{27}Al , the magnitude of this quadrupole interaction is typically in the MHz range and can be expressed as a quadrupole coupling constant (C_Q), relating the quadrupole moment Q with the local EFG tensor as:

$$C_Q = \frac{e^2 q Q}{h} \quad (1)$$

with e the elementary charge, eQ the electric quadrupole moment and $eq = V_{zz}$. The principal axis components of the traceless EFG tensor are defined as $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ and allow to define an asymmetry parameter, $\eta_Q = (V_{xx} - V_{yy}) / V_{zz}$.²² The quadrupole moment Q is unique for every quadrupolar nucleus, typically expressed in femtometer² (fm^2) or millibarns (mb). For ^{27}Al , Q equals 146.6 mb. For ^{27}Al , C_Q usually falls in the range 1–10 MHz, though there are some rare cases with exceptionally high values.^{23,24} The magnitude of C_Q also reveals information on the symmetry of the local Al environment as deviations from spherical symmetry increase the effective EFGs at the nucleus and in turn the quadrupole coupling.^{25,26} When the quadrupole perturbation is large the first order approximation is not sufficient to describe the system completely. Higher order interactions can also play an important role. In the case of ^{27}Al NMR of solids second order quadrupole interaction is present for most cases, except for some extremely symmetric systems. Second order quadrupole broadening is inversely proportional to the external field B_0 . Therefore going to higher magnetic fields decrease quadrupole broadening and increase the resolution.

In liquid state NMR, first and second order quadrupole interactions are averaged out. In solids only the first-order quadrupole interaction can be fully averaged by very fast magic-angle spinning (MAS). However, second-order quadrupole interaction is not averaged with this single-angle sample spinning. This not only results in anisotropically broadened solid state spectra of the central ^{27}Al transition ($m_{+5/2} \leftrightarrow m_{-5/2}$), it also gives rise to a quadrupole-induced chemical shift:

$$\Delta\nu_{m,m-1} = -\frac{3}{40} \frac{C_Q^2 I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2} \left(1 - \frac{\eta_Q^2}{3}\right) \quad (2)$$

; where I is the spin number and ν_L is the Larmor frequency. The influence of this relation can be seen directly from Figure 4. The chemical shift in solid-state NMR is the average of the sum of all principal components of the chemical shift tensor. For a spin-1/2 nucleus, the maximum intensity of the NMR peak indicates

its isotropic chemical shift. For a quadrupolar nucleus, the isotropic chemical shift cannot simply be derived from the maximum intensity, unless the nucleus resides in a highly symmetric site, rendering the quadrupolar interaction negligible. Figure 4 shows the impact of differences in the EFG tensor on the simulated MAS NMR resonances resulting from a central transition of a quadrupolar nucleus with isotropic chemical shift at 20 ppm. Figures 4(e) and 4(f) show simulated ^{27}Al CT NMR line shapes respectively demonstrating the impact of a distribution in only the quadrupole coupling and the

Figure 4: Simulated ^{27}Al central transition spectra under MAS of (a) without quadrupole coupling and (b)–(f) with a quadrupole coupling (C_Q) of 2 MHz. The asymmetry parameter (η) varies from 0.0 to 0.5 and to 1.0 in (b), (c) and (d). A distribution of C_Q is simulated in (e) and a distribution of C_Q and chemical shift are simulated in (f).

combined effects of quadrupole and chemical shift distributions. The image readily demonstrates the potential issues with older datasets reported using peak maxima and full widths at half maximum (FWHM) and the essential role of spectral decomposition and chemical shift referencing in quadrupolar NMR.

In case of ^{27}Al , IUPAC recommends to use a fresh aqueous (D_2O) solution of $\text{Al}(\text{NO}_3)_3$ (1.1 M) as the ^{27}Al primary chemical shift reference standard at 0 ppm.¹² An aqueous solution of 0.5/0.5 M $\text{Al}(\text{NO}_3)_3/\text{HNO}_3$ is usually used in case long shelf-life is desired. The range of ^{27}Al isotropic chemical shifts (δ_{iso}) for different Al- O_x coordinations is usually between -20 to $+90$ ppm. The hexa coordination (Al-O_6) exhibits ^{27}Al isotropic chemical shifts in the range between -21 and $+37$ ppm,^{27–33} while for the tetra-coordinated species (Al-O_4) it is between $+39$ and 85 ppm.^{27–31} The penta-coordinated aluminium (Al-O_5) usually shows shifts in the range between $+20$ and $+52$ ppm.^{24,34–38} Since each coordination exhibits a typical chemical shift, ^{27}Al NMR provides an easy way to identify and quantify Al structural units in materials.^{23,39} For most materials, the ^{27}Al NMR resolution is sufficient to distinguish between different coordinations. Especially in the case of Al(V) , quadrupole broadening is less than that in Al(IV) and Al(V) .

In addition to chemical shift referencing, also pulse calibration is essential for ^{27}Al characterisation of materials. The nutation of half-integer spin quadrupoles (like ^{27}Al) in solution state is different from that in solid-state. The 90° pulse calibrated for a solution standard should be divided by a factor of $1+1/2$ to obtain that for solid-state systems when the quadrupole frequency ($\nu_Q = C_Q/[2I(2I-1)]$) is higher than the nutation frequency. At infinite rotation frequency only the second-order quadrupole broadened central transition survives. The nutation of quadrupole central transition in solid-state heavily depends on the quadrupole interaction. Therefore, very small flip angles ($\pi/12$ or lower) are recommended to remain in the quantitative regime for the central transition signals with different quadrupole couplings.

Once correct chemical shift referencing and pulse calibration are ensured, separation of overlapping resonance contributions broadened by the second-order quadrupole coupling becomes experimentally accessible using high-resolution NMR methods such as double rotation (DOR),^{40,41} dynamic-angle spinning (DAS),^{42,43} multiple-quantum magic-angle spinning (MQMAS)^{44,45} and satellite-transition magic-angle spinning (STMAS).^{46,47} While in case of ^{27}Al , DOR or DAS experiments don't benefit, as the MAS frequencies which can be used for these experiments cannot average the ^{27}Al - ^{27}Al dipolar interactions, MQMAS or STMAS experiments do provide an advantage, as they can have very high MAS frequencies. Using correctly acquired experimental data, distributions of quadrupole parameters can be simulated and fit with Gaussian distributions of each of the EFG tensor components, using the Cjzek model^{48,49}, a feature that has been incorporated in one of the more popular NMR spectral analysis programs, DMFIT.^{50,51}

MQMAS, a 2D experiment correlating single and multiple quantum transitions (3Q and 5Q), is the most popular and convenient choice to achieve high resolution in the case of spin $1/2$ quadrupolar nuclei (e.g. ^{27}Al) exhibiting central transitions broadened by a second-order quadrupole interaction.⁵² Isotropic chemical shifts can be directly be obtained from the indirect dimension of the experiment. Quadrupole parameters (C_Q and η_Q) and their distributions can be extracted by fitting resolved single quantum (horizontal) slices of the 2D experiment.

As the quadrupole coupling constant C_Q is impacted by the local symmetry, this parameter reveals information on the coordination of Al atoms. Distortions from perfect octahedron or tetrahedron usually result in large quadrupole interactions (of the order of MHz), especially in the case of Al-O coordinations in alumina. Tetra-coordinated species exhibit larger quadrupole coupling than the hexa-coordinated species; penta-coordinated Al typically exhibit a broad distribution in quadrupole coupling and/or chemical shift, due to their preferential occurrences at surfaces of the solids and at grain boundaries. 3D correlating δ_{iso} , C_Q and η_Q consequently yields a fingerprint of the local environment of an ^{27}Al nucleus.

