Peer Review File

Resolving Intermediates during the Growth of Aluminum Deuteroxide (Hydroxide) Polymorphs in High Chemical Potential Solutions

This manuscript has been previously reviewed at another Nature Portfolio journal. This document only contains reviewer comments and rebuttal letters for versions considered at *Communications Chemistry*.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The main experiment performed here (in situ crystallization with neutron total scattering) is an interesting one, and the analysis seems OK. However, it is not clear to me how this work really contributes to solving any of the gaps in understanding that the authors describe in the introduction. In particular I suggest the authors try to make it clearer how the changes in coordination link to the changes in stacking structure that are analysed in an interesting and detailed way using the dPDF. Total scattering analysis of the samples used in the NMR study would help to make this link clearer. At present this seems like two different papers.
Some specifics:
Line 155: Commonly, the non-uniform peak broadening in powder diffraction data and dependency on Miller indices hkl planes are indicative of the lack of translational order along the stacking direction (33,34) or finite-sized nanoparticles with anisotropic dimensions (35,36) , e.g., suspended monolayers.
This sentence isn't very clear, I would suggest splitting the two concepts of non-uniform peak broadening and hkl-dependent broadening, then explaining the structural features that lead to them. For $Al(OH)_3$ I think you also ought to mention turbostratic disorder. The references given, although relevant are not very general and do not represent the state of the art. A good, and reasonably recent overview of the effects of defects on powder diffraction data can be found in International Tables for Crystallography vol. H.

Fig 1b the time information text is written over the data
Can the dPDFs in fig1b be plotted out to slightly higher radial distances (say 20 Å) so the extent of order is more obvious? At least in supporting information.
The dG(r) data were obtained from dS(Q) up to 28 Å-1- why do we only get to see up to 20 Å-1?

It's not clear in the main text that (as seems to be shown in the SI) the PDF at the end point in fig 2 is taken after moving the solid sample into the beam.
I think it would make fig 2 clearer if you plotted the difference between the single layer model and the observed data on its own, before showing the comparison with the different interlayer correlation models. I find it hard to see any similarity between the difference plot and the (yellow) gibbsite layer correlation model in the current version of the figure, while Bayerite (blue) seems to match almost perfectly apart from a small region from 19-25 Å. Also, I think you could explain the process you have carried out here a bit more clearly, i.e. you take the single layer model and fit it to the dPDF, then compare the difference to the four different models of how the layers could interact, to see which one matches best. Right?

Reviewer #2 (Remarks to the Author):

The manuscript of Wang et al explores the mechanism for the growth of Aluminum Deuteroxide (Hydroxide) and the intermediate phases that form during the reaction. The results include 2 sets of experiments. 1) in-situ neutron PDF data that addresses the time scale 0-36 hrs for the product in the synthesis solution, and 2) diffraction/NMR that evaluate the product after 6 days, 45 days, and 3 months.
I applaud the authors efforts to apply complementary tools to gain insights into this complex system. However, it is a major weakness of the work is that there is no overlap between the timescales and physical treatment of the samples (in solution vs washed and recovered as a solid) that serves as a benchmark between the sets of samples. For the neutron PDF, the authors show in situ F(Q) and G(R) data, but because of the low signal to noise in the data, only include quantitating analyze the data for the sample at a single time point, 36 hrs. This means that the in situ experiments themselves do not provide mechanistic insights. The mechanistic insights are only possible through comparison of the PDF data point and the 3 ex situ samples
Do the authors have PDF of pre-reacted samples at the longer time points? Or NMR/diffraction for the sample after 36 hrs (as in the PDF)? Without these, the work seems more like 2 separate sets of independent experiments rather than a cohesive study. Accordingly, it seems overly speculative

to propose multiple different nucleation and growth when these could also be attributed to transformations that occur when recovering samples.
Some specific comments

