Revisiting Edge-Sites of γ -Al₂O₃ Using Needle-Shaped Nanocrystals and Recoupling-Time Encoded $\{^{27}\text{Al}\}$ - ^1H *D*-HMQC NMR Spectroscopy

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ABSTRACT: Despite being widely used in numerous catalytic applications, our understanding of reactive surface sites of high surface-area γ -Al₂O₃ remains limited to date. Recent contributions have pointed towards the potential role of highly reactive edge-sites contained in the high-field signal of the ^1H -NMR spectrum of γ -Al₂O₃ materials. This work combines the development of needle-shaped γ -Al₂O₃ nanocrystals having a high relative fraction of edge sites with the use of state of art solid-state NMR – ^1H - ^1H Single-Quantum (SQ) Double-Quantum (DQ) and Arbitrary-Indirect-Dwell (AID) dipolar Heteronuclear Multiple Quantum Coherence (*D*-HMQC) – to

significantly deepen our understanding of this specific signal. We identify two distinct hydroxyl sites which possess altered isotropic chemical shifts, different positions within the dipole-dipole network and distinct proximities to different aluminum surface sites. Moreover, the use of recoupling-time encoded *D*-HMQC data allows us to partially revise previous assignments of *D*-HMQC data of γ -Al₂O₃ materials. While previous work has ascribed the high-field signal to be correlated to a single four-coordinate Al-site with substantial quadrupolar broadening we can identify the presence of two four-coordinate Al-sites with similar isotropic chemical shifts but different quadrupolar coupling constants. Recoupling-time-encoded data are thus able differentiate sites that would otherwise only be achievable with access to multiple fields or usage of highly advanced NMR techniques.

1. INTRODUCTION

Among all high surface area transitional alumina, the gamma-polymorph (γ -Al₂O₃) has received an outstanding research interest within the last decades. Although being used in numerous catalytic applications,¹ the bulk structure of γ -Al₂O₃ remains unsolved, limiting understanding of catalytically relevant surface sites such as reactive hydroxyl species or Lewis acidic aluminum

centers becomes especially challenging.² Density functional theory (DFT) calculations for surface sites of γ -Al₂O₃ emphasize the dependence of spectroscopic signatures on the relative exposure of specific crystal facets^{3,4,5} and thus the morphology of the studied γ -Al₂O₃ material. While these studies are mainly centered around the predominantly exposed (110), (100) and (111) facets, Busca and co-workers have pointed only recently towards the potential role of edge and corner sites, more specifically the (100)/(110) edges, of γ -Al₂O₃ within this scheme⁶. In a combined experimental and computational work, Batista and co-workers provide further evidence for the presence of specific edge features by comparing the solid-state ¹H-NMR magic angle spinning (MAS) spectra of two morphologically distinct γ -Al₂O₃ materials.⁷ These findings demonstrate the outstanding potential of NMR studies on γ -Al₂O₃ materials possessing well-defined morphologies with high edge-to-surface ratios to significantly broaden our understanding of γ -Al₂O₃ surface sites. As it dictates the final shape of the γ -Al₂O₃ material by topotactic transformation, controlling the boehmite growth is of prime importance and in the recent years, great advances have been made to better understand how parameters such as pH⁸⁻¹¹ or ionic additives^{10,12-14} influence the morphology of boehmite crystallites. However, boehmite and thus γ -Al₂O₃ materials were previously mainly tailored towards exposure of specific facets, while little attention has been paid to their fraction of edge sites.

Here, a tailored γ -Al₂O₃ support with a needle-shaped morphology and thus high proportion of edge sites is prepared by using dodecanoic acid as a structure directing agent (SDA) during the synthesis of the Boehmite (γ -AlO(OH)) material. As evidenced by IR and NMR spectroscopy, our support displays discrete OH groups including those that have been attributed to edge features. Using recoupling-time encoded and thus “pseudo-3-dimensional” $\{^{27}\text{Al}\}$ -¹H Arbitrary-Indirect-Dwell dipolar Heteronuclear Multiple Quantum Coherence (AID *D*-HMQC)¹⁵ spectra enables us

to refine the results of previous NMR studies on γ -Al₂O₃ materials and to further disentangle the components of broad aluminum signals without the need for advanced pulse sequence engineering or access to multiple magnetic fields. In combination with findings from ¹H-¹H Single-Quantum (SQ) Double-Quantum (DQ) spectroscopy, we can significantly deepen our understanding of the potential edge-sites of γ -Al₂O₃ by resolving two sites within the high-field signal and identifying surface-Al sites in their proximity. Overall, we demonstrate a robust yet simple methodology for the NMR characterization of pristine γ -Al₂O₃ materials and provide a novel basis for potential further computational and experimental studies.

