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Article type : Article

NMR study on reaction processes from aluminum chloride hydroxides to alpha alumina powders

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Abstract

Starting from gelatinous aluminum chloride hydroxide, the transformation process towards α -Al₂O₃ was examined by using ²⁷Al NMR, both in the liquid and solid states, as a main analytical tool. By increasing the hydrolysis ratio (h , defined as [OH⁻]/[Al³⁺]) of the starting aqueous precursor up to $h = 2.5$, the transition temperature to the final product, α -Al₂O₃, decreased to as low as 500 °C. In this case, the structural change from amorphous alumina to α -Al₂O₃ took place without intermediate transition Al₂O₃ phases.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/jace.16108

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Examining the process of networking during the transition from aqueous sol —through the state of xerogel— to final anhydrous oxide by NMR revealed the presence of highly polymeric species mainly ascribed to δ -[Al₂O₈Al₂₈(OH)₅₆(H₂O)₂₄]¹⁸⁺ (δ -Al₃₀). δ -Al₃₀ species were found in the solution phase and became predominant after drying. We conclude that the lower temperature synthesis of α -Al₂O₃ became possible due to preformation of polymerized AlO₆ construction units in the precursor, reducing the energy barrier for the nucleation of the final α -Al₂O₃ phase.

1. Introduction

α -Al₂O₃ is a widely used ceramic material applied in the fields of construction, electronics, optical or biotechnology, due to its outstanding mechanical strength, chemical and electrical resistance, or thermal insulation¹. Conventionally, α -Al₂O₃ is fabricated by calcining aluminum hydroxides obtained from the source mineral, bauxite. It is also possible to synthesize α -Al₂O₃ from various aluminum salts, e.g. chloride², sulphate³ or nitrate⁴. Temperatures needed for α -Al₂O₃ synthesis from aluminum hydroxides or salts are usually above 1100 °C¹. A general transformation process includes several transition Al₂O₃ phases, which are denoted by Greek characters. Two representative transformation routes are $\chi \rightarrow \kappa \rightarrow \alpha$ and $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ^{1,5,6}. Transition Al₂O₃ phases differ from each other by different partition of Al atoms in the octahedral and tetrahedral voids of the oxygen sublattice, as well as by various defects in the sublattice. In α -Al₂O₃, all Al atoms are localized in octahedral sites. Whereas transformations among the transition phases are displacive with low activation energies, the final stage of the transformation to the α modification is reconstructive, and hence requires a higher activation energy for its nucleation⁷. The only exception is diaspore, α -AlO(OH), which directly transforms to α -Al₂O₃ at relatively low temperatures, since its structure is similar to that of α -Al₂O₃¹. However, diaspore occurs in nature to a very low

extent and its synthesis is laborious requiring hydrothermal conditions with high temperature and pressure⁸. Therefore, diasporite is not suitable as a starting material of α -Al₂O₃ on a production scale.

The aim of this work is to examine the reaction processes from non-conventional starting materials in a liquid phase and to find a transition temperature as low as possible to the final product, α -Al₂O₃. A decrease in the synthesis temperature is favorable not only from economic and environmental aspects, but also with regard to smaller crystallite or particle sizes in a highly dispersed state.

Some attempts of decreasing the synthesis temperature of α -Al₂O₃ have already been reported. The lowest α -Al₂O₃ synthesis temperature of 420 °C was reported by Brand et al.². In some other works α -Al₂O₃ was synthesized at around 500 °C⁸⁻¹¹. The precursors in the reported cases could be categorized as gelatinous aluminum hydroxides, however, this designation is indefinite without elucidating features specific to the starting materials.

Here we focus on the low-temperature synthesis of α -Al₂O₃ from gelatinous aluminum chloride hydroxide (ACH). We examine ACH xerogels with different hydrolysis ratio h ($= [\text{OH}^-]/[\text{Al}^{3+}]$) prepared by sol-gel partial hydrolysis. Apart from conventional analyses by thermal analysis and powder X-ray diffraction analysis, we focus on ²⁷Al nuclear magnetic resonance (NMR) spectroscopy both in the liquid and solid phases. This enables us to reveal the states and their variation in short-range ordering in terms of networking and polymerization of Al-containing clusters throughout the entire processes from the starting solution to the final α -Al₂O₃ powders.