- For the full modelling of the 36 h product as a individual layers. – I was looking for a brief description of this non-standard modeling strategy within the manuscript itself.
- The authors plot the residual with the layer stacking of other phases. Then simply state that the residual resembles the interlayer peaks of bayerite below 15 Å but resembles the interlayer peaks of gibbsite above 19 Å. This is an interesting suggestion but is highly subjective. The statement needs to be supported by some quantitative metrics (an R2 - value?) comparing the correspondence of the features in the residual/interlayer features over different length scales.
- I am curious as to how the low neutron scattering cross-section of Al influences the structural analysis. Perhaps the authors could comment on how diagnostic the Al positions are relative to the D/O positions?
- The authors should show the Rietveld fits with the residual that demonstrates the fidelity of the analysis, and not simply the resulting phase distribution.
- The diffraction data on the ex situ samples were used to estimate the phase distribution including a significant amorphous component. PDF is sensitive to amorphous structure – do the authors also have PDF data for the ex situ samples? This would strengthen the manuscript.
- The authors refer to “pentahedral” coordination. This is not term used to describe coordination geometry. I guess the authors mean 5-coordinate? In this case the possible geometries are square pyramidal and trigonal bipyramidal
- Can the authors comment on the sensitivity of the 27Al NMR measurements identifying the 5 coordinate Al? In the data, this is magnified by a factor of 128. Is this below the detection limit of the 3QMAS NMR? Can the authors compare these to the 5 coordinate surface acid sites previously seen by NMR and PDF in gamma-al2o3? And thereby exclude the possibility that the 5-coordinate features are associated with a minority phase vs being involved in the transformation mechanism.

Other comments

- Figure 1b, the data labels overlap with the plot lines and are difficult to read.222
- The address for PNNL is listed as being in Washington, DC

MANUSCRIPT ID: COMMSCHEM-24-0115A

>>We outlined our replies (in blue) and revisions (in red) in the text below. Changed paragraphs and sentences in the resubmitted manuscript are marked in yellow.<<

Response to Reviewers' Comments

Reviewer 1

The main experiment performed here (in situ crystallization with neutron total scattering) is an interesting one, and the analysis seems OK. However, it is not clear to me how this work really contributes to solving any of the gaps in understanding that the authors describe in the introduction.

Author Reply: We thank the Reviewer for the positive feedback and useful comments on our manuscript. We agree that the exact molecular processes leading to monolayer formation (as intermediate states) remains inconclusive. We, however, showed evidences for the presence of nanosheets and amorphous intermediates, and proposed two protentional pathways for the nucleation and growth of gibbsite from supersaturated aluminate solutions. Theoretical simulations using our newly developed reactive force field and a semiempirical model to study aluminate oligomerization and transition between different coordination states, are underway to provide a complete understanding of nucleation and growth processes at the molecular level.

In particular I suggest the authors try to make it clearer how the changes in coordination link to the changes in stacking structure that are analysed in an interesting and detailed way using the dPDF. Total scattering analysis of the samples used in the NMR study would help to make this link clearer. At present this seems like two different papers.

Author Reply: We think changes in Al^{3+} coordination from tetrahedral to octahedral are linked to the $Al(OD)_3$ monolayer formation. This transformation processes are postulated via either route-1 or route-2 (Figure 6) for the reaction pathways based on our observations. How the layers are stacked with respective to each other to form stacking structures, however, does not relate to Al^{3+} coordination changes. We viewed the layer assemblage processes as a different length-scale problems, i.e., not involving the coordination changes in the individual atoms, but a whole layer translates with respective to each other. Putting together in-situ neutron total scattering with ex-situ NMR characterizations, the observation of $Al(OH)_3$ monolayer formation (from total scattering) and the range of Al^{3+} coordination states (revealed by NMR) leads us to postulate the two distinct nucleation and growth pathways.

Some specifics:
Line 155: Commonly, the non-uniform peak broadening in powder diffraction data and dependency on Miller indices hkl planes are indicative of the lack of translational order along the stacking direction (33,34) or finite-sized nanoparticles with anisotropic dimensions (35,36) , e.g., suspended monolayers. This sentence isn't very clear, I would suggest splitting the two concepts of non-uniform peak broadening and hkl-dependent broadening, then explaining the structural features that lead to them. For $Al(OH)_3$ *I think you also ought to mention turbostratic disorder. The references given, although relevant are not very general and do not represent the state of the art. A good, and reasonably recent overview of the*

effects of defects on powder diffraction data can be found in International Tables for Crystallography vol. H.