EXPERIMENTAL SECTION

Experimental details of material preparation and solid-state NMR measurements are provided in the Supporting Information (Section S1 and S2).

RESULTS AND DISCUSSION

Synthesis of Needle-Shaped γ -Al₂O₃ Nanocrystals

With the aim to investigate the role of sites on the (100)/(110) edge of alumina using solid-state NMR, the possibility of increasing the aspect ratio of hexahedral nanocrystals and thus the proportion of edge over surface sites was explored. In general, acidic conditions favor formation of hexahedral Boehmite nanorods while platelet-like morphologies are obtained in basic regimes. Ionic additives can further fine-tune these morphologies via adsorption and thus anisotropic suppression of crystal growth. A previous study employing long alkyl chain carboxylic acid as

modifiers during the hydrothermal treatment of boehmite nanoparticles has shown the ability of carboxylic acid to suppress the growth along the shorter axis, namely the (010) and (001) facets of boehmite through surface capping¹³, generating narrow hexagonal shaped boehmite crystallites. In this work, building on previous studies,¹⁶ we chose dodecanoic acid as the long chain carboxylic acid (C_{12}) in combination with aluminum basic acetate as the aluminum source in a 0.5 molar ratio (C_{12}/Al). Hydrothermal treatment performed at 160 °C for 48 hours, results in the formation of needle-shaped $\gamma-Al(OOH)$, confirmed by powder XRD and TEM (Figure 1). This synthetic procedure provides a simple and robust route for the formation of homogeneously distributed needle shape $\gamma-Al(OOH)$ nanocrystals. Further topotactic transformation of the material by calcination at high temperature and dehydroxylation at 500°C leads to the formation of morphologically defined, needle-shaped $\gamma-Al_2O_{3-500}$, a suitable candidate for in depth characterization of well-defined $\gamma-Al_2O_3$. We will refer to this material as Needle- Al_2O_{3-500} throughout the following discussion.

Figure 1. Crystal phase and morphology were verified at the boehmite ($\gamma\text{-Al(O)(OH)}$) stage (b, d) and after calcination to $\gamma\text{-Al}_2\text{O}_3$ (c, e) using powder X-ray diffraction (P-XRD) and transmission electron microscopy (TEM). Since boehmite transforms into $\gamma\text{-Al}_2\text{O}_3$ in a topotactic manner, the needle-shaped morphology of the nanocrystals is retained upon calcination. For the P-XRD of Boehmite the miller indices of the respective crystal planes are indicated for the individual reflections to simplify comparison with the standard reflection pattern. The morphology was tailored by using dodecanoic acid in the synthesis (a) .

^1H NMR and IR Studies of Needle- $\text{Al}_2\text{O}_{3-500}$

The structural homogeneity of Needle- $\text{Al}_2\text{O}_{3-500}$ manifests in relatively well-resolved ^1H solid-state NMR and FTIR signals from distinct types of surface facets and edge -OH sites. Specifically,