This has been done for a set of transition alumina samples with the help of values reported in literature (infra). 3D ellipsoid representations are a suitable method to present such correlations, as they allow to also include the spread of the on

the reported values by plotting an average value of each parameter (ellipsoid centre) along with its spread (ellipsoid axis). In case of alumina, such correlations have to be built for Al(IV), Al(V) and Al(VI) coordinations separately. In case of transition alumina such 3D ellipsoids were found to be extremely useful in the identification of all alumina phases as they have minimal overlap (infra). Additionally, ^1H - ^{27}Al correlation NMR methods are extremely useful which provide extra information on structure of alumina and other aluminium containing solid systems. In case of surface studies dynamic nuclear polarization (DNP) enhanced NMR detection crucial information on ^1H - ^{27}Al connectivity.^{53–59}

2. Aluminium hydroxides and oxyhydroxides with $\text{H}/\text{Al} \geq 1$

Aluminium (oxy)hydroxides are the common precursors to generate transition alumina phases by thermal treatment (Figure 1). Typical for all structures is the presence of Al-bonded hydroxyls which take part in hydrogen bonding. The idealized structure formula for the hydroxides and oxyhydroxides is $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$, respectively, although real materials may contain extra physisorbed water molecules, leading to an Al/H ratio for the hydroxides in the range of 3-3.2, and for oxyhydroxides roughly in the range of 1-2. Furthermore, all these phases exclusively contain hexa-coordinated Al-ions leading to a ratio $\text{Al}_{\text{tet}}/\text{Al}_{\text{hex}}$ equalling zero. These water-rich phases occur naturally in bauxite, containing the hydroxide gibbsite and the oxyhydroxides boehmite and diaspore as main aluminous components, next to traces of the other three hydroxides, viz. bayerite, nordstrandite and doyleite. The Bayer process, introduced in 1888, still today is the most important pathway to refine bauxite.³ Leaching of aluminate from the bauxite mineral followed by precipitation leads to gibbsite, currently the most used precursor for alumina and aluminium synthesis.

2.1. Aluminium hydroxides

Only four Al-hydroxides are known: gibbsite, bayerite, doyleite and nordstrandite. Whereas gibbsite and bayerite are common minerals found naturally and produced synthetically, nordstrandite and doyleite are rare. Among the latter two, only nordstrandite can be obtained synthetically. Hence, reports on these two hydroxides, especially on doyleite are limited.

Al-hydroxides are built up from octahedral (6-coordinated Al^{3+}), edge-linked into hexagonal sheets, isomorphous to brucite type sheets with $2/3$ occupancy of the metal positions, resulting in the typical honeycomb-like appearance. Each sheet is composed of two densely packed oxygen planes, with AB sequence (Figure 5). The four hydroxide structures differ in their vertical stacking, leading to different vertical Al distributions and to different hydrogen bonding within and between the hexagonal layers. This not only results in different Al-environments, but also in different sequences of transition alumina upon calcination. Upon thermal treatment only

nordstrandite and bayerite are reported to follow a same transformation sequence.

2.1.1.1. Gibbsite

Gibbsite $\rightarrow \chi \rightarrow \kappa \rightarrow \alpha$ -alumina

Gibbsite, the end-product of the commercial Bayer process, is produced on large scale by alkaline precipitation of Al^{3+} . It is widely used as fire retardant, additive in polymers and paper, toothpaste fillers, for stabilization of titania and in the production of artificial marble.

gibbsite ($\gamma\text{-Al}(\text{OH})_3$) crystallizes as a monoclinic structure (space group $P2_1/b$)⁶⁰ where consecutive hexagonal layers of Al-octahedra are systematically mirrored. This results in an overall stacking sequence of AB BA AB BA in the oxygen sublattice (Figure 5). Aluminium ions in different layers are vertically aligned. The intra- and interlayer hydrogen bonding occurring in gibbsite results in two crystallographically different Al environments with a ratio of 1:1.⁶¹ While their chemical shift differences are small, the two Al-sites experience significantly different EFGs, reflected in their quadrupole coupling constants. Like most of Al-containing materials, the direct excitation ^{27}Al MAS NMR spectrum of gibbsite contains a very wide spinning side-band manifold, owing to its large quadrupole interaction. The ^{27}Al CT spectrum of gibbsite under MAS shows two overlapping Al resonances (see simulated spectrum in Table 2) which differ in their second-order quadrupole coupling pattern assigned to two different sites.^{7,9,62–64} Al occupying the first site is surrounded by hydroxyl groups taking part in four intra-layer and two inter-layer hydrogen bonds with an isotropic chemical shift

Figure 5 The crystal structures of (from top to bottom) gibbsite,⁶⁰ bayerite and nordstrandite (Al in blue polyhedra, O in red and H in grey).⁶⁷

of 13.6 ppm, C_Q of 4.6 MHz and η_Q of 0.4. The second Al site exhibits a similar isotropic shift (11.3 ppm), but a smaller C_Q (2.2 MHz) and a larger η_Q (0.7). In this case, four hydroxyls point towards the neighbouring layers, while the other 2 engage in intra-layer interaction.⁶¹ Spectral decomposition of the ^{27}Al NMR resonance of the central transition, recorded quantitatively with a $\pi/12$ pulse, revealed two equally occupied octahedral Al-sites in accordance with the structural model. Also high-resolution ^1H decoupled ^{27}Al 2D 3QMAS spectra showed two isotropic resonances in corresponding to the two Al sites.^{63,64} Proton decoupling is highly recommended for quadrupolar NMR, especially for MQ experiments in hydroxides and oxyhydroxides⁶⁵.

Dehydroxylation of gibbsite follows different routes (sequence of transition alumina species) when performed in wet air, in dry air, and in vacuum. Heating in presence of excess water vapour (60–300 °C), transforms gibbsite to boehmite,⁶⁶ being the main route for synthesis of the latter. In dry air it transforms to χ -alumina (300–500 °C) and κ -alumina (800–1150 °C) before turning into α -alumina.⁶ In this sequence,⁹ the population of the

Figure 6: ^{27}Al MAS NMR spectra of untreated and thermally treated gibbsite in air from 100 to 1200 °C (373 to 1473 K in the inserted legend). Reproduced from ref. 7 with permission from Elsevier, copyright 2018.

Figure 7. ^{27}Al NMR spectra of synthetic bayerite and derivatives obtained by heating at the indicated temperatures. Reproduced from ref. 69 with permission from Elsevier, copyright 2018.

4-coordinated Al (Al-O_4) increases gradually and reaches a maximum of $\text{Al}_{\text{tet}}/\text{Al}_{\text{hex}} \approx 30\%$ around 1000°C in the kappa phase (Figure 6). Under vacuum, gibbsite transforms to ρ -alumina ($100\text{--}400^\circ\text{C}$), which then turns into η -alumina ($270\text{--}500^\circ\text{C}$) and θ -alumina ($870\text{--}1150^\circ\text{C}$), before reaching α -alumina (above 1200°C). Also in this series, the percentage of tetrahedral Al increases and reaches values of 50% in the theta phase. Unlike most other discussed alumina phases the highly disordered ρ -alumina with strongly fractured, nanosized particles contains a significant fraction of five-fold coordinated aluminium in addition to the tetra and hexa-coordinated Al species.

Grinding has significant influence on the gibbsite properties as confirmed with ^{27}Al NMR by MacKenzie *et al.*⁶⁶ The mechanically activated surfaces of the fractured gibbsite particles are postulated to adsorb water, resulting in five-fold coordinated Al-species. Ground gibbsite, showed a small fraction ($\sim 10\%$) of AlO_5 , which remained present on heating from room temperature up to 600°C , before diminishing. These observations demonstrate the generally observed sensitivity of alumina transformation to crystallite size, moisture, heating rate, etc.

2.1.2. Bayerite

Natural bayerite occurs only rarely compared to the more stable gibbsite. Synthetically, it readily forms by pH-controlled precipitation from Na-aluminate solutions. Even though it has no major direct industrial applications, bayerite serves as precursor for the production of catalytically interesting η -alumina.

The aluminium hydroxide bayerite ($\alpha\text{-Al}(\text{OH})_3$) crystallizes in monoclinic structure in the space group $\text{P}2_1/a$.⁶⁷ Similar to all crystalline $\text{Al}(\text{OH})_3$ phases it consists of layers of edge sharing AlO_6 -octahedra with hexagonal symmetry. Like in gibbsite the sheets are congruently aligned. Unlike gibbsite however, the stacking of the oxygen ions in the anionic sublattice follows a sequence AB AB AB..., i.e. each octahedral layer can be generated by simple vertical translation from the layer below. Also like gibbsite, bayerite has two crystallographically distinct Al-sites in a ratio 1:1, owing to the hydrogen bonding in and between the layers.