2. Experimental Procedure

2.1 Preparation

Whereas ACHs are mostly synthesized by neutralization of Al^{3+} solution by basic solution, the ACH gels in this work were prepared by dissolving Al metal in aqueous AlCl_3 solution so that most of the conditions remain the same with different hydrolysis ratio, $h = [\text{OH}^-]/[\text{Al}^{3+}]$ (i.e. the same molar concentration of Al in solution assured by constant solution volume, absence of other cations beside Al). Gelatinous ACH samples with different hydrolysis ratio were synthesized by dissolving chopped Al wire (99.5 %, 3 mm in diameter, Kadaň, Slovakia) in AlCl_3 solution with fixed volume of 50 ml prepared from $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ (98 %, Lachema Brno, Czech Republic) and deionized water. The amounts of Al metal and $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ were varied while keeping the molar concentration of $[\text{Al}^{3+}]$ constant at 1.85 M. The temperature of synthesis was 95 °C and the range of tested h was 0–2.5. We henceforth denote our ACH samples with h values as ACH- h . At values of h exceeding 2.5, crystalline aluminum hydroxides or oxyhydroxides start to precipitate. These precipitates lead to the known transformation sequence to $\alpha\text{-Al}_2\text{O}_3$ requiring temperature treatment above 1100 °C¹. As-synthesized viscous liquids (ACH solutions) were dried at 95 °C for 2–3 days to obtain a series of ACH xerogels. The samples prepared at varying hydrolysis ratio are summarized in Table 1. The ACH xerogels were heated in a laboratory furnace CLASIC CZ 1013L in static air atmosphere with a heating rate of 10 °C/min and held for 2 h at the selected plateau temperatures. A scheme of the experimental procedure is shown in Figure 1.

2.2 Characterization

Powder X-ray diffraction analyses (XRD) were carried out with a Philips PW 1050 diffractometer with Bragg-Brentano geometry and CuK_α radiation.

TG-DTA measurements were performed by using a TA Instruments SDT 2960 up to 1200 °C with a heating rate of 10 °C/min in air flow.

Liquid state ^{27}Al NMR measurements of as-prepared ACH solutions were carried out with a Varian Mercury Plus 300 MHz spectrometer with a Varian 1H/19F/X 5 mm PFG ATB probe. ^{27}Al has a Larmor frequency (ν_0) of 78.2 MHz at this magnetic field strength. The length of an excitation pulse for ^{27}Al was 5.8 μs at 53 dB. 1024 scans were accumulated for each spectrum.

For solid-state ^{27}Al MAS-NMR measurements, two spectrometers were used, and the spectra were recorded in a single pulse sequence. As-synthesized ACH xerogels were studied using a Bruker Avance III 600 MHz NMR spectrometer providing a magnetic field of 14.1 T, which corresponds to a ^{27}Al NMR Larmor frequency of 156.4 MHz. A 1.3 mm MAS probe (Bruker, Germany) was used with 40 kHz spinning rate (ν_{rot}). The $\pi/2$ -pulse length was 1.0 μs , and the recycle delay of 10 s ensured full spin-lattice relaxation. 256 scans were accumulated for each spectrum. The heat-treated ACH samples were studied with a Bruker Avance III 300 MHz NMR spectrometer with a magnetic field of 7.0 T, which corresponds to a ^{27}Al NMR Larmor frequency of 78.2 MHz. A 4 mm MAS probe (Bruker, Germany) and a spinning rate of 15 kHz were chosen. The $\pi/2$ -pulse length was 2.0 μs and the recycle delay of 10 s ensured full spin-lattice relaxation. At least 1024 scans were accumulated for each spectrum.

All NMR measurements were performed at room temperature and all NMR spectra were referenced to an aqueous $\text{Al}(\text{NO}_3)_3$ solution. Characterization techniques are also summarized in Fig. 1 with the number of the associated figure to be displayed below.

3 Results and Discussion

3.1 Characterization of the Precursors

3.1.1 Solution ^{27}Al NMR

The course of hydrolysis of Al^{3+} in our ACH solutions with increasing h is consistent with literature data^{12,13}. In diluted acidic aqueous Al^{3+} solutions, the dominant form of aluminum is a hydrated cation, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Polarization of H_2O molecules by Al^{3+} leads to deprotonation of hydrated cations according to Eq. 1. These deprotonated hydrated cations then may form dimers (Eq. 2) and higher polymeric species according to conditions such as temperature, pH and presence of different anionic species.