the ^1H NMR spectrum (20 kHz MAS, 16.4 T) of Needle- $\text{Al}_2\text{O}_{3-500}$ exhibits a high-field signal at -0.2 ppm (A), surprisingly well resolved features in the region spanning from 0.9 to approximately 2 ppm with peak intensities at 0.95 ppm (B), 1.55 ppm (C) and 2.05 ppm (D) and a broad shoulder above 2.5 ppm (Figure 2a). In parallel, the IR spectrum (Figure 2b) also possesses several distinct features at 3722, 3758, 3728 and 3667 cm^{-1} . Both ^1H NMR and IR spectroscopy are commonly used to distinguish the bridging state ($\mu_1\text{-OH}$ vs $\mu_2\text{-OH}$ vs $\mu_3\text{-OH}$) of the corresponding hydroxyl as well as its involvement in hydrogen bonding. The ^1H -NMR spectra of $\gamma\text{-Al}_2\text{O}_3$ have generally been reported to consist of a high field signal around -0.2 ppm, a broad signal at about 1.8 ppm and a shoulder in the region between 3 and 4 ppm^{7,17,18}, which is consistent with the herein reported spectral signatures although the resolution of individual features in the 0.5-2.5 ppm region is unique for Needle- $\text{Al}_2\text{O}_{3-500}$ and has not been reported previously. In earlier works from De Canio *et al.*¹⁷ and Taoufik *et al.*¹⁸ the high field signal is assigned to $\mu_1\text{-OH}$ sites, the signals around 1.8 ppm to $\mu_2\text{-OH}$ and the shoulder at 3-4 ppm is interpreted as $\mu_3\text{-OH}$ or hydrogen bonded hydroxyls. The work of Batista *et al.*⁷ suggests an alternate assignment which accounts for edge sites and assigns the high field signal mostly to isolated $\mu_1\text{-OH}$ sites on the edges of alumina crystallites with minor contributions of both free and H-bond acceptor species on the (111) surface. The signals between 1-3 ppm are assigned to non-isolated $\mu_1\text{-OH}$ and $\mu_2\text{-OH}$ sites free from H-bonds on both the surfaces and the edges while the shoulder above 3 ppm is attributed to $\mu_1\text{-OH}$ and $\mu_2\text{-OH}$ species involved in hydrogen bonding. The strong intensity for the signal at -0.2 ppm for our high edge-to-surface ratio Needle- $\text{Al}_2\text{O}_{3-500}$ is consistent with this recent assignment by Batista *et al.* and corroborates our strategy of optimizing the synthesis towards a needle-shaped, high-aspect-ratio morphology for spectroscopic studies of potential edge sites. For the interpretation of IR data different models exist, for example the ones of Tsyganenko, Knözinger, Busca and Digne.^{5, 19-21}

While all models share the common trend of decreasing stretching frequencies $\nu(\text{OH})$ (cm^{-1}) with increasing acidity of the hydroxyls, resulting in the general trend $\nu(\mu_1 - \text{OH}) \geq \nu(\mu_2 - \text{OH}) \geq \nu(\mu_3 - \text{OH})$, they differ in their exact assignments of the reported features.

Figure 2. a) ^1H NMR spectrum of Needle-Al₂O₃₋₅₀₀ was acquired using a rotor synchronized echo with a 2 s recycle delay and echo delays spanning two rotor periods. In addition to an isolated signal at -0.2 ppm (A), features are resolved at 0.95 ppm (B), 1.55 ppm (C) and 2.05 ppm (D) in addition to a shoulder above 2.5 ppm. Conventional and more recent assignment strategies are indicated below the spectrum. b) IR spectrum of Needle-Al₂O₃₋₅₀₀ shown together with possible interpretations of the observed features based on various existing models (roman numerals (I, II, III) indicate bridging state of the hydroxyls, lower case letters (v, p, o) indicate coordination environment of the Al-site(s) the hydroxyl is bound to).

To gain further insight into the nature of the hydroxyl sites we conducted studies on the ^1H longitudinal and transverse relaxation behavior. The results for the analysis of the longitudinal relaxation times (T_1) are summarized in the supporting information and were used to choose suitable recycle delays for 2D measurements. Due to the resemblance of the $\{^{27}\text{Al}\}\text{-}^1\text{H}$ D -HMQC

sequence to rotor-synchronized echo experiments on the proton channel we approximated the relevant relaxation behavior of the protons for the *D*-HMQC experiments by comparison with rotor synchronized echoes of varying echo delays instead of using the standard CPMG-technique for characterization of transversal (T_2 / T_2^*) relaxation behavior. Indeed, the signals at 2.05 ppm and -0.2 ppm dominate the ^1H NMR spectra at prolonged echo delays while the signals at 1.5 ppm and 0.95 ppm as well as the shoulder above 2.5 ppm are significantly reduced in intensity pointing towards reduced coherence lifetimes for these sites (Figure S4). As shortened coherence lifetimes can stem from various origins such as i) inclusion of the site in a dense dipolar coupling network ii) proximity of the site with a large quadrupolar coupling constant a clear interpretation of this finding is not possible. It is nevertheless detrimental to the acquisition of $\{^1\text{H}\}$ - ^{27}Al D-HMQC experiments with different recoupling periods as these signals might decay upon prolonged recoupling.