Author Revisions: We have modified this sentence and updated references as follows: "Commonly, non-uniform peak broadening in powder diffraction data is an indicative of anisotropic crystallite (or domain) size/strain line broadening[33]. For example, anisotropic crystallite size can result from crystal growth, where specific bonding interactions produce layered or columnar structures. Atomic dislocation-induced strain in comparison is a typical example of anisotropic strain broadening in a crystal[34]. Here, only the 4.32 Å^{-1} reflection is noticeably narrower than other reflections, and its Miller index nicely matches to the expected intralayer lattice plane in the four $Al(OD)_3$ polymorphs. Thus, the observed non-uniform peak broadening and dependency on Miller indices for the 4.32 Å^{-1} reflection suggest the lack of translational order along the stacking direction[33,35,36], e.g., random or turbostratic stacking, or finite-sized nanoparticles with anisotropic dimensions[37-39], e.g., suspended monolayers."

Fig 1b the time information text is written over the data. Can the dPDFs in fig1b be plotted out to slightly higher radial distances (say 20 Å) so the extent of order is more obvious? At least in supporting information.

Author Reply: We plotted only up to 10 Å in Figure 1b to facilitate discussions on the first 4 peaks in the difference PDF ΔG(r) dataset.

Author Revisions: We have modified the labelling positions in Figure 1b, so the texts are not shown on top of the data curves. Figure plotted up to high-r distances are now provided in Supplementary Information, Figure S2c.

The dG(r) data were obtained from dS(Q) up to 28 Å-1- why do we only get to see up to 20 Å-1?

Author Revisions: In Supplementary Information, we modified Figure S2a and added Figure S2b for the extended q-region plot, so that the S(q) (Figure S2a) and ΔS(q) (Figure S2b) datasets are now displayed up to 28 Å^{-1}.

It's not clear in the main text that (as seems to be shown in the SI) the PDF at the end point in fig 2 is taken after moving the solid sample into the beam. I think it would make fig 2 clearer if you plotted the difference between the single layer model and the observed data on its own, before showing the comparison with the different interlayer correlation models.

Author Revisions: Yes, thanks for the suggestions. Figure 2 is modified accordingly.

I find it hard to see any similarity between the difference plot and the (yellow) gibbsite layer correlation model in the current version of the figure, while Bayerite (blue) seems to match almost perfectly apart from a small region from 19-25 Å. Also, I think you could explain the process you have carried out here a bit more clearly, i.e., you take the single layer model and fit it to the dPDF, then compare the difference to the four different models of how the layers could interact, to see which one matches best. Right?

Author Reply: The Reviewer is correct about our single layer model fitting approaches. Details about the method are provided in sections 1 and 2 of the Supplementary Texts, due the to the length restrictions for the communication article (limited to ~5,000 words). To facilitate discussions on layer stacking sequences and comparison between the residual PDF and calculated interlayer correlations, we added R_w analysis for every 5 Å segments of the residual data. These results are displayed in Figure 2b.

Author Revisions: Figure 2 is modified accordingly. R_w values (in every 5 Å segments of the residual data) are displayed in Figure 2b. Details about the single-layer model fitting are presented in section 1 of the Supplementary Text. We also added more method descriptions in section 2 of the Supplementary Text.

Reviewer 2

The manuscript of Wang et al explores the mechanism for the growth of Aluminum Deuteroxide (Hydroxide) and the intermediate phases that form during the reaction. The results include 2 sets of experiments. 1) in-situ neutron PDF data that addresses the time scale 0-36 hrs for the product in the synthesis solution, and 2) diffraction/NMR that evaluate the product after 6 days, 45 days, and 3 months. I applaud the authors efforts to apply complementary tools to gain insights into this complex system.

Author Reply: We thank the Reviewer for their time in evaluating our manuscript.