It was long thought that ^{27}Al NMR could not resolve the two Al sites, since they are very similar from a crystallographic point of view resulting in isotropic chemical shifts differing only slightly (9.1 and 13.1 ppm). In contrast with gibbsite, also the C_Q values of the two Al sites of bayerite are almost identical (1.9 and 1.4 MHz), leaving only the η_Q values (0.25, 0.80) to distinguish the two sites. While in double rotation (DOR) NMR experiments no resolution of the 2 sites was achieved⁶⁸, exploiting ^{27}Al 3QMAS NMR, Damodaran *et al.*⁶⁴ could resolve the two ^{27}Al NMR resonances. Quantification succeeded with quadrupolar parameters extracted from MQMAS.⁶⁴

Thermal treatment of bayerite converts it into η -alumina at $300\text{--}600^\circ\text{C}$, followed by the formation of θ -alumina at $800\text{--}1000^\circ\text{C}$, reaching α -alumina above 1100°C (Figure 1). However, a complete transformation to α -alumina without co-existing additional phases has rarely been observed by ^{27}Al NMR (as in

Figure 6).⁶⁹ This may be related to the ready conversion of bayerite into boehmite, which follows a different transition route.⁷⁰

The changes of the ^{27}Al MAS NMR spectrum upon calcination of bayerite are illustrated in Figure 7. During bayerite calcination 6-coordinated Al is converted into AlO_4 , reaching a maximum $\text{Al}_{\text{tet}}/\text{Al}_{\text{hex}}$ ratio of 50:50 at $800\text{--}900^\circ\text{C}$. Further heating decreases the AlO_4 content again. The broadening of the AlO_6 ^{27}Al MAS NMR resonance increases with temperature (from 300°C to 800°C), indicating an increased C_Q and its distribution. On calcination from 800°C to 1200°C , the mean C_Q of the 4-coordinated Al increases from 4.7 MHz to 5.5 MHz, while the C_Q of the 6-coordinated Al decreased from about 3.7 MHz to 3.0 MHz.⁷¹ In the transition sequence, the illustrated deconvolution of the spectra suggests the presence of five-coordinated Al, but NMR parameters were not reported. Ashbrook *et al.* reported ^{27}Al NMR of bayerite mechanically mixed with silicic acid.⁶³ Two-

dimensional 3QMAS experiments were carried out to resolve a third Al site at around 60 ppm corresponding to Al (IV) coordination indicating the formation of Al-O-Si bonds in tetrahedral coordination. Longer grinding also produced five-coordinated Al at the surface as shown by the ^{27}Al NMR peak at around 32 ppm. 2.2. Aluminium oxyhydroxides Despite of their quite different structures, the aluminium oxide monohydroxides diasporite and boehmite exhibit a very similar stability,⁷² with slight preference for boehmite. Both are built-up from edge and corner sharing Al octahedra, but while diasporite is a truly 3D connected octahedral framework, boehmite displays hydrogen-bonded octahedral layers (Figure 7).

2.2.1. Boehmite

Gibbsite $\searrow$

Used in the production of ceramics, as catalyst binder, catalyst support and as a flame retardant, boehmite ($\gamma\text{-AlOOH}$) is the aluminium oxyhydroxide of greatest practical interest. It is produced by hydrothermal synthesis starting from gibbsite and can also be obtained by controlled calcination of bayerite. Boehmite crystallizes in the orthorhombic space group *Amam*,

Figure 8: Structure of boehmite and diasporite

with one crystallographic site for Al and two for oxygen. It is built up from edge-sharing octahedra arranged in stepped layers, cross-linked by hydrogen bonds.⁷³ Within the octahedral layers the oxygen planes follow an ABC ABC... arrangement. However, H-bonding between Al-octahedra, causes systematic offsets within oxygen planes spanning neighbouring Al-layers (Figure 8). Boehmite exhibits severe variation of hydration level and particle size.^{74,75} With increasing water content, layer distance is slightly increased and crystallites tend to decrease in size. The resulting compound is called pseudoboehmite.⁷⁶ This flaky material has grown in only two crystallographic directions and exhibits a poorly defined X-ray powder pattern. Boehmite-like arrangement of aluminium octahedra persists within the layers.

Boehmite and Pseudoboehmite show a single ²⁷Al MAS NMR resonance with isotropic chemical shift at 12.6 ppm (Figure 9).^{69,71,77–79} From the combined analysis of the spinning side-band manifold and the 3QMAS spectrum, the range of C_Q and η_Q for boehmite were deduced as 1.8–2.8 MHz and 0.5–1.0, respectively. While the boehmite ²⁷Al CT resonance exhibits a small distribution in quadrupole couplings and chemical shifts, the pseudoboehmite resonance is significantly broadened. This renders the estimation of C_Q and chemical shift difficult. Grinding of boehmite, similar as in the case of gibbsite, has been observed to generate five-fold coordinated Al, a feature which quite often is reported also for Pseudoboehmites.⁸⁰ Upon heating, boehmite sequentially transforms into γ -alumina (500–

700 °C), δ -alumina (800–900 °C), θ -alumina (~1000 °C) and α -alumina (above 1100 °C) (Figure 1).⁶ In the delta phase the ratio Al_{tet}/Al_{hex} reaches a maximum of up to 0.6. Calcination of pseudoboehmite follows the same sequence, but phase transformations occur in broader temperature ranges. For the highly disperse and partially disordered pseudoboehmites, commonly complex mixtures of transition aluminas are obtained and, unlike boehmite, five-fold coordinated Al could be observed.⁷⁷ As boehmite can form from bayerite as well as from gibbsite by calcination, the occurrence of varying amounts of transition aluminas assigned to the boehmite pathway upon thermal transformation of both hydroxides is not surprising. As shown in Figure 9, ²⁷Al NMR is ideally suited to follow the evolution of the AlO_4/AlO_6 ratio as function of the calcination temperature.^{71,77–79} The development of 4-coordinated Al centers (δ_{iso} 70–80 ppm) starts at 300 °C. As the fraction of AlO_4 increases, the resonance of the residual AlO_6 broadens due to an increase in the distribution of its C_Q .⁶⁹ De-composition of the spectra at even higher temperatures might even reveal the presence of five-coordinated Al, especially when pseudoboehmite is used as starting material.⁶⁹ From 1200 °C onwards, only the octahedral Al of α -alumina remains.

2.2.2. Diaspore

Diaspore → α -alumina

Diaspore (α - $AlOOH$) is a naturally occurring mineral that can be obtained synthetically by hydrothermal synthesis at high temperature and pressure.⁸¹ It crystallises in the orthorhombic space group $Pbnm$ with a single Al and two O atoms per asymmetric unit.⁸² The structure consists of a hexagonally ordered, close packed oxygen sublattice with AB AB ... sequence and Al occupying octahedral sites in such a way as to generate edge-sharing ribbons which connect via corners to a 3D network. The reported ²⁷Al NMR parameters for the octahedral Al in diaspor are $\delta_{iso} = 17$ ppm, $C_Q = 3.4$ MHz and $\eta_Q = 0.8$.⁸³ Diaspore topotactically converts to α -alumina when heated in air above 500 °C, without passing through any transition phases. The structural similarity of the anionic sub lattices of diaspor and α -alumina facilitates this transformation. Tsuchida⁸¹ observed the transformation using ²⁷Al MAS NMR. The peak maximum of the AlO_6 resonance shifted about 5 ppm down-field on calcination in the temperature range 450–500 °C. In contrast to boehmite, grinding of diaspor did not result in any additional species.⁸¹ Upon vacuum dehydration however, formation of a transition alumina phase containing up to 20% of tetra-coordinated Al is reported.⁸⁴ This α' alumina phase was detected with ²⁷Al NMR and exhibits peak maxima of the hexa- and tetra-coordinated peaks at 0 and 60 ppm respectively. No other NMR parameters were reported. Interestingly, transformation from α' -alumina to corundum is catalysed by water vapour. Moist air-catalysed transformation of diaspor to

Figure 9: ²⁷Al NMR spectra of synthetic boehmite and derivatives obtained by heating at the indicated temperatures. Reproduced from ref. 69 with permission from Elsevier, copyright 2018.

α -alumina has been suggested as the reason for the absence of transition alumina's in the diasporite series.

3. Transition alumina phases

Transition alumina's typically are microcrystalline phases exhibiting a certain degree of disorder in their structure. Their complexity and disordered nature defines the reactivity of activated or partially calcined alumina hydrates, which are known to be excellent catalyst supports. Phases like χ , ρ , η and γ have ill-defined structures. This structural diversity manifests in badly resolved X-ray diffraction patterns and ^{27}Al NMR spectra making the structural interpretation complex. The NMR resonance of the six-coordinated Al sites in all the transition alumina's shows a tailing towards smaller chemical shifts. Distributions of NMR parameters like the quadrupole coupling and chemical shifts are the reason for this asymmetry. Surface species of transition alumina's can be considered as highly dynamic. Proton motion on the surface (from chemisorbed or physisorbed water) takes place at great speeds compared to bulk diffusion. This fast re-orientation of the protons randomly creates and annihilates large electric field gradients on the surface, resulting in an efficient quadrupole relaxation.