Even though the ^1H NMR spectrum exhibits relatively well-defined features, it is very likely that these arise from distinct hydroxyl sites with overlapping ^1H chemical shifts. To further resolve potential species and to gain insights into their relative proximities we measured the 2D ^1H - $\{^1\text{H}\}$ SQ-DQ^{22,23} spectrum of Needle- $\text{Al}_2\text{O}_{3-500}$ (Figure 3). The spectrum overall parallels previous findings,^{7,17,18} however the improved resolution provided by structurally defined alumina allows us to deepen the previous assignments. We can thus provide the following more detailed picture of the features of the ^1H NMR spectrum:

- The high field signal (A in figure 2) is not a single feature, but consists of at least two distinct groups with slightly differing isotropic chemical shifts of -0.2 ppm and -0.4 ppm that we will refer to as A1 and A2 in the following discussion. In addition to a strong self-correlating diagonal-peak at (-0.2 ppm, -0.4 ppm) which seems to be dominated by signal

A2, the 2D spectrum reveals additional correlations of signal A1 and signals at 1.9 and 3.2 ppm as well as an intense cross-correlation of signal A2 to a signal at 2.3 ppm. It is possible that multiple additional signals are further contained within A1 and A2; we will comment further on this in the following discussion.

- The region around 1.8 ppm reveals at least five different signals at 0.95 ppm, 1.3 ppm, 1.6 ppm, 1.9 ppm and 2.3 ppm. The signals at 1.3 ppm and 1.6 ppm seem to be strongly correlated, as previously reported.¹⁸ This is consistent with the observed short coherence lifetime for this region of the ¹H spectrum as well as the previous REDOR studies.¹⁸
- The shoulder around 3 ppm reveals a correlation to the signal at 1.9 ppm with no detectable self-correlations.

The most notable of these findings is the disentanglement of the high field signal into at least two different contributions, indicating the presence of two structurally similar yet distinct hydroxyl sites. Although not shown in this work, we could further verify this differentiation based on different reactivities of A1 and A2 sites towards an organometallic compound. Taking into account the most recent assignments for the high field signal of γ -Al₂O₃ to μ_1 -OH sites at edges⁷ at least two distinct edge hydroxyl features with different local structures and correspondingly different dipole-dipole couplings to nearby OH species are present. One of these sites (A1) is in close proximity to other sites of the same type while the other site (A2) is mainly close to μ_2 -OH sites.

Figure 3. b) The ^1H - ^1H SQ-DQ correlation²² spectrum of Needle- $\text{Al}_2\text{O}_{3-500}$ was acquired using one rotor period of BaBa recoupling²³, a 2s recycle delay and 768 scans for each of the 96 t_1 -increments and is depicted together with the rotor synchronized echo (a) of Needle- $\text{Al}_2\text{O}_{3-500}$ that was acquired under analogous conditions (i.e. same rotor, same recycle delay). The spectrum is dominated by a strong self-correlation of the -0.2 ppm signal, and cross-correlations of the signals at 1.3 and 1.8 ppm, -0.4 and 2.3 ppm as well as 1.9 and 2.8 ppm. c) The high field signal (A) consists of two distinct hydroxyl sites with isotropic chemical shifts of -0.2 (A1) and -0.4 ppm (A2). The A1 sites reveal a strong self-correlation while the sites at -0.4 ppm reveal a correlation to the sites at 1.9 ppm.