Higher amounts of OH^- in a solution, i.e. higher h values, promote condensation reactions by neutralization, leading to a higher degree of polymerization¹³. This trend is universal no matter the aluminum salt used as starting material¹⁴.

Nevertheless a large number of polymeric Al species in Al^{3+} solutions have been theoretically proposed¹, yet, only a few of them have been characterized (vide infra). Al-containing polymeric species are divided into two categories according to their morphology. The first group of these species is formed by connecting trimers of AlO_6 into “flat” structures. Its representative is the tridecamer $\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}^{15+}$ (M- Al_{13}) with so-called “Mögel” structure, which consists merely of interconnected AlO_6 octahedra¹⁵. The second group differs from the first one by the presence of Keggin moiety, which consists of AlO_4 tetrahedra surrounded by AlO_6 units forming a more spacious structure. Several polymeric Al species possessing different isomers of Keggin ions (denoted by Greek character prefix) have been

characterized, e. g. ϵ - $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (ϵ -K- Al_{13})¹⁶ and δ - $[\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{24}]^{18+}$ (δ - Al_{30})¹⁷.

In our ACH solutions with low h , only monomers and small oligomers, mainly dimers and trimers, are observed according to ²⁷Al NMR (Fig. 2). All samples with a hydrolysis ratio up to 2.0 exhibit main resonance peaks with a chemical shift at around 0 ppm. The peak was assigned either to hydrated Al monomers ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ ^{13,18}) or to peripheral AlO_6 in M- Al_{13} ¹⁹. The other signal assigned to M- Al_{13} has a chemical shift in the range of 2–15 ppm¹⁹. Therefore, ACH-0.0 consists only of hydrated Al monomers. For ACH-0.5, the resonance peak at 0 ppm remained predominant. However, small peaks at around 4 ppm were observed, as shown in the magnified inset. They might be ascribed to dimers or trimers of Al²⁰, and/or M- Al_{13} ¹⁹. Exact assignment of the latter small peak is not possible since the signals reported for these species are in the same region and are also broadened due to the surrounding electric field gradients^{19–22}. The intensity of the 0 ppm signal diminishes with increasing hydrolysis ratio due to the polymerization of Al monomers¹³. The signal of Al dimers/trimers at around 2–5 ppm is present in the range of $0.5 \leq h \leq 2.0$. The distinct peak at 62.9 ppm was assigned to AlO_4 in a highly symmetrical environment of ϵ -K- Al_{13} ^{21,22}. ϵ -K- Al_{13} is present in the ACH samples possessing $1.2 \leq h \leq 2.5$. The samples with hydrolysis ratio 2.0 and 2.5 exhibit a signal at 10–12 ppm, which, theoretically, may originate from the AlO_6 moieties present in either δ - Al_{30} or ϵ -K- Al_{13} ¹⁷. In contrast to δ - Al_{30} , the NMR signal in this region originating from AlO_6 is not observable for ϵ -K- Al_{13} at ambient temperature due to large electric field gradients¹⁹. A very broad signal at ca. 71 ppm present in the spectrum of ACH-2.5 also points to the presence of δ - Al_{30} ^{18,23}.

3.1.2 Solid-State ^{27}Al MAS-NMR

Solid-state ^{27}Al MAS-NMR spectra of as-synthesized ACH xerogels are shown in Fig. 3.

The spectrum of the ACH-0.0 (Fig. 3a) contains only one narrow signal at -1.0 ppm. This indicates that all the Al atoms are situated in a very symmetrical octahedral environment of oxygen atoms. The spectrum of the ACH-0.5 (Fig. 3b) shows also a narrow signal at -0.9 ppm which is one-side broadened downfield up to ca. 15 ppm suggesting some degree of disorder of octahedral Al sites^{24,25}.