However, it is a major weakness of the work is that there is no overlap between the timescales and physical treatment of the samples (in solution vs washed and recovered as a solid) that serves as a benchmark between the sets of samples. For the neutron PDF, the authors show in situ F(Q) and G(R) data, but because of the low signal to noise in the data, only include quantitating analyze the data for the sample at a single time point, 36 hrs. This means that the in situ experiments themselves do not provide mechanistic insights. The mechanistic insights are only possible through comparison of the PDF data point and the 3 ex situ samples

Author Reply: We disagree with the Reviewer that the in-situ neutron experiments do not provide mechanistic insights on gibbsite/bayerite formation process. Although the signal-to-noise ratio is difficult to overcome, the overall intensities increasing with increasing reaction time and analysis applied in neutron ΔS(q) and ΔG(r) data suggest that the $Al(OD)_3$ monolayer is an intermediate particle phase during gibbsite/bayerite nucleation and growth from alkaline sodium aluminate solutions. The life time of $Al(OD)_3$ monolayer is on the order of less than 36 hours. Our in-situ observations also suggest that the precipitation is not a simple reaction involving the direct growth of ordered gibbsite or bayerite somatoids from supersaturated solutions. In addition, because of the slow precipitation rates in our solution system, we viewed recovered solid sample as a reference to follow the reaction at longer time-scales. We also feel it is unfair to disqualify the work for ~5 days time-gap between the end of the neutron experiments and the recovered solid sample characterized at 6 days.

Author Revisions: A new solution sample was prepared using the same preparation protocol. Additional in-situ characterization using ^{27}Al MAS NMR was performed on this newly prepared solution to follow the growth of gibbsite/bayerite phases over two weeks period. As illustrated in Figure S6, we observed initially a single Lorentzian line corresponding to tetrahedral aluminate species in solution. After ~3 days, signal intensity in the octahedral region starts to show, which displays a quasi-Lorentzian line attributing to the slow spinning rate. Under the performed acquisition conditions (see Method), individual resonances for bayerite-like or gibbsite-like nanolayers remain unresolved, and instead, a single octahedral resonance is observed, representing the combined octahedral coordination in both polymorphs. Signals for pentacoordinate Al^{3+} are not resolved, likely due to their low abundance compared to the dominated tetrahedral Al^{3+} signal in solution. Note that we do not have enough precipitates for XRD characterization at 3 days.

We also added a brief discussion in the main text (at the end of the in-situ results section) for the variation in the induction time observed between the two in-situ measurements. They are described below: "We note the variation in the induction time between the two in-situ measurements under the same solution concentration. If one considers the stochastic nature of nucleation and the formed nuclei have to grow to appreciable sizes before they can be detected experimentally, studies have shown that variation in the induction times determined from a large number of measurements under well-defined/identical conditions typically results an exponential distribution function[44,45]. Thus, ruling out concentration errors, variation in the induction times observed here may result from differences between neutron and NMR experiment conditions, such as temperature and solution volume used. Another possibility for such variation could originate from multiple nucleation and growth processes, i.e., not a single nucleation/growth mechanism."

Also, to reduce the texts in the manuscript, we moved NMR experimental details to section 3 in the Supplementary Text.

Do the authors have PDF of pre-reacted samples at the longer time points? Or NMR/diffraction for the sample after 36 hrs (as in the PDF)? Without these, the work seems more like 2 separate sets of independent experiments rather than a cohesive study. Accordingly, it seems overly speculative to propose multiple different nucleation and growth when these could also be attributed to transformations that occur when recovering samples.

Author Reply: We do not measure neutron PDF of recovered solid sample at the longer time point. The neutron experiment was conducted during COVID shutdown period. We were off-site and not able to do any follow up experiments for limited neutron beamtimes. We also cannot think of any reasons that could cause changes or transformation when simply scoping and vacuum filtering (no washing) of solid precipitates out of the bottom of the solution bottle. In our revised manuscript, the time-gap issues are fixed with added in-situ ^{27}Al MAS NMR characterizations.

Some specific comments
- For the full modelling of the 36 h product as an individual layers. – I was looking for a brief description of this non-standard modeling strategy within the manuscript itself.

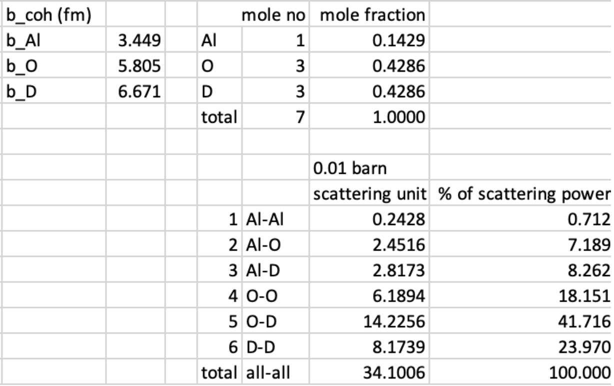
Author Reply: Details about the model are provided in sections 1 and 2 of the Supplementary Texts, due the to the length restrictions for the communication article (limited to ~5,000 words).