Recoupling-Time Encoded $\{^{27}\text{Al}\}$ - ^1H D-HMQC NMR Spectroscopy

To further understand the nature of the newly resolved hydroxyl features we turned towards $\{^{27}\text{Al}\}$ - ^1H D-HMQC spectroscopy. D-HMQC experiments are a robust technique to investigate heteronuclear correlations between protons and quadrupolar nuclei and are suited for NMR studies of alumina materials.²⁴⁻²⁶ For the present study we decided to employ $\{^{27}\text{Al}\}$ - ^1H type experiments

in which polarization is initially transferred from protons to surrounding ^{27}Al nuclei and then back-transferred for proton-detection to obtain increased sensitivity and a high resolution in the proton dimension. In cases where the proton relaxation times significantly exceed those of the ^{27}Al species, the reverse $\{^1\text{H}\}$ - ^{27}Al scheme might be preferable.²⁶ Two important characteristics of the *D*-HMQC experiment are the chosen recoupling method and the scheme for time incrementation in the indirect dimension of the experiment. As it has been reported to be a very versatile and robust technique,²⁷ we have decided to use the SR4_1^2 recoupling sequence,²⁸ an R-type rotor synchronized recoupling sequence and a super-cycled version of the basic R4_1^2 sequence. In order to minimize relaxation losses in the indirect dimension we employ the arbitrary indirect dwell (AID) variant of the *D*-HMQC experiment that has been introduced recently by Venkatesh *et al.*⁸ The incrementation protocol is such that the echo period on the ^1H channel is not constant (CT *D*-HMQC) but rather the minimum multiple of rotor periods compatible with the current time increment.

Figure 4. a) In previous studies ^1H - ^{27}Al correlations of γ - Al_2O_3 materials were determined based on a single D -HMQC experiment with a fixed recoupling length that is typically chosen as short as possible to remain selective for surface over bulk species. b) In this work, we encourage acquisition of a series of D -HMQC experiments with different recoupling lengths to differentiate a single quadrupolar broadened site from multiple species. c) The ^1H NMR spectrum of Needle- $\text{Al}_2\text{O}_{3-500}$ was acquired using a rotor synchronized echo with echo-periods spanning six rotor periods and a recycle delay of 2s in order to simulate the relaxation behavior present in the 2D spectrum below. All features that could be identified in the fully relaxed ^1H NMR spectrum at short echo delays remain present to a sufficient extent to be detected in the 2D experiment. d) AID- D -HMQC spectrum of Needle- Al_2O_3 using six rotor periods of SR4 $_1^2$ recoupling.

Chemical shifts of the main features (A, B, C, D) of the ^1H NMR spectrum are indicated with dashed lines, intensity maxima of aluminum signals obtained from direct excitation aluminum measurements are indicated with solid lines. The spectrum reveals a broad correlation of the ^1H signal A with ^{27}Al signals spanning from 10 to 70 ppm. For the remaining features of the ^1H NMR spectrum correlations to three types of aluminum signals are detected, corresponding to ^{27}Al sites with different coordination numbers Al_{IV} , Al_{V} and Al_{VI} . e) Calculated ^{27}Al projections of AID-D-HMQC spectra at different recoupling times are for sites A, B, C and D. The color of the projections encodes the recoupling length that was used in the respective 2D experiment, ranging from 6 (dark purple) to 30 (light pink) rotor periods. While for species B, C and D no additional insights can be gained using this strategy, it allows to revisit the assignment of the signal A. One can differentiate three different contributions to the signal. The ^{27}Al species giving rise to the signal maximum around 20 ppm disappears quickly upon prolonged recoupling time and therein reveals two additional underlying signals.

Previously, 2D ^1H - ^{27}Al correlations of $\gamma\text{-Al}_2\text{O}_3$ materials were analyzed on the basis of a single 2D D-HMQC experiment with a fixed recoupling length spanning m rotor periods (for SR4_1^2 recoupling $m = 6, 12, 24 \dots$) that is typically chosen as short as possible to remain selective for surface over bulk species (Figure 4a). The acquisition of a single $\{^{27}\text{Al}\}$ - ^1H D-HMQC spectrum for Needle- $\text{Al}_2\text{O}_{3-500}$ using six rotor periods of SR4_1^2 recoupling ($m = 6$) reproduces previous findings (Figure 4c). Different ^{27}Al signals corresponding to ^{27}Al species in 6, 5 or 4-coordinate environments (Al_{VI} , Al_{V} or Al_{IV} , respectively) are resolved on established correlations between coordination number of the aluminum site and its chemical shift²⁹. In figure 4d, each of the ^1H