3.1. Early transition aluminas and tohdite with $\text{H}/\text{Al} \geq 0.2$

3.1.1. Rho alumina

In vacuo calcination of gibbsite at 200 °C generates a highly amorphous and disperse phase called ρ -alumina. It has rarely been characterized owing to its amorphous nature according to X-ray diffraction⁶² and it is highly sensitive towards moisture. Rho-alumina often is referred to as hydratable alumina, since contact with water converts it to a mixture of hydroxides and oxyhydroxides. In construction and building industries rho-alumina is a common additive for cements and as a bonding agent, also known as Alphabond.⁸⁵ Phenomenologically it may be described as the borderline case between a disordered oxyhydroxo compound and early transition alumina, occurring in a broad range of H/Al ratios roughly between 0.6–0.2. The ^{27}Al MAS NMR spectrum reveals three types of overlapping resonances corresponding to different Al coordinations (AlO_6 , AlO_5 and AlO_4)^{7,62}. The disorder typical for ρ -alumina can clearly be seen from the large distribution of quadrupole couplings (See Figure 10). The intensities of the AlO_4 , AlO_5 and AlO_6 resonances are approximately 25:20:55, respectively (Figure 10). The corresponding isotropic chemical shifts occur around 68, 34 and 9.8 ppm.

Meinhold *et al.*⁷ proposed a model with a random distribution of EFG's to fit the experimental line shapes exhibiting unusually

long tailings, typical for disordered alumina phases. However, a detailed analysis with a Gaussian isotropic model with Czek distribution is essential for the proper analysis of such spectra.⁴⁸ Slade *et al.* and Meinhold *et al.*,^{7,62} did not carry out the extraction of the mean quadrupole couplings of ρ -alumina,

except for those of the AlO_6 site (4.8 MHz). Rho-alumina obtained from gibbsite has been reported to convert to eta-alumina upon heating in air, which then follows the bayerite path³. Amorphous alumina³ thin films produced by atomic layer deposition often exhibit ^{27}Al NMR spectra^{86–92} similar to that of ρ -alumina, but with a population of five-coordinated Al varying with the layer thickness. If the layer thickness is of the order of a few nanometers, the ^{27}Al NMR spectra resemble ρ -alumina. For sample thickness of the order of tens of nanometers, the AlO_5 population dominates⁹⁰. The relative occupancy of different Al-O sites in films has been reported to evolve with temperature^{92,93} similar as in the gibbsite series, finally reaching α -alumina⁹⁰.

Tohdite cannot be classified as transition alumina, as it can only be synthesised hydrothermally⁷² or found in as the natural mineral akdalaite⁹⁴. Still it will be briefly discussed in this section as it displays the typical H/Al ratio of 0.2 associated with the early transition alumina and because it transforms into kappa-alumina before alpha alumina is formed, similar as observed for chi-alumina (*vide infra*). Tohdite also known as akdalaite is well

Figure 10. ^{27}Al MAS spectra (and decomposition: grey) of ρ -alumina simulated using the NMR parameters from ref. 7

Figure 11. Structure comparison of tohdite, chi, eta and gamma alumina

crystalline, shows a defined $\text{Al}_{\text{tet}}/\text{Al}_{\text{hex}}$ ratio of 0.25 and displays the same specific stacking of oxygen planes (ABCB...) encountered in kappa alumina. Though lacking disorder in site occupation and having different order of oxygen planes as the spinel-based transition aluminas eta and gamma, it also consists of alternating layers of octahedral and mixed octahedral/tetrahedral aluminium ions. No ^{27}Al study of tohdite is known.

3.1.2. Chi alumina

Gibbsite $\rightarrow \chi \rightarrow \kappa \rightarrow \alpha$ -alumina

Chi alumina is the first member of the gibbsite calcination series. It forms between 250 and 650 °C and spans a range of H/Al values between 0.9 and 0.1. Despite several efforts since the 1950's,^{1,95–99} the crystal structure of χ -alumina remains uncertain. This poorly characterized transition alumina eluded most crystallographic studies. It has a very diffuse powder X-ray diffraction pattern with few broad lines, and appears to have stacking faults or fully disordered domains. One cubic¹ and two hexagonal⁹⁸ structures have been proposed. Recently, a study combining *ab-initio* calculations, IR and X-ray diffraction⁹⁹ suggested the probability of an average hexagonal structure. Also high resolution TEM analysis supports a hexagonal arrangement.¹⁰⁰ However, all authors agree the oxygen sublattice is best described as a dense packing of oxygen planes with either a fully random stacking sequence one that is ordered only locally. Therein, tetrahedral and octahedral Al sites are both considered to be disordered, and typically in a ratio of roughly 0.3. Dimensions of one of the suggested hexagonal unit cells closely resembles tohdite and kappa-alumina, both with layer sequence ABCB...

Slade *et al.*⁷⁹ reported the ^{27}Al MAS spectrum of chi-alumina prepared by calcination of gibbsite. They observed two main resonances (peak maxima at 5.7 and 63.8 ppm), corresponding to the hexa- and the tetra-coordinated Al sites. In addition, there was a small shoulder around 40 ppm, the region where five-coordinated Al is expected.

Consequently this peak could be representing species at stacking faults. The high-resolution ^{27}Al NMR spectrum of a χ -alumina phase was reported later, along with line-shape simulations using distributions in

quadrupole parameters (Figure 12).⁸ The isotropic chemical shifts of AlO_6 , AlO_5 and AlO_4 resonances were 11.5, 38.0 and 71.5 ppm, with intensity ratios of 70.0, 7.5 and 22.5 percent respectively. The mean of the distributions of quadrupole couplings are 4.5, 2.7 and 5.0 MHz, respectively. All three resonances were simulated with an η_Q of 0.3, although small differences in η_Q did not affect the simulated line shape significantly.

3.2. Intermediate transition aluminas

Though derived from different precursors, eta and gamma alumina show some similarities,² and even have been considered identical at some point.¹⁰¹ Both are based on an anionic sublattice of ABC.. sequence, and both display a tetragonal distortion with respect to the ideal cubic fcc symmetry. Both also show disorder in the cation occupation, though with differing emphasis on tetrahedral and octahedral sites. This results in diffraction patterns, which for both are poorly resolved, and quite similar. Nonetheless, both structures are best described by defective Spinel phases with vacancies owing to their stoichiometry¹⁰², and both may contain additional protons up to a H/Al ratio of 0.2. The archetype Spinel with formula MgAl_2O_4 contains hexa-coordinated Al^{3+} and tetra-coordinated Mg^{2+} in such a way as to minimise electrostatic repulsion. This results in layers of edge-sharing Al octahedra, which are connected to layers of mixed octahedra, sharing edges with upper or lower layer, and tetrahedra, which strictly are corner-sharing. In eta and gamma alumina, tetrahedral and octahedral sites are both occupied by aluminium, which results in a defective occupation owing to stoichiometry. For both phases some occupation of nominally 'forbidden' sites is observed, which also may arise from the lower occupation of cation sites or from local twinning, i.e. local disorder in the ideal ABC stacking of oxygen planes. Owing to the similarity of the phases it is extremely difficult to distinguish them based on diffraction, unless the history of the material is known.

3.2.1. Eta alumina

ρ Bayerite $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$ -alumina

Calcination of bayerite around 300 °C produces η -alumina. On calcination, η -alumina transforms to θ -alumina, before restructuring to alpha. In the case of η -alumina, the occupation of the four-coordinated positions is fairly high, with a $\text{Al}_{\text{tet}}/\text{Al}_{\text{hex}}$ ratio of maximally 0.6. With other words, eta-alumina can be described by an idealised Spinel formula of $\text{Al}_{\text{tet}}\square_{2/3}\text{Al}_{\text{hex}5/3}\text{O}_4$, with $\square$ indicating vacancies on octahedral sites. The higher number of tetrahedral aluminium also has been postulated to explain the higher Lewis acidity compared to gamma alumina

Figure 12. ^{27}Al MAS NMR centre-band (right) of eta alumina showing (a) the experimental data, (b) complete simulation and the individual components (c) AlO_6 , (d) AlO_4 , and (e) AlO_5 . Reproduced from ref. 91 with permission from ACS, copyright 2018.