In the NMR spectra of the samples with $h > 0.5$, all signals are markedly broadened. The broadening and asymmetry of the line shapes of AlO_4 , and to lower extent also of AlO_6 , stems from the second-order quadrupolar broadening in solid samples^{24,25}. ACH-1.2 (Fig. 3c) contains 3 broad signals with maxima at 5.1, 35.6 and 64.3 ppm. They correspond to Al atoms coordinated by 6, 5 and 4 oxygen atoms, respectively²⁶. The signal at 64.3 ppm is very close to the signal at 64.5 ppm firstly assigned to the derivate of K-Al_{13} distorted by lack¹⁸ or excess²⁷ of one AlO_6 unit. More recently, it was assumed to be the δ -isomer of Al_{13} with Keggin structure ($\delta\text{-K-Al}_{13}$)²⁸. ACH-2.0 (Fig. 3d) possesses also all three types of coordination of Al. The 75.1 ppm signal corresponding to 4-coordinated Al is downfield shifted and narrower than the AlO_4 signal found in ACH-1.2. The peak at 75.1 ppm was assigned to AlO_4 in the γ -isomer of Al tridecamer with Keggin structure ($\gamma\text{-K-Al}_{13}$)^{29,30}. The signal of 5-coordinated Al (34.6 ppm) has the same peak position as in the ACH-1.2 sample, but its intensity is lower, suggesting a lower amount of 5-coordinated Al present in the ACH-2.0 sample. The lower amount of AlO_5 may be caused by a higher amount of Al atoms that form specific polymers containing only AlO_4 and AlO_6 at higher h . At lower h , the species seem to contain more Al atoms in a transient AlO_5 state. The NMR lines of highest intensity in the spectrum of ACH-2.0 (Fig. 3d) are attributed to 6-coordinated Al atoms. Two distinct components at 3.9 and 10.1 ppm are clearly visible in the spectrum. The NMR spectrum of

the ACH-2.5 sample (Fig. 3e) reveals the presence of 6- and 4-coordinated Al, with 5-coordinated Al being absent. It contains 6-coordinated Al signals (10.2 ppm, 4.5 ppm) similar to that of ACH-2.0. The most intense one is the component at 10.2 ppm. Besides the NMR lines of 6-coordinated Al, the ACH-2.5 spectrum contains a signal at -27.6 ppm, and two signals at 74.5 and 67.5 ppm, being typical for AlO_4 . Very similar looking spectra to that of ACH-2.5 were assigned by Phillips et al.³¹ to $\delta\text{-Al}_{30}$ polycations. They assigned the broad NMR lines at around -50 ppm in their spectra to edge-linked AlO_6 trimers surrounding a tetrahedrally coordinated Al atom in the ϵ -Keggin-like structures. In the ^{27}Al MAS-NMR spectrum of ACH-2.5, the feature near -27.6 ppm corresponds to the same moieties with respect to the different magnetic field strength compared to that used in the work of Phillips et al.³¹. However, the presence of other than $\delta\text{-Al}_{30}$ species in ACH-2.5 to a minor extent may not be excluded.

3.1.3 Changes in the Short-Range Order from Sol to Xerogel

Herein, the rearrangement of Al species during the drying process is discussed by comparing solid and liquid state ^{27}Al NMR spectra. In general, there are well-known differences between liquid and solid-state NMR spectra mainly due to the lack of averaging of the dipolar interactions, the chemical shift anisotropy and the second-order quadrupole interaction in the latter. Under the MAS-NMR measuring conditions used in this study the dipolar interactions and the chemical shift anisotropy are effectively averaged; however, the second-order quadrupole interaction persists. This becomes critical when we consider the rearrangement within the transformation from liquid to solid phase.

Drying at 95 °C promotes the aging process of the solutions, leading to the formation of high polymeric Al species from monomeric and low-order polymeric hydrated Al

species^{21,22,27}. The transformations of the Al species during aging were extensively discussed from the viewpoints of hydrated Al polyoxocation in the literature³².