- The authors plot the residual with the layer stacking of other phases. Then simply state that the residual resembles the interlayer peaks of bayerite below 15 Å but resembles the interlayer peaks of gibbsite above 19 Å. This is an interesting suggestion but is highly subjective. The statement needs to be supported by some quantitative metrics (an R2 - value?) comparing the correspondence of the features in the residual/interlayer features over different length scales.

Author Revisions: Thanks for the suggestions. To facilitate discussions on layer stacking sequences and comparison between the residual PDF and calculated interlayer correlations, we added R_w analysis for every 5 Å segments in the residual data. These results are displayed in Figure 2b.

- I am curious as to how the low neutron scattering cross-section of Al influences the structural analysis. Perhaps the authors could comment on how diagnostic the Al positions are relative to the D/O positions?

Author Reply: In neutron total scattering (and diffraction), Al atom has coherent a scattering length of 3.449 fm (1 fm = 10^{-15} m), D atom has a length of 6.671 fm and O atom has a length of 5.803 fm (https://www.ncnr.nist.gov/resources/n-lengths/). The scattering power (cross-section) from each atom is equal to the square of the scattering length multiplied by 4π. Since O/D atoms are three times more than Al atom in the $Al(OD)_3$ stoichiometry and Al atom has a slightly smaller scattering power than O/D atoms, neutron total scattering has a higher sensitive for O and D pair correlations than correlations involving Al atom. This information is shown in the table below, where the calculated neutron total scattering weights (as %) for the six pair-wise partial correlations expected in the $Al(OD)_3$ stoichiometry are listed. Here, about 84 % of the measured neutron intensities comprises contributions from the O-O, O-D, and D-D pair correlations. Al-Al, Al-O, and Al-D contribute ~16% of the total intensity. This ~16% contribution is nonnegligible.



b_coh (fm)				mole no	mole fraction	
b_Al	3.449		Al	1	0.1429	
b_O	5.805		O	3	0.4286	
b_D	6.671		D	3	0.4286	
			total	7	1.0000	
					0.01 barn	
					scattering unit	% of scattering power
			1	Al-Al	0.2428	0.712
			2	Al-O	2.4516	7.189
			3	Al-D	2.8173	8.262
			4	O-O	6.1894	18.151
			5	O-D	14.2256	41.716
			6	D-D	8.1739	23.970
			total	all-all	34.1006	100.000

- The authors should show the Rietveld fits with the residual that demonstrates the fidelity of the analysis, and not simply the resulting phase distribution.

Author Revisions: Rietveld fits are now provided in Figure S8 in Supplementary Information.

- The diffraction data on the ex situ samples were used to estimate the phase distribution including a significant amorphous component. PDF is sensitive to amorphous structure – do the authors also have PDF data for the ex situ samples? This would strengthen the manuscript.

Author Reply: As mentioned above, we do not have neutron PDF data for the ex-situ samples. In the in-situ neutron total scattering datasets, since the solution background scattering were removed via a difference PDF ΔG(r) approach, we also suspect that the minor amorphous phase signals may have been removed accidentally during the background scaling between the time-sequenced PDF and the initial first 4 hours PDF dataset. Although we are very careful about the solution background removal during data reduction and analysis, we cannot guarantee over- subtraction of background would not occur. Even if the amorphous phase signals are preserved in the final reduced PDF ΔG(r), its disordering character and low-abundance also lead to weak scattering signal when compared to the ordered $Al(OD)_3$ nanosheets. This is a common issue in the differences PDF analysis approaches. Thus, we performed a suite of ex-situ characterizations to prevent erroneous interpretation of nucleation and growth mechanisms and to support the PDF results.

- The authors refer to "pentahedral" coordination. This is not term used to describe coordination geometry. I guess the authors mean 5-coordinate? In this case the possible geometries are square pyramidal and trigonal bipyramidal

Author Revisions: Thanks for pointing it out, we mean 5-coordinate Al^{3+} species, regardless the exact geometric shapes the species could be. The term "pentahedral" is now changed to "pentacoordinate" throughout the manuscript.