¹⁰³, an important feature of η -alumina for catalytic applications ^{103–105}.

²⁷Al NMR reports on pure-phase η -alumina are scarce, though almost all ²⁷Al NMR studies of the bayerite transition series report the η -alumina phase, which exists over a fairly large temperature range (300–600 °C). One of the initial reports was from John *et al.* ², in which the authors determined a higher Al(IV) concentration in η -alumina as compared to γ -alumina. Pecharroman *et al.* ⁷¹ observed hexa- and tetra-coordinated Al resonances with isotropic chemical shifts of around 15 and 77 ppm, respectively. The corresponding mean C_Q values were 3.9 and 4.6 MHz, with a higher η_Q for AlO₄ (0.7) than for AlO₆ (0.4). Chagas *et al.* ⁶⁹ reported the occurrence of the η -phase co-existing with θ -alumina in an even larger temperature range (300–1000 °C) when slow heating rates are applied. In this case, the intensity of the tetra-coordinated Al resonance continuously increased from 300 to 700 °C and then remained almost constant. The same authors also confirmed the often observed co-existence of eta and gamma aluminas as a result of the possibility of formation of boehmite from bayerite and the consecutive formation of gamma alumina next to the eta phase formed directly from unconverted bayerite.

3.2.2. Gamma alumina

Boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ -alumina

Gamma alumina is formed by thermal dehydroxylation of boehmite between 500–750 °C and then transforms to the delta phase with increased cation ordering. Gamma is often employed in heterogeneous catalysis and like many other aluminas its catalytic activity is affected by the crystallite size. The structure of gamma alumina (γ -alumina), the most investigated transition alumina phase, was already characterized decades ago ^{106,107}. Like eta alumina, γ -alumina crystallizes as (non-stoichiometric) spinel with some degree of disorder and may contain protons up to a ratio of H/Al of 0.2. Despite of its extensive characterisation there is still some debate on the details of the structure, but most authors agree the defect sites in gamma alumina are mostly found on tetrahedral sites, which leads to an idealised Spinel formula of Al_{tet2/3}□_{1/3}Al_{hex2}O₄, with □ symbolising vacancies on tetrahedral sites. Like for eta-alumina a tetragonal distortion to space group $I4_1/amd$ from the ideal cubic fcc packing of the anion sublattice is reported. ^{108–111} In theoretical studies, the difficulty to account for defect sites has occasionally been overcome, by simulating orthorhombic structures with full order on the cation sites. ^{112–114} *Ab initio* ²⁷Al NMR calculations found a close match using the spinel-type structure with the space group $Fd3m$ ¹¹⁵ and Al distributed in different sites as follows: Al(VI) 64%, Al(IV) 34.4% and Al(V) 1.6%. Currently the most widely accepted description of gamma alumina consists of a spinel model with partial occupation of non-spinel positions and considerable disorder next to presence of surface hydroxyl groups ⁴.

Like most transition aluminas, the surface of γ -alumina is hydroxylated to a large extent, as can be observed with ¹H MAS

Figure 13. Typical 14.1 T ²⁷Al MAS NMR spectra of unground and ground γ -Al₂O₃ unheated and heated for 15 min as indicated. (A–E) Unground; (F–J) ground. Reproduced from ref. 67 with permission from Elsevier, copyright 2018.

NMR. ^{14,56} A combined theoretical and NMR study revealed that the chemical shift and quadrupole coupling of ²⁷Al in γ -alumina strongly depend on the extent of surface hydroxylation. ¹¹⁶ Unlike the related eta-alumina, gamma alumina frequently shows the presence of five-fold coordinated aluminium. In a ²⁷Al NMR study, Slade *et al.* ⁷⁹ proposed the presence of the penta-coordinated species as reason for the crystallographic distortion in gamma alumina. However, usually Al(V) species are assumed to arise from surface species. Disorder and related presence of 'non-spinel' species are considered to provide only a negligible number of five-coordinated Al. This is supported by the observation that mechanical milling, diminishing the particle size, can increase the fraction of 5-coordinated Al up to 20% ¹¹⁷. From this perspective Al(V) content can be used as a measure of activated surface area or, in other words, a measure for particle size. The 5-coordinated Al was suggested to be responsible for the thermal instability of γ -alumina ¹¹⁸. γ -alumina can be also produced from the calcination of Pseudoboehmite. ⁷⁷ In this case the material displays higher surface area and a higher fraction of five-coordinated Al. Mechanical grinding of γ -alumina also facilitates its thermal transformation to α -alumina. While α -alumina was formed at 1000 °C from ground γ -alumina, 1200 °C was necessary for the unground sample (Figure 13) ⁷⁸. High-energy mechanical milling alone is enough to convert γ -alumina to α -alumina, as shown in the ²⁷Al NMR study of Düvel *et al.* ^{117,119}

Figure 14. Structure comparison of kappa, delta and theta alumina

gamma alumina, or if the other, less studied early transition aluminas like eta and chi show similar diversity.

3.3. Late transition aluminas with $H/Al < 0.1$

Progressing the calcination to higher temperatures, the X-ray diffraction signatures observed along all different pathways towards alpha alumina show increasing resolution. While the early transition aluminas all show disorder in Al distribution and in the case of chi-alumina also in the oxygen sublattice, the late transition aluminas all can be satisfactorily described by ordered structure models. All late transition aluminas have an increased amount of tetrahedral Al-species compared to their early transition counterparts, before the Al_{tet}/Al_{hex} decreases again to reach zero during final reconstruction to the alpha phase.

As evidenced by the above mentioned studies, the detailed history of a given γ -alumina strongly impact the relative populations of its Al-sites and in turn also its properties like surface area, Lewis acidity, and transformation behaviour. For example, an alumina species "Super5" known for its activity and acidity exhibits chemical shifts similar to γ -alumina, but has a very high percentage ($\sim 35\%$) of Al(V)^{120,121}. A recent paper on the ^{27}Al NMR of highly porous γ -alumina, however, did not observe any significant amount of Al(V)¹¹⁰. Tungsten oxide (WO_x) impregnated γ -alumina lacks the penta-coordinated Al sites immediately on increasing the loading. Most probably anchoring of WO_x on the surface of γ -alumina occurs preferentially at the penta-coordinated surface sites.. In addition, multiplicities of both hexa- and tetra-coordinated Al sites have been observed as a function of WO_x concentration, as has been proven by ^{27}Al MAS and 3QMAS experiments¹²². In short, in the case of γ -alumina a regular ratio of Al populations at different Al-O coordination cannot be predicted as it depends too heavily on the synthesis conditions.

Gamma alumina is the most studied transition alumina. So it remains unclear if the manifestation of so varying properties is typical for

3.3.1. Kappa alumina

$Gibbsite \rightarrow \chi \rightarrow \kappa \rightarrow \alpha$ -alumina

Kappa alumina is obtained by thermal treatment of χ -alumina or of tohdite and is observed in a temperature range between 650 and 1000 °C. With tohdite kappa alumina shares the same

Figure 15. ^{27}Al NMR spectra of κ - Al_2O_3 : (a) MAS spectra at 7.0 and 11.7 T; (b) 3Q MQMAS spectra at 7.0 T. The very distorted site Al(2) is only visible at the higher field in MAS while the Al(1), Al(3) and Al(4) sites are fully resolved in the MQMAS spectrum. Reproduced from ref.¹¹⁴ with permission from RSC, copyright 2018.

anionic sublattice with ABCB... sequence of oxygen planes, but with different cation distributions. Ollivier *et al.* determined the crystal structure with X-ray diffraction, electron microscopy and ^{27}Al NMR,¹²³ and described it in the orthorhombic space group $Pna2_1$.^{123,124} Four non-equivalent Al and six non-equivalent O atoms construct the unit cell. Of the four Al-sites one is in tetrahedral coordination (Al3), the other three (Al1, Al2, Al3) reside in distorted octahedral environment, which arises from slight vertical displacement of oxygen in the anion sublattice. In the case of kappa alumina Al1 is quite regular, while Al2 and Al4 show severe distortion. Based on the shortest bond length in each octahedron this results in nominal coordination numbers of roughly 6 for Al1, 5+1 for Al4, and 4+2 for Al2. All three sites have been resolved by MAS and 3QMAS NMR (Figure 15).¹²³ Compared to other transition alumina phases, reported C_Q values for κ -alumina appear very small, possibly owing to discrepancies in reporting quadrupole parameters in Ref¹²³.