signals B, C and D are correlated to resolved ^{27}Al signals from Al_{VI} , Al_{V} , and Al_{IV} , consistent with the presence of multiple types of hydroxyls bridging between aluminum sites of different coordination number. The shoulder above 3 ppm is solely coordinated to Al_{IV} species. By comparison, ^1H signal A is correlated to a very broad ^{27}Al feature between 10 and 70 ppm. However, it is not possible to fully deconvolute this feature on the basis of a single such measurement due to the complex quadrupolar lineshapes of ^{27}Al signals, particularly for species with large C_Q such as surface sites. Even taking into account an additional measurement at a second magnetic field strength, it is not possible to fully discriminate multiple signals from a single and quadrupolar broadened spectral feature. For further insights into the nature of the surface edge sites that give rise to these correlated intensities, an additional dimension of information is required. “Pseudo-three-dimensional” NMR experiments can be obtained with relative ease by acquiring a series of the same two-dimensional NMR spectra while varying a specific parameter. This parameter can be either an external factor, e.g. the temperature³⁰ or a characteristic of the actual NMR experiment. In analogy to variable contact time CP experiments in biological NMR we decided to acquire a series of *D*-HMQC spectra with varying duration of the SR4_1^2 recoupling length spanning $m(i) = 6, 12, 24, 18$ and 30 rotor periods respectively (Figure 4b). To the best of our knowledge, this strategy of “recoupling-time encoded” *D*-HMQC has not been employed to study surface species of alumina materials up to date even though for the studies of surface species the chosen recoupling time is an especially critical parameter as it determines the selectivity for surface over bulk signals.

The intensity variation of the observed correlations over the different recoupling times (Figure 4d) is a function of two main factors: i) the distance between the proton and the ^{27}Al site as the

transfer is mediated via the heteronuclear dipole-dipole coupling and ii) the relaxation of the magnetization during the recoupling. Unfortunately, these effects cannot be fully disentangled. As discussed earlier one may slightly correct for occurring relaxation via comparison with rotor synchronized echoes at similar overall echo delays (e.g. comparing a 6-rotor-periods echo delay echo with a 6-rotor periods recoupling *D*-HMQC) but since relaxation behavior under free evolution and recoupling pulses are not necessarily identical this is a rather crude approximation. However, a full disentanglement of these concurring effects is not necessary for our further analysis as we do not aim at the extraction of specific distances but rather want to use the recoupling-encoded data to distinguish different ^{27}Al resonances that underly the broad feature. For a first analysis we focus on species A, B, C and D and do not further distinguish the additional sites that could be separated based on the proton correlation data. Regarding the B, C and D signals the benefit of the recoupling-time-encoded *D*-HMQC is less pronounced as these signals are already relatively well resolved using a single *D*-HMQC spectrum with fixed recoupling length. While the correlations for B and C disappear quickly upon increasing recoupling times, signal D reveals pronounced correlations even at 30 rotor periods of SR4_1^2 recoupling. The decay rates parallel our initial analysis of rotor synchronized echoes. For signals B, C and D and the shoulder above 2.5 ppm we extracted isotropic chemical shifts δ_{iso} and quadrupolar coupling constants C_Q of the correlated Al sites using solely the spectrum with $m = 6$ rotor periods recoupling and a second data set at comparable acquisition parameters but elevated magnetic field strength of 20 T for a best fit of sites with substantial gaussian line broadening. The Al_{IV} sites can be modelled using $\delta_{iso} = 72$ ppm, $C_Q = 7$ MHz, Al_V sites with $\delta_{iso} = 44$ ppm, $C_Q = 7$ MHz and Al_{VI} sites as $\delta_{iso} = 16$ ppm, $C_Q = 6$ MHz. These values are similar to those extracted by Taoufik *et al.* based on Cjzjek-

type models and differ mainly in the C_Q values for Al_{IV} and Al_V sites which were reported to be around 12 MHz instead of 7 MHz in their study¹⁸.