In the case of the samples containing mostly monomers (ACH-0.0, ACH-0.5), the correlation between solid (Fig. 3) and liquid state (Fig. 2) NMR spectra is obvious. The samples contain only octahedral signals ascribed to Al monomers both in liquid and solid states. Polymerization to higher polymers was not observed after drying. However, in the spectra of the samples with higher hydrolysis ratio, some discrepancies occur, as a consequence of structural change during the aging process. In addition to signals for AlO_6 and AlO_4 in the liquid spectrum of ACH-1.2, a signal of 5-coordinated Al appeared in the spectrum of the solid. Employing molecular dynamics simulations, Rustad et al.³³ suggested the presence of metastable 5-fold coordinated Al in ϵ -K- Al_{13} . As the origin thereof, breaking of the bond between Al in octahedral coordination and μ_4 -O linked to central tetrahedrally coordinated Al was put forward – which is the initial step in oxygen exchange process for the bridging hydroxyl groups³³. Similar mechanism may occur in the case of ACH-1.2 during drying leading to cluster condensation, which requires replacement of terminal H_2O groups by OH groups³³. The broad, weak signal in the ^{27}Al MAS-NMR spectrum of ACH-1.2 at 64.3 ppm may be ascribed to the δ -Keggin-structure formed by modification of ϵ -K- Al_{13} ²⁷ present in the liquid sample. The largest discrepancy between the liquid sample and the xerogel was observed for ACH-2.0. The signal for ϵ -K- Al_{13} disappears completely and a signal at ca. 75 ppm appears, suggesting that the ϵ -K- Al_{13} transformed, at least partly, to γ -K- Al_{13} during drying. This is also confirmed by the simultaneous occurrence of an NMR line at 10 ppm matching the 7–11 ppm region, assigned to the AlO_6 in γ -K- Al_{13} ²⁹. However, we cannot exclude the formation of other polymeric Al species, which cannot be tracked by ^{27}Al NMR. As observed for ACH-1.2, also in the ACH-2.0 a signal caused by 5-coordinated Al occurs, but with lower intensity compared to the ACH-1.2 sample. For the ACH-2.5 sample,

both liquid and solid-state NMR spectra suggest the presence of δ -Al₃₀. However, in the liquid NMR spectrum, also ϵ -K-Al₁₃ was present, which is absent in the solid-state NMR spectrum. This ambiguity may be explained by assuming that ϵ -K-Al₁₃ polymerized to δ -Al₃₀ during drying the liquid sample to xerogel, which could occur upon heating³⁴. The presence of the feature near -30 ppm in MAS-NMR spectrum of ACH-2.5 indicates retention of the liable terminal H₂O groups after drying, which enhance further reactivity (vide infra)³¹. The summarized results from solution and solid-state NMR are shown in Tab. 1

3.2 Heat-Treatments of the ACH Xerogels

3.2.1 Thermal Analysis

Thermal analyses of the ACH xerogels are shown in Fig. 4. After dehydration of adsorbed H₂O at temperatures up to 100 °C, ACH-0.0 decomposes in a single step exhibiting an endothermic effect with peak minimum at 191 °C to amorphous Al₂O₃, which contains some amount of remaining -OH groups. The phase transformation of amorphous Al₂O₃ to γ -Al₂O₃ is accompanied by an exothermic peak with a maximum at 846 °C and the transformation of γ -Al₂O₃ to α -Al₂O₃ by a broad exothermic peak with a maximum at 1135 °C. At about 800 °C, further weight loss occurs due to dehydroxylation. In all samples the largest weight losses occur up to 300 °C. With rising value of *h*, the weight losses are divided into several steps, revealing the samples consist of several differently bound -OH groups. This is also reflected by DTA curves, in which the corresponding endothermic peaks broaden, comprising several overlapping components up to 400 °C. For ACH-0.5, the exothermic peaks at 827 °C and 1119 °C corresponding to the transformation to γ -Al₂O₃ and α -Al₂O₃, respectively, occur at slightly lower temperatures comparing to ACH-0.0. The exothermic effects for ACH-1.2 caused by the transformations to γ -Al₂O₃ (834 °C) and α -Al₂O₃ (1118 °C) are similar to previously mentioned samples. However, ACH-1.2 contains

an additional exothermic peak at 678 °C due to the direct low-temperature transformation of a part of the sample to α -Al₂O₃. A similar exothermic peak occurs in ACH-2.0 at 687 °C. For the two samples with the highest h , the exothermic peak ascribed to the transformation of γ -Al₂O₃ to α -Al₂O₃ diminishes, with no recognizable peak in ACH-2.5. The fluctuations of the DTA curves above 600 °C are caused by simultaneous transformations of multiple phase systems to final α -Al₂O₃.