However, if the reported values were quadrupole frequencies (η_Q) instead of C_Q 's, then they are in agreement with the *ab initio* calculations reported in Ref ¹¹⁵. While Al1 and Al4 showed C_Q values of 3.33 and 5.67 MHz, respectively, the Al2 site was estimated to exhibit values higher than 6 but less than 10 MHz. The tetra-coordinated Al resonance was analysed with a C_Q of 5.07 MHz and an η_Q of 0.3. In a combined XRD, XPS and NMR study, Malki *et al.* ⁹ have estimated the ratio of Al_{tet}/Al_{hex} in κ -alumina to be 27%, which is below the ideal ratio according to the proposed structure (33%). The same authors also pointed out that XPS analysis of kappa as well as chi alumina revealed a nonstoichiometric excess in Al versus oxygen and related both observations to the large surface area of the highly dispersed materials.

3.3.2. Delta alumina

Boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ -alumina

In a similar temperature range where chi alumina turns into the more ordered kappa form, also the diffraction pattern of gamma alumina sharpens, indicating increasing regularity. This new phase, called delta-alumina, emerges around 800 °C before further transforming to the theta phase around 950 °C.^{107,125} In delta alumina the ABC... stacking of oxygen planes already present in gamma alumina is retained. The cations show significantly higher degree of order compared to its gamma predecessor. All structure models for delta alumina are based on superstructures of the Spinel type. Originally a tetragonal structure was proposed in 1961¹²⁶, but nowadays intergrowths of at least two structurally related (pseudo)orthorhombic forms, are accepted as good description of delta alumina¹²⁷. A recent study combining XRD, TEM and DFT calculations used two representative models, described in space groups $P212121$ (delta1) and $P21$ (delta2; pseudo-orthorhombic). Similar as in gamma alumina, both structures show layers of edge-sharing octahedra, alternating with mixed hexa/tetra-coordinated layers in a densely packed oxygen sublattice with ABC... sequence. Occupation of cation sites is explicit within the ordered domains and without vacancies. Combination of both structure models described the TEM observation well and suggested a Al_{tet}/Al_{hex} ratio as high as 0.6, which is in rough agreement with experimental data. The study also demonstrated the enthalpy of formation of these variants are very similar to θ -alumina, which explains the common observation of delta next to the theta phase in the boehmite calcination series¹²⁷.

There are only a few ²⁷Al NMR spectra of pure δ -alumina available in literature. MacKenzie *et al.* ⁷⁸ followed the formation of δ -alumina (1000 °C) in the boehmite series. They observed a clear δ -alumina XRD pattern and reported two ²⁷Al MAS NMR resonances, corresponding to hexa- and tetra-coordinated Al, with intensity maxima at 8 and 68 ppm, respectively. The corresponding Al population ratio was estimated to be approximately 60:30. Similar NMR

characteristics were displayed by δ -alumina produced by directly heating γ -alumina at 1000 °C. However, the δ -alumina phase according to XRD was completely absent when ground (1h) boehmite or γ -alumina was calcined⁷⁸, although this may have been due to an extremely small particle size⁷⁸. ²⁷Al MAS NMR spectra of a gel of hydrolysed $Al(OPh)_3$ fired at 900 °C was interpreted as δ -alumina, based on the high content of Al tetrahedra¹²⁸. Pecharroman *et al.* ⁷¹ also observed the high ²⁷Al tetra/hexa coordination intensity ratio upon calcination of boehmite calcination at 950 °C, and estimated the corresponding isotropic chemical shifts (14, 77 ppm), C_Q 's (5.1, 3.3 MHz) and η_Q 's (0.7, 0.4). The relative Al populations in the reported δ -alumina spectra seem to be consistent, although the unambiguous synthesis appears to be dependent on optimum crystallite sizes of the precursor. A recent paper reported ²⁷Al 3QMAS NMR experiments (Figure 16) on nano-crystalline alumina which has mixed γ -, δ - and θ -phases. In combination with calculated shift predictions and 1D line-shape decompositions, the 3QMAS NMR experiments helped to

Figure 16. Simulated ²⁷Al NMR spectrum (and decomposition: grey) of δ -alumina using the NMR parameters from ¹²⁹).

resolve the different species evolved at different temperatures, for varying crystallite sizes. In the mixture, however, the transformation to α -alumina did not occur at 1100-1200 °C, but took place later, at 1300 °C¹²⁹.

3.3.3. Theta Alumina

Theta alumina is the common late transition alumina in the series starting from bayerite and boehmite. In the former it arises from eta, in the latter from delta alumina, in temperature ranges of 800-100 °C and 900-1000 °C, respectively. Like its precursors it shows ABC... ordering of the oxygen planes and it clearly follows the trend of increasing order with increasing temperature, observed for all calcination pathways. Owing to

its high crystallinity and clear X-ray diffraction pattern, its structure was reported as early as 1957¹³⁰ and found isostructural to beta-Ga₂O₃. Theta crystallises in monoclinic

Figure 17. ²⁷Al MAS NMR simulations of the sol-gel prepared alumina sample annealed at 1200 °C recorded at (a) 8.45 T and (b) 14.1 T. The top lines show the experimentally obtained spectra, the middle lines are the simulated spectra, and the bottom lines show the individual simulated peaks. Reproduced from ref. 123 with permission from Elsevier, copyright 2018.

symmetry with space group *C2/m*, and contains alternating layers of hexa- and tetra-coordinated Al in a ratio $Al_{tet}/Al_{hex} = 1$. Syntheses of theta-alumina from bayerite or boehmite both rarely yield pure-phase θ -alumina. Similar enthalpies of delta alumina make it a common side-phase at temperatures up to 950 °C and small amounts of α -alumina phase may be present as an impurity already below 1000 °C. Slade *et al.* observed this effect with ²⁷Al MAS NMR.⁷⁹ Overlap between six-coordinated Al resonances from α - and θ -alumina, prevented confirmation of the expected equality of Al(IV) and Al(VI) content without detailed spectral decomposition. In the bayerite series, however, the θ -alumina -phase starts to form already at lower temperatures (900–1000 °C). Consequently, bayerite-derived θ -alumina provides a higher chance to allow observation of its 1:1 distribution of AlO₆ and AlO₄ with NMR. This effect can be seen in the ²⁷Al NMR spectra of the transition alumina series reported by Pecharrroman *et al.*⁷¹ The decomposition and the quantification of the θ -alumina spectra at different magnetic fields were carried out by O'Dell *et al.* (Figure 17)¹³¹. C_Q values obtained from the deconvolution were 6.4 and 3.5 MHz for AlO₄

and AlO₆ species, respectively, while the corresponding η_Q values were 0.65 and 0.00. Isotropic shifts were 80 and 10.5 ppm for AlO₄ and AlO₆, respectively. These parameters are in very good agreement with the parameters obtained from *ab initio* calculations¹¹⁵.

4. Alpha-alumina

The final outcome of a calcination of any precursor consisting of Al, O, and H beyond 1350 °C is α -alumina. Alfa alumina has the same structure as naturally occurring corundum. Many precious stones like rubies or sapphires exhibiting bright colours are corundum single crystals with isomorphic substitution of Al with Fe or Cr. Synthetic single crystals of corundum are used as substrates for epitaxial growth of superconductors and semiconductors. The microcrystalline α -alumina obtained by calcination of aluminium (oxy) hydroxides is widely used as catalyst supports, porcelain, advanced ceramics manufacture, refractories and abrasives and also as source for aluminium metal.¹³²

Figure 18. The crystal structure of α -alumina (Al in blue polygons and O in red)¹⁵⁶.

Figure 19. ²⁷Al (130.3 MHz) MAS NMR spectra of α -alumina, $\nu_r = 7500$ Hz. (a) Experimental spectrum. (b) Simulated spectrum using the experimental parameters $C_Q = 2.38$ MHz and $\eta = 0.00$.

Figure 20. Tree plot of alumina structural transformations and associated changes in the NMR spectra from the hydroxide and oxyhydroxide precursors to α -alumina phase. The monoclinic and orthorhombic alumina species were identified relatively easily, while the others have either a disordered structure or an amorphous nature.