The advantages of the recoupling-time encoded data set reveal themselves in the intensity variation for the ^{27}Al signals that are correlated to 1H signal A, which undergo a much more complicated evolution of the line-shape as a function of the chosen recoupling duration. A more detailed analysis for the newly differentiated A1 and A2 sites reveals that at least three different ^{27}Al signals are contained within their calculated ^{27}Al projections. First, there is a broad ^{27}Al signal with an intensity maximum at 20-30 ppm, which decays quickly upon prolonged recoupling delays. There are two additional narrower ^{27}Al signals with intensity maxima at approximately 60 ppm and 11 ppm that build up towards prolonged recoupling durations. Similar signals are observed for both A1 and A2, however the position of the ^{27}Al intensity maxima for the broad correlated signal differs slightly. For both, A1 and A2, we conducted a very simple line shape analysis of their correlated ^{27}Al signals using three different ^{27}Al sites each with significant gaussian line broadening (Table S1, Table S2, Figure 5). Again, the exact NMR parameters for the individual sites were chosen based on a comparison with additional data sets recorded at elevated magnetic field strength of 20 T but otherwise similar conditions (Figure S7). Keeping the NMR parameters constant while only varying the relative weights of the sites we are able to reproduce the observed lineshapes of the ^{27}Al projections for the A1 and A2 signals over a series of recoupling times. Remaining deviations between simulated and experimental line-shapes could stem from: i) slightly altered NMR parameters, ii) additional presence of minor species, or iii) the necessity for a Czjzek-type noise³¹ instead of a Gaussian broadening. Taking into account data sets which were acquired at different recoupling lengths, the low field end of the ^{27}Al projections cannot be modelled by a single quadrupolar broadened

Al_{IV} species. In contrast to previous assignments which describe the presence of a single Al_{IV} species with $\delta_{iso}=69$ ppm, $C_Q=11.5$ MHz²⁶, we interpret the low field end as two separate Al_{IV} sites with similar isotropic shifts around 72 ppm but different quadrupolar coupling constants of approximately 8 and 13.5 MHz for A1 and 7 and 11.75 MHz for A2. In addition, we can confirm the presence of Al_{VI} sites with chemical shifts of roughly 19 ppm and quadrupolar coupling constants around 6 MHz for both A1 and A2. For both, A1 and A2, the Al_{IV} site with the largest quadrupolar coupling constant decays faster and is only observable at short recoupling times while the other sites persist in the spectrum upon prolonged recoupling periods. As already pointed out by Wischert *et al.*, sites with very large C_Q values might simply be invisible due to their inherent reduced sensitivity as well as insufficient coherence lifetimes.²⁹ The small C_Q values of some sites could either result from very specific surface geometries, might be related to dynamics since all our spectra have been acquired at room-temperature or could point towards a sub-surface rather than surface nature of these sites.

Figure 5. Simulated line shapes (*black lines*) for calculated ^{27}Al projections (*solid pink lines*) of A1 (*left*) and A2 (*right*) signals for AID-*D*-HMQC spectra with recoupling lengths of 6, 12 and 24 rotor periods (*from bottom to top*). Three distinct ^{27}Al signals each (dashed lines) were used for A1 and A2 to simulate the spectra. The ^{27}Al NMR parameters of the signals were kept constant for the spectra at different recoupling times while the relative intensities of the sites were varied in order to follow the evolution of the line-shapes. Broad ^{27}Al signals from Al_{IV} sites dominate the spectra at short recoupling times while narrower ^{27}Al signals from Al_{IV} and Al_{VI} sites build up towards longer recoupling times. Usage of recoupling-time encoded *D*-HMQC data thus allows the differentiation of multiple overlaying signals.

To conclude, the potential edge sites that give rise to ^1H signals A1 and A2 possess similar but not fully identical ^{27}Al correlation patterns which further supports the distinct nature of the sites. Both A1 and A2 sites appear to be in proximity to Al_{IV} surface sites with significant quadrupolar coupling constants $C_Q > 10$ MHz. If one assumes that A1 and A2 are indeed $\mu_1\text{-OH}$ sites and therefore only bound to a single aluminum surface site, two different interpretations are possible for the additional correlations to the small- C_Q Al_{IV} as well as Al_{VI} sites. If one interprets A1 and A2 as a single type of hydroxyl each, the second Al_{IV} as well as the Al_{VI} site have to be either subsurface species or surface sites which are in the further surroundings of A1 and A2 but not directly bound to them. However, one should not exclude the possibility that further sites which are not resolved in the ^1H - ^1H SQ-DQ spectrum are contained in A1 and A2. In this case additional scenarios are possible, e.g. one of these sites could be correlated to the large- C_Q site and the second one to the small- C_Q site. Based on our experimental data we cannot advocate one interpretation over the other, but we hope that our work will be taken as an input for further computational studies which might have the potential to allow for an unambiguous interpretation.