- Can the authors comment on the sensitivity of the 27Al NMR measurements identifying the 5 coordinate Al? In the data, this is magnified by a factor of 128. Is this below the detection limit of the 3QMAS NMR? Can the authors compare these to the 5 coordinate surface acid sites previously seen by NMR and PDF in gamma-al2o3? And thereby exclude the possibility that the 5-coordinate features are associated with a minority phase vs being involved in the transformation mechanism.

Author Reply: The Reviewer is correct. The trace 5-coordinate Al^{3+} is indeed below the detection limit of 3QMAS NMR. As for the second part of the question about the 5-coordinate Al^{3+} species, in the manuscript (under section of "multiple nucleation and growth processes"), we suggest that the 5-coordinated Al^{3+} detected here can be either presented at the edge of octahedrally-coordinated Al^{3+} nuclei or associated with the amorphous phase. In each of the cases, the trace 5-coordinate Al^{3+} potentially facilitates Al^{3+} coordination changed from tetrahedral in solution species to octahedral in $Al(OD)_3$ nanoplatelets. The transformation processes are postulated via either route-1 (through transient pentacoordinate species) or route-2 (amorphous-to-ordered transitions) for the reaction pathways based on our observations (Figure 6).

Other comments

- Figure 1b, the data labels overlap with the plot lines and are difficult to read.222

Author Reply: Figure 1b is changed in accordance with suggestions.

- The address for PNNL is listed as being in Washington, DC

Author Reply: Fixed.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

I think the authors have addressed the comments from myself and the other referee well. However the new XRD data and Rietveld fits and QPA presented are not fully explained and further information is needed for proper assessment of the results:
XRD and Rietveld fits- Please add details of the data collection (capillary?, flat plate?) and refinement. what parameters were refined? Was PO considered (if flat plate data on a layered material)? What were the final agreement factors (Rwp, GooF)? What/whose anisotropic strain macros were used (note there is no hard coded anisotropic strain model in TOPAS)? Is TiO_2 a suitable standard for amorphous content in aluminum hydroxides? I would have used dry aluminum oxide. Scattering power of the standard relative to the sample can actually make a big difference in amorphous content determination. Why is the fit on the first 2 diffraction peaks so poor in the 6 and 45 day samples but near perfect in the 3 month sample?

MANUSCRIPT ID: COMMSCHEM-24-0115A

>>We outlined our replies (in blue) and revisions (in red) in the text below.<<

Response to Reviewers' Comments

Reviewer 1 (Remarks to the Author)

I *think the authors have addressed the comments from myself and the other referee well. However, the new XRD data and Rietveld fits and QPA presented are not fully explained and further information is needed for proper assessment of the results:*

Author Reply: We thank the Reviewer for the positive feedback and further comments on our XRD analysis.

XRD and Rietveld fits- Please add details of the data collection (capillary?, flat plate?) and refinement. what parameters were refined? Was PO considered (if flat plate data on a layered material)? What were the final agreement factors (Rwp, GooF)? What/whose anisotropic strain macros were used (note there is no hard coded anisotropic strain model in TOPAS)? Is TiO2 a suitable standard for amorphous content in aluminum hydroxides? I would have used dry aluminum oxide. Scattering power of the standard relative to the sample can actually make a big difference in amorphous content determination. Why is the fit on the first 2 diffraction peaks so poor in the 6 and 45 day samples but near perfect in the 3 month sample?

Author Reply: To address the above questions, we added section 4 in the supplementary text to show details about XRD sample preparation and Rietveld-internal standard refinement procedures. We also corrected our wrong statement about using anisotropic strain macros (in TOPAS) to account for peak broadening. When we revisited these data, we realize that only crystallite size broadening was analyzed by interpreting the Lorentzian coefficients refined in TOPAS. Finally, because disorder was not included in the model, our Rietveld refinement results are considered semi-quantitative within the scope of the work.

Author Revisions: Please see section 4 of the Supplementary Text. Also note that the only changes made in the main text are the X-ray diffraction method section, where a sentence referring to Section 4 of the supporting text is added at the end of the paragraph.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Thanks for addressing the remaining questions. I am now happy for the paper to be published.