Alpha alumina is the most stable Al_2O_3 phase and its structure has first been reported by Linus Pauling in 1925.¹³³ The structure differs from phases discussed above, in the presence of face-sharing octahedra and shows the highest symmetry in space group $R\text{-}3c$, with one Al and one O site. The structure can be described as being composed of layers of octahedra, similar as encountered in the $\text{Al}(\text{OH})_3$ phases, but stacked in such a way that alternating pairs of face sharing octahedra are formed where the layers are merged. The oxygen sublattice follows hcp packing ABAB. This implies that upon transformation of late transition aluminas derived from the gibbsite, bayerite, and boehmite series, i.e. kappa, and theta alumina, the materials not only have to change cation arrangement but also need to re-construct the anion sublattice. Transformation of these occurs at quite high temperatures usually above 1000 °C.

Calcined diaspore, which shares the same oxygen arrangement as alpha alumina has been observed to already show the presence of alpha alumina at temperatures as low as 600 °C.⁸⁴ As the crystal structure contains a single crystallographic Al site, α -alumina is expected to have a single resonance in its ^{27}Al NMR spectrum. The first ^{27}Al NMR spectrum of α -alumina was reported by Pound,¹³⁴ who deduced a C_Q of 2.39 MHz from single crystal NMR investigation. Huggins and Ellis put forward the structural models for the surface of several alumina materials including α -alumina in a ^{27}Al static NMR study. However, one of the first reports on quantitative ^{27}Al MAS NMR spectroscopy of $\alpha\text{-Al}_2\text{O}_3$ together with line shape simulations was from Jakobsen *et al.*¹³⁵ They observed the central ($m_{+1/2} \leftrightarrow m_{-1/2}$) transition and the satellite transitions ($m_{\pm 3/2} \leftrightarrow m_{\pm 1/2}$ and $m_{\pm 5/2} \leftrightarrow m_{\pm 3/2}$) corresponding to a single octahedral Al-site. Accurate estimations of C_Q (2.38 MHz) and η_Q (0.00) were carried out for a rather symmetric octahedral environment. Even though a broadening due to the second-order quadrupole interaction was proposed, the central transition (CT) resonance was fairly featureless, lacking the characteristic pattern for an axially symmetric system. An isotropic chemical shift of 12.7 ppm was determined after considering the quadrupole-induced shift correction. These values were later confirmed by Skibsted *et al.*¹³⁶ in a study mainly focused on the simulation of the satellite transition (ST) manifold in the ^{27}Al spectrum of α -alumina (Figure 19).

The ^{27}Al spin-lattice relaxation (SLR) behaviour of α -alumina and the quantitative excitation using radio-frequency (RF) pulses were carefully studied by Kentgens *et al.*¹³⁷ Crushed synthetic single crystal samples showed extremely long SLR times compared to natural corundum, which might contain paramagnetic impurities. To measure accurate SLR times, an adiabatic passage was realized by frequency stepping, ensuring proper inversion of the CT and ST magnetization. The influence of the length of the RF pulses on the selective excitation of CT or ST was also discussed. Most literature mentioned in this section showed some disagreements on the ^{27}Al isotopic chemical shift of α -alumina, mostly due to the difficulty to correct for quadrupole-induced shifts. However, by now it has been generally accepted to be in the range of 13.5–16 ppm. Mechanical crystallite size reduction in α -alumina was reported to increase distributions in electric field gradients with the help of ^{27}Al MAS and 3QMAS NMR experiments. Upon size reduction from 52 nm to 12 nm, an up-field shift of about 4 ppm was observed at the peak maximum, but no additional Al coordination beside the octahedral one could be detected.¹³⁸

5. Tabulation and correlation of NMR parameters

The structural transformation in transition alumina series occurs with severe reorganization of atoms driven by the thermal dehydroxylation process. The most stable alumina phase, alpha has a hexagonal-rhombohedral structure. The phases gamma and eta have similar (cubic disordered spinel) structures. Other stable alumina or precursor phases are either monoclinic or orthorhombic. The rest of the phases are with either amorphous or with disputed structures (Figure 20).

The experimentally determined NMR parameters of aluminium hydroxides and oxyhydroxides and transition alumina phases reported in most recent and reliable literature are collected in Table 2. Table 2 reports the most recently reported NMR parameters. Some phases possess site multiplicity with same coordination number, as explained in the presentation of the different phases above. Moreover, there is a spread of these NMR parameters due to the physical conditions of the investigated samples (particle size, humidity, pH etc.). Ellipsoid graphs presented in Figure 21 are more suited to include the distributions in reported ^{27}Al NMR parameters of transition alumina phases.

The three-dimensional ellipsoid plots (Figure 21) correlate the most important NMR parameters of ^{27}Al NMR of alumina, namely the isotropic chemical shift (δ_{iso}) quadrupole coupling constant (C_Q) and the asymmetry parameter (η_Q). All the three Al-O coordination types (tetra-, penta- and hexa-) were considered for these graphs. These 3D-plots provide important information, which eventually leads to easy identification of an alumina phase under analysis.

The following strategy is proposed to use the 3D ellipsoid plots for identifying an alumina phase. All transition alumina phases have tetra-coordinated Al. The left plot in Figure 21 provides the NMR parameter correlations of the tetra-coordinated Al. As the first step, one may explore one parameter at a time, like chemical shifts alone. Additional screening through quadrupole coupling constants and asymmetry parameters gives clear indication of the phase. These parameters are useful to add extra-resolution to the 1D ^{27}Al spectrum under analysis. The 2D-projections of the 3-D figures (See Supplementary information) will be helpful in detailed investigations. The same strategy can also be applied to the hexa-coordinated Al and further on to penta-coordinated Al. The $\text{Al}(\text{OH})_3$ and AlOOH precursors have large distributions of NMR parameters of hexa-coordinated Al. Gibbsite and bayerite have two hexa-coordinated Al sites each, adding to the spread of the ellipsoid. Similarly, reports on the boehmite quadrupole parameters show distributions. Transition alumina phases show a smaller spread of NMR parameters of hexa-coordinated Al. None of them have tetra-coordinated Al. Therefore, one can concentrate entirely on the Al(VI) plot for the phase identification of transition aluminas, which show high-resolution in the 3D-representation. An exception is κ -alumina, with multiple AlO_6 sites. However, the lower chemical shifts of these sites separate it from the other alumina phases. Only three alumina phases show five-coordinated Al, namely γ , χ and ρ -alumina. The observation of this Al species in the alumina under analysis brings in an additional advantage in the identification process.

Table 2. ^{27}Al solid-state NMR parameters of transition alumina phases and their precursors. The spread of the parameters are represented in the ellipsoid plot of Figure 21.

Material	^{27}Al MAS	^{27}Al MQMAS	Coordination (occupancy)	δ_{iso} / ppm	C_Q / MHz	η_Q	Ref.
gibbsite			$\text{Al}_{\text{hex}(1)}$ (50%)	11.3	2.2	0.7	61
			$\text{Al}_{\text{hex}(2)}$ (50%)	13.6	4.6	0.4	
bayerite			$\text{Al}_{\text{hex}(1)}$ (50%)	9.1	1.9	0.25	64
			$\text{Al}_{\text{hex}(2)}$ (50%)	13.1	1.4	0.80	
boehmite			Al_{hex} (100%)	12.6	1.8-2.8	0.5-1.0	64
diaspore			Al_{hex} (100%)	17.0	3.4	0.8	83
α -alumina			Al_{hex} (100%)	13.5	2.38	0.0	131
				16.0	2.40	0.05	138
ρ -alumina			Al_{hex} (30-55%)	9.8 ^b	4.8	0.6 ^b	7
			Al_{pent} (20-50%)	34.0 ^b	4.5 ^b	0.6 ^b	
			Al_{tet} (25-15%)	68.0 ^b	5.6 ^b	0.6 ^b	
χ -alumina			Al_{hex} (70-75%)	11.5	4.5	0.3	8
			Al_{pent} (5-10%)	38.5	2.7	0.3	
			Al_{tet} (20%)	71.5	5.0	0.3	
γ -alumina			Al_{hex} (70-40%)	10.0	5.1	0.31	120
			Al_{pent} (0-20%)	44.0	3.55	0.00	
			Al_{tet} (30-60%)	71.5	5.1	0.19	

Material	^{27}Al MAS	^{27}Al MQMAS	Coordination (occupancy)	δ_{iso} / ppm	C_Q / MHz	η_Q	Ref.
δ-alumina			Al_{hex} (70-55%)	15.2	3.6	0.4	71
			Al_{tet} (30-45%)	78.5	4.7	0.7	
θ-alumina			Al_{hex} (50%)	10.5	3.5	0.0	131
			Al_{tet} (50%)	80.0	6.4	0.65	
η-alumina			Al_{hex} (80-50%)	14.5-15.1	3.9	0.4	71
			Al_{tet} (20-50%)	76.5-77.5	4.5-4.7	0.7	
κ-alumina			$\text{Al}_{\text{hex}(1)}$ (25%)	0.0	3.33 ^a	0.33 ^c	123
			$\text{Al}_{\text{hex}(2)}$ (25%)	5.0	5.07 ^a	0.33 ^c	
			Al_{V+I}^d (25%)	4.4 ^c	>10 ^a	0.77 ^c	
			Al_{tet} (25%)	68.5	5.67 ^a	0.3	

^a assuming the reported values in Ref ¹²³ are quadrupole frequencies ν_Q ; ^b estimated from the spectra shown in Ref ⁷; ^c predicted by *ab initio* calculations ¹³⁹ and deduced from the experimental spectra ¹²³; ^d Al2 site having five regular and one elongated Al-O bond.