Figure 6. Summary of novel structural insights that are obtained in our in-depth spectroscopic analysis of a well-defined $\gamma\text{-Al}_2\text{O}_3$ material: Features that could be identified in the ^1H - ^1H SQ-DQ correlation experiment (*blue*) with their respective relative proximities (*blue lines*) are grouped into the broader features that can be distinguished already from the 1D ^1H NMR Spectrum (*pink*). For all species ^{27}Al sites to which correlations are visible in D -HMQC experiments are indicated (*green*). Please note that for improved visibility the bridging character of the hydroxyls is not indicated, especially those that are contained in groups B, C and D may be $\mu_2\text{-OH}$.

Conclusion

Using a well-defined tailored $\gamma\text{-Al}_2\text{O}_3$ material with a large abundance of edge sites and highly resolved signals in both IR and NMR in combination with state-of-the-art 2D and pseudo-3D solid-state NMR spectroscopy, we went beyond established NMR studies on $\gamma\text{-Al}_2\text{O}_3$, more specifically the high-field ^1H -NMR signal that has been in the focus of recent interest due to its potential link

to highly reactive edge sites. The combined results of our NMR analysis and the structural implications are summarized in Figure 6, including all distinct hydroxyl sites and relative proximities that we could identify based on 1D and 2D measurements as well as the NMR parameters of the ^{27}Al sites to which they are correlated. Overall, the high homogeneity of our alumina material has allowed us to reveal a variety of distinct hydroxyl sites that could not be resolved beforehand. Most importantly, from 2D ^1H - $\{^1\text{H}\}$ SQ-DQ NMR spectroscopy we can show that the ^1H NMR signal which has been the subject of recent investigations and edge-theories in fact corresponds to at least two distinct hydroxyl sites with different local environments and proximities to surface -OH and Al sites. These differences manifest in distinct ^1H chemical shifts, and different correlations in the 2D ^1H - ^1H and ^1H - ^{27}Al correlation spectra. Using recoupling-time encoded $\{^{27}\text{Al}\}$ - ^1H D-HMQC spectra, we were furthermore able to go beyond previous interpretations of the ^{27}Al projections for the high field signal which seems to contain more sites than accounted for in earlier works. Since our strategy circumvents measurements at different magnetic fields or application of further advanced NMR techniques to separate ^{27}Al signals based on their different quadrupolar coupling strengths, it might be especially useful for more synthetically-oriented groups which do not have access to multiple high field magnets or a variety of such pulse sequences.

The methodology presented here has the potential to improve structural assignments and provide experimental constraints for refining computational models of surface species, not just for catalytic materials based on $\gamma\text{-Al}_2\text{O}_3$, but also for other functional materials with complex surface structures. Our work also serves as an important demonstration on the synergetic effects of combined efforts of materials research and NMR spectroscopy. We hope that the herein presented methodology inspires further work, not only on $\gamma\text{-Al}_2\text{O}_3$ materials with different well-defined morphologies and

tailored surface chemistries but also on other functional materials containing complicated line-shapes due to the presence of multiple overlapping broadened sites. We also advocate that recoupling-time encoded $\{^{27}\text{Al}\}$ - ^1H *D*-HMQC NMR studies should be pursued on a broad range of γ - Al_2O_3 materials in order to evaluate the presence of multiple Al_{IV} species.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge:

Experimental details on materials preparation and solid-state NMR measurements, additional TEM data, additional NMR spectra, numerical values for line shape analysis (PDF)

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‡ These authors contributed equally. J.M developed the synthesis route to Needle Al_2O_3 -500.

L.V. and J.M synthesized all molecules/materials and performed routine characterization. L.R.

performed TEM measurements. L.V. designed and performed the ss-NMR experiments at 16.4 T. Z.B. performed the ss-NMR experiments at 20 T. Results were analyzed by L.V. and C.C. Initial drafts were written by L.V. Further editing of the manuscript was conducted by L.V., J.M., Z.B., L.R., J.A.v.B. and C.C. All authors have given approval to the final version of the manuscript.

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