3.2.2 Powder X-Ray Diffraction

The phase compositions of heat-treated ACH xerogels tracked by XRD are shown in Fig. 5. All heat-treated samples were amorphous up to a temperature of 400 °C according to XRD and thus their XRD patterns are omitted in the figure. The lowest temperatures of α -Al₂O₃ formation from the five different ACH xerogels after 2 h heat-treatments are summarized in Tab. 1. The lowest temperature was 500 °C starting from ACH-2.5. Since no transition Al₂O₃ was observed by XRD up to heat-treatment at 500 °C, it can be assumed α -Al₂O₃ formed from amorphous Al₂O₃ following an unusual transformation sequence without passing through transition Al₂O₃ polymorphs. The low-temperature transformation to α -Al₂O₃ may take place due to the structures of the Al polycations present in xerogels with higher h . Contrary to the case of diaspore, these Al polycations do not possess a hexagonal close packed arrangement of an oxygen sublattice similar to α -Al₂O₃; however, their approximately cubic close packed oxygen sublattice may be more easily rearranged to hexagonal close packed one due to low energy barrier presumably originating from the terminal H₂O group sites³³. The starting temperature of α -Al₂O₃ synthesis for ACH-1.2 and ACH-2.0 was 600 °C. The intensity of the diffraction series of α -Al₂O₃ is quite low and increases with increasing h . The intensities of the α -Al₂O₃ diffractions after heat-treatment at 600 °C are recognizably higher for ACH-2.5 than for the other samples.

After the heat-treatment at 600 °C, broad diffractions assigned to γ -Al₂O₃ —all broad unassigned diffractions in Fig. 5— appeared in all the samples except ACH-0.0 and ACH-0.5. γ -Al₂O₃ formed from the residual material of the samples that had not yet been transformed to α -Al₂O₃ at low T. An increase of the diffraction intensities of both α -Al₂O₃ and γ -Al₂O₃ occurs with rising temperatures up to 1000 °C. After heating at 800 °C and 1000 °C, the ACH-0.5 exhibits γ -Al₂O₃ as well, which transforms to α -Al₂O₃ at higher temperatures. All samples contain only α -Al₂O₃ after heating at 1200 °C for 2 h. These results from XRD are in line with those from DTA-TG. Slightly higher transformation temperatures observed by DTA compared to XRD are caused by kinetic factors, since the heating regimes during thermal analyses and heat-treatments in laboratory furnace were not the same.

It should be noted that Brand et al. proposed, that the removal of reaction gases — particularly HCl and H₂O— released within the transformations during the heat-treatments of aluminum chloride hydroxide gel² is necessary to obtain α -Al₂O₃ at a temperature of around 500 °C. In our case, α -Al₂O₃ is formed from ACH-2.5 at 500 °C even in static air atmosphere, without removing the gases by air stream compared to work of Brand et al.². However, we cannot conclude whether or not the removal of the reaction gases is crucial, since we do not have any further information about gases' partial pressures in the systems to compare.

3.2.3 *Solid-State ²⁷Al MAS-NMR*

The transformations of the ACH samples after heat-treatments were tracked also by ²⁷Al MAS-NMR as shown in Fig. 6. After the heat-treatments at lower temperatures (200 °C and 400 °C) the signal of 5-coordinated Al occurred in all samples together with diminishing intensities of AlO₆ and increasing intensities of AlO₄. The latter is apparent after heat-

treatment at 400 °C. The NMR spectra reveal that the formation of amorphous alumina during dehydration/dehydroxylation of ACHs proceeds by eliminating oxygen atoms from the 6-coordination sphere of Al atoms to form transient AlO_5 and AlO_4 besides AlO_6 ^{33,35}. Crystallization of Al_2O_3 further requires rearrangement of oxygen atoms and elimination of AlO_5 units. This correlates with the phase transformations observed by the XRD measurements (Fig. 5). Vanishing of the AlO_5 signal at the lowest temperature is evident for ACH-2.5 (Fig. 6e). After the heat-treatment at 500 °C, its NMR spectrum contains predominantly AlO_6 with a bit of AlO_4 units, indicating the coexistence of a small amount of γ - or amorphous Al_2O_3 besides α - Al_2O_3 . After heating at 1200 °C, all samples contain solely α - Al_2O_3 with only one NMR signal from 6-fold coordinated Al at 9.5–9.8 ppm.