Figure 21. Plots of ^{27}Al NMR parameters (isotropic chemical shift, quadrupole coupling constant and asymmetry parameter) of tetra-, penta- and the hexa- Al-O coordinations in transition alumina phases (α , χ , κ , θ , γ , δ , η , ρ) and their precursors (bayerite (Ba), boehmite (Bo) and gibbsite (G) and diasporite (D)). 2D projections of all graphs are available in the Supplementary Information (Figures S1 – S3). The phase κ also has an additional highly distorted V+1-coordinated site with a high quadrupole coupling of around 10 MHz (See Supplementary Information Figure S4).

This 3D-ellipsoid representation of NMR parameters is a much more powerful tool for phase identification as compared to diffraction methods, especially for complex and rather X-ray amorphous transition alumina phases like ρ , χ or η -alumina. All those phases are sufficiently resolved in the correlation plots of NMR parameters. The three ellipsoid plots in Figure 21 introduce significant resolution to the NMR data to enable unique identification. That makes this method equivalent to other application fields of NMR spectroscopy for analytical purposes, like high-throughput ^1H or ^{13}C NMR spectroscopy of organic compounds with signature peaks uniquely assigned to chemical functions.

6. Quantum chemical calculations of NMR parameters of alumina

Although ^{27}Al NMR is highly sensitive, elucidating chemical and physical nature of the local crystal structures of aluminium-containing solids, requires an updated state of the art of coupling quantum calculations to NMR data. NMR data are average over the sample in time and space, with different time windows than diffraction methods. Therefore modelling can assess the plausibility of a structural set of models by producing computed NMR observables as a way to validate the most probable model. By considering both the quality of the agreement and the number of parameters required to reach such an agreement a Bayesian probability can be attached to the model selection. A deeper understanding of the system can be obtained from this additional input from quantum structure calculations. The recent developments in first-principles calculations of NMR parameters are found to be adequately complementing NMR experimental data. The chemical shielding and quadrupole interaction parameters derived from such calculations establish the unique relationship between the NMR data, quantum chemistry and structural environment. Density functional theory (DFT) remains as the basis for shielding and EFG tensor calculations for solids. A DFT based algorithm known as gauge-including projector augmented wave (GIPAW)¹⁴⁰ is one of the most successful methods to predict NMR parameters. There are several examples in literature which use DFT-GIPAW with the generalization of plane wave basis sets and pseudopotentials to calculate ^{27}Al NMR parameters and simulate NMR spectra^{141–144}. This approach is highly useful for exploring the NMR characterization of transition alumina systems, unlike aluminosilicates where periodic molecular origin of NMR parameters make more sense, starting from different alumino siloxy cluster units¹⁴⁵. However, studies

comprising quantum chemical NMR calculations on all alumina phases are still missing in literature.

Force field calculations are also employed to obtain NMR parameters¹⁴⁶. Mostly they are used for molecular systems, along with molecular modelling, predicting potential energy landscapes in molecular dynamics (MD) simulations. NMR chemical shift of bonded systems is the parameter which is usually estimated in such exercises. However, a modification known as Clay force field (ClayFF) has been developed to extend the applications to non-bonded systems, like in binding molecules (like water) or ions¹⁴⁷. Using ClayFF calculations, largely hydrogen-bonded systems like gibbsite and boehmite were studied with MD simulations^{148,149}. But the extraction of NMR parameters is still preferred with the help of DFT calculations. Nowadays, different DFT methods are implemented in popular software packages such as WIEN2K¹⁵⁰ and CASTEP¹⁵¹ which yield extremely accurate NMR chemical shielding and quadrupole interaction parameters.

One of the initial investigations was from Choi et al.¹⁵² exploring α -alumina and θ -alumina structures and predicting NMR shielding and EFG tensors using ab initio calculations. The calculations for the α -alumina model obtained ^{27}Al δ_{iso} of 16.66 ppm, C_Q of 2.09 MHz and η_Q of 0.00. For θ -alumina, the four and six coordinated Al sites were predicted to have δ_{iso} of 79.46 and 11.3 ppm, C_Q of 6.03 and 3.15 MHz and η_Q of 0.37 and 0.23, respectively. These values were close to the experimental NMR parameters. Also, gibbsite and bayerite structures were subjected to ab initio calculations obtaining shielding and quadrupole coupling values close to experimental data⁶⁴. However, improvements in the field of DFT-GIPAW calculations facilitated data with better agreements to experimental data. Generalized gradient approximation (GGA) was implemented using Perdew-Burke-Ernzerhof (PBE)¹⁵³ exchange correlation functional for the studies of alumina structures. Lizarraga et al.¹³⁹ calculated NMR parameters for some of the most ordered alumina phases (α , θ , κ and γ alumina) with high accuracy. A comprehensive study by Ferreira et al.¹¹⁵ used PBE, revised PBE¹⁵⁴ and van der Waals density [19] functionals to extract precise values for NMR parameters of α , θ , κ and γ alumina, gibbsite and boehmite. These are the results which have the best agreements with the experimental data until now. For κ -alumina, the chemical shift and quadrupole coupling values obtained in this study remain as the most important reference, as the NMR experimental efforts did not analyze the results properly.

Furthermore, the DFT studies of ^{27}Al NMR parameters focused on the surface of alumina phases, especially of γ -alumina. Modelling the surface of alumina was not trivial, with the presence of penta-coordinated Al, dangling bonds, surface-hydroxyls and hydrogen bonds. However, the effect of surface on the NMR spectra was mostly limited to the intensity of the AlO5 resonance showing up in between 20 and 50 ppm. Recently, Wischert et al.¹¹⁶ have shown that the selective cross-polarization from the hydroxyl protons in the surface can improve the sensitivity of the surface aluminium species, with the support of first principles calculations in periodic boundary conditions. It was shown that very high ^{27}Al quadrupole

couplings (>30 MHz) are possible with very low concentration of hydroxyls on the surface, as it leads to highly asymmetric surface structures. In another effort to model different γ -alumina surfaces to do DFT calculations, the chemical shift of penta-coordinated Al was predicted to be between 32 and 39 ppm¹²². But in a DFT study involving χ and η alumina, the experimental and theoretical correlation of ^1H and ^{27}Al chemical shifts showed that the surface terminal hydroxyls of these phases are linked to tetra-coordinated Al¹⁵⁵.

Conclusions

A literature overview on ^{27}Al NMR studies of known transition alumina phases reveals the strength of this spectroscopy for disentangling the different phases and their transitions. A library of NMR spectroscopic fingerprints of the different phases is provided. Some structural disorder is always present in transition alumina phases. For disordered materials, NMR can further structural characterization compared to diffraction methods. The different kinds Al-O coordination can be sorted with high accuracy and in quantitative mode. Analysis of the nuclear quadrupole interaction provides insight in deviations from spherical symmetry and their distribution across the crystal structure. The nature and relevance of alumina surface and the dependence of physical properties of the material on the surface is reflected in the NMR spectra. A high contrast between disordered, amorphous and periodic and aperiodic parts of samples allows to characterize on the same footing periodic, amorphous or ill-crystalline, as well as intrinsic coexistence of periodic and disordered situations.

Most of the NMR investigations date a few decades back. There have been remarkable improvement on solid-state NMR since, both methodologically and technologically. There are still several transition alumina phases with poorly described structure, the elucidation of which will benefit from the application of recent NMR advances. A complete NMR characterization of all transition alumina phases with high-resolution methods and extraction of parameters using a unified model which takes the inherent disorder into account, is now feasible. ^{27}Al NMR is obviously the most suited method for studies of transition alumina synthesis and transformation.

Conflicts of interest

There are no conflicts to declare.

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