The lowest α - Al_2O_3 synthesis temperature of 420 °C was reported by Brand et al.², by using aluminum chloride hydroxide gel prepared from partially thermally decomposed $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$. The composition of the starting gel was, however, not determined. It was assumed from IR that its structure is similar to diaspore, and from ^{27}Al MAS-NMR that it contains 6- and 4-coordinated Al (9.1, 58.6 ppm)³⁶. During the heat-treatment, the amount of 5-coordinated Al increased and subsequently diminished to form α - Al_2O_3 with the signals at 12.9 and 62.7 ppm³⁷. It should be noted, that pure α - Al_2O_3 should produce a single octahedral signal in NMR, so the latter signal in tetrahedral region originates most probably from some structural defects or not-yet converted transition Al_2O_3 . Despite our finding, that the transformations of ACH xerogels to α - Al_2O_3 proceeding via 5-coordinated Al state, is consistent with that for the sample referred in the work of Brand et al.², the ^{27}Al MAS-NMR signals of the ACH-2.5 xerogel differ slightly from those of the aluminum chloride hydroxide gel referred in². Despite such a subtle difference, it is likely, that the sample referred in² contained high polymeric Al species similar to those in ACH-2.5, leading to low-temperature crystallization of α - Al_2O_3 .

Mackenzie et al.³⁷ assumed that low temperature α -Al₂O₃ formation was associated with a 5-coordinated Al signal in the precursor. However, 5-coordinated Al does not seem to be the sole factor promoting the transformation to α -Al₂O₃. For example, crystallite size of the starting precursor plays a significant role in the transformation of γ -Al₂O₃ to α -Al₂O₃³⁸. In our case, the ACH xerogels as precursors for α -Al₂O₃ possessing a signal of AlO₅ (ACH-1.2 and ACH-2.0) do not lead to the lowest temperature of α -Al₂O₃ synthesis. In fact, non-heat-treated ACH-2.5 xerogel, which does not show an AlO₅ NMR signal, leads to low-temperature α -Al₂O₃ synthesis. We assume, that highly polymeric species in ACH-2.5 lower the activation energy barrier to α -Al₂O₃ crystallization due to the structural units similar to those of α -Al₂O₃. These units serve as nucleation sites for the rest of Al atoms, which rearrange via 4- and 5-coordinated states of amorphous Al₂O₃ to form solely 6-coordinated state of α -Al₂O₃. The occurrence of 4- and 5-fold coordinated Al species after heat-treatment of the xerogels, usually observed in amorphous Al₂O₃, could be explained by dehydroxylation. On the other hand, 5-coordinated Al in the structures of ACH-1.2 and ACH-2.0 xerogels represent structural units less similar to those in α -Al₂O₃, which may hinder the nucleation of α -Al₂O₃ and hence, do not contribute to the lowering of the α -Al₂O₃ synthesis temperature. The crystallization of α -Al₂O₃ from those samples proceeds via conventional route forming at first transition Al₂O₃ phases and then α -Al₂O₃ by nucleation at 5-coordinated Al, preferentially localized on the surface of transition Al₂O₃. This process is reconstructive, requiring higher activation energy^{1,38}. The latter crystallization path is followed also by the rest of the ACH-2.5 sample that had not transferred to α -Al₂O₃ at low temperature.

4 Conclusion

In this work, structural changes from gelatinous aluminum chloride hydroxide, ACH, to α -Al₂O₃ powder was examined by liquid and solid-state ²⁷Al NMR as a main analytical tool. The hydrolysis ratio, h , defined as $[\text{OH}^-]/[\text{Al}^{3+}]$ was chosen as a varying parameter. The lowest temperature of α -Al₂O₃ synthesis, 500 °C, was attained by starting from ACH-2.5, i.e. the solution with $h = 2.5$. By comparing liquid and solid-state NMR spectra, the process of networking during the transition from ACH solution to anhydrous oxide, passing through ACH xerogel, was examined. Highly polymeric species, mainly ascribed to δ -[Al₂O₈Al₂₈(OH)₅₆(H₂O)₂₄]¹⁸⁺, were revealed already in the solution phase with $h = 2.5$ and became much more predominant in xerogel after drying. We conclude that the synthesis of α -Al₂O₃ at 500 °C was feasible due to the preformation of the construction units in the precursor, which result in reducing of the energy barrier for its nucleation. Direct kinetic analyses for the explicit evaluation of the activation energy are yet to be done.

Declaration of Interest

Declarations of interest: none.

Acknowledgements

The authors thank Mr. S. Stahl (Institute of Nanotechnology, Karlsruhe Institute of Technology) for assistance with NMR measurements.

Funding: This work was supported by the Scientific Grant Agency VEGA of The Ministry of Education, Science, Research and Sport of the Slovak Republic [grant numbers 2/0092/14, 1/0712/18]; and the Deutsche Forschungsgemeinschaft [grant number SE 1407/4-1]. P. H. is grateful to the State of Lower Saxony (Germany) for a Niedersachsen Professorship, from which also D. N. was supported.

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List of Table and Figure Captions

Fig. 1. Scheme of synthesis procedure and characterizations of the samples.

Fig. 2. ^{27}Al NMR spectra of as-synthesized ACH solutions with different magnification ($\nu_0 = 78.2$ MHz); a) ACH-0.0, b) ACH-0.5, c) ACH-1.2, d) ACH-2.0, e) ACH-2.5.

Fig. 3. Solid-state ^{27}Al MAS-NMR spectra of as-synthesized ACH xerogels with different magnifications ($\nu_0 = 156.4$ MHz, $\nu_{\text{rot}} = 40$ kHz); a) ACH-0.0, b) ACH-0.5, c) ACH-1.2, d) ACH-2.0, e) ACH-2.5.

Fig. 4. Thermal analyses (DTA above, TG below) of the ACH xerogels; a) ACH-0.0, b) ACH-0.5, c) ACH-1.2, d) ACH-2.0, e) ACH-2.5.

Fig. 5. XRD patterns of heat-treated ACH xerogels at 500 °C, 600 °C, 800 °C, 1000 °C, 1200 °C; a) ACH-0.0, b) ACH-0.5, c) ACH-1.2, d) ACH-2.0, e) ACH-2.5. * = $\alpha\text{-Al}_2\text{O}_3$, broad unassigned diffractions belong to transition Al_2O_3 .

Fig. 6. ^{27}Al MAS-NMR spectra of as-synthesized (below) and heat-treated ACH xerogels at 200 °C, 400 °C, 500 °C, 600 °C, 800 °C, 1000 °C, 1200 °C ($\nu_0 = 78.2$ MHz, $\nu_{\text{rot}} = 40$ kHz); a) ACH-0.0, b) ACH-0.5, c) ACH-1.2, d) ACH-2.0, e) ACH-2.5.

Tab. 1. Summarized results for aluminum chloride hydroxide samples from NMR and XRD.

Tables

Tab. 1. Summarized results for aluminum chloride hydroxide samples from NMR and XRD

Label	<i>h</i>	Al species from solution ²⁷ Al NMR of ACH solutions with respective NMR signals in ppm*	Signals of ACH xerogels from ²⁷ Al MAS-NMR (ppm*)			<i>T</i> of α-Al ₂ O ₃ formation from XRD
			AlO ₄	AlO ₅	AlO ₆	
ACH-0.0	0.0	monomers (0)	-	-	-1	800 °C
ACH-0.5	0.5	monomers (0); dimers, trimers (4)	-	-	-1	600 °C
ACH-1.2	1.2	monomers (0); dimers, trimers (4) ; ε-K-Al ₁₃ (63)	64	36	5	600 °C
ACH-2.0	2.0	monomers (0); dimers, trimers (4); ε-K-Al₁₃ (63) ; δ Al ₃₀ (13)	75	35	-2; 0; 4; 10	600 °C
ACH-2.5	2.5	monomers (0); ε-K-Al ₁₃ (63); δ Al₃₀ (11;71)	67; 75	-	-28; 0; 5; 10	500 °C

* The signals and the species with higher-intensity signals in ²⁷Al NMR and ²⁷Al MAS-NMR are in bold font

PREPARATION**SYNTHESIS**
Al(s)+AlCl₃(aq.), 95 °C**ACH SOLUTIONS****DRYING**
95 °C**ACH XEROGELS****HEAT-TREATMENT**
200 - 1200 °C, 2 h, air**HEAT-TREATED
ACH SAMPLES****CHARACTERIZATION****²⁷Al NMR**
 $\nu_0 = 78.2 \text{ MHz}$
Fig. 2**²⁷Al MAS-NMR**
 $\nu_0 = 156.4 \text{ MHz}$
Fig. 3**TG-DTA**
Fig. 4**XRD**
Fig. 5**²⁷Al MAS-NMR**
 $\nu_0 = 78.2 \text{ MHz}$
Fig. 6





