EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Interaction of capping agents on Aluminum based NPs – in-situ PDF study	**Experiment number**: SC-4354
Beamline: ID31	**Date of experiment**: from: 08.11.2016 to: 11.11.2016	**Date of report**: 21.12.2016
Shifts: 6	**Local contact(s)**: Maria Valeria Blanco	*Received at ESRF:*

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Report:

The aim of the proposal referred to, was the study of the nucleation and formation of ultra-small AlOOH nanoparticles with the Pair Distribution Function (PDF) Technique. In particular, the focus was set on ligand interactions to the nanoparticle surface and the very early steps of agglomeration and nanoparticle growth.
In order to resolve the signal and its time dependent change we had to measure close to the limit of the detector time resolution by at the same time acquiring an adequate data quality.

In preparation to the beamtime we advanced our flowcell setup towards a small reaction reactor in which reactants were mixed in a controlled fashion and the start of the reaction can be monitored with much higher time accuracy. A homogeneous solution was established in the reaction chamber within less than one second for which external conditions such as temperature as well as the ligand addition rate are tuneable.

The first test of the new reaction vessel was successful as high Qs without the observation of any setup shadowing (e.g. from the stirring magnet or the flight tube extension). The Perkin Elmer detector enabled us to measure at a maximum of 2 s/scan (6 sec in total) in order to collect satisfactory statistics. Figure 1a depicts a data set series in which the signal of the amorphous AlOOH precursor structure is isolated and background subtracted.

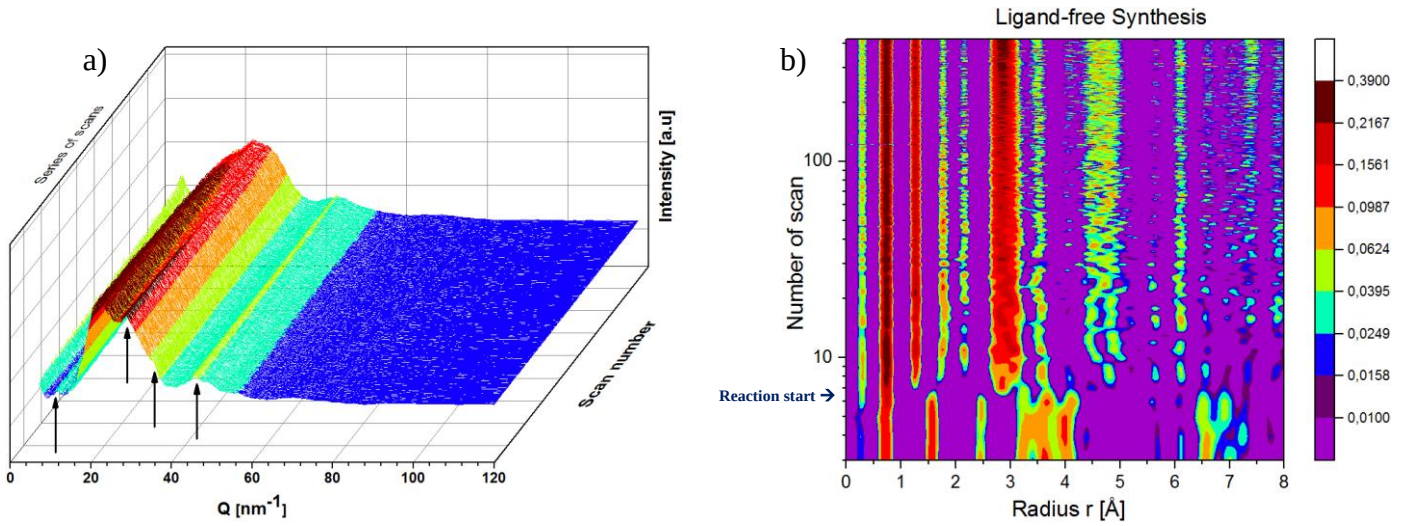

Fig. 1: In-situ synthesis of pure boehmite precursor structures at room temperature. a) Background corrected data in which tiny particles and clusters result in amorphous appearing broad signals in particular at the beginning of the synthesis. Slowly, peaks of flat boehmite layers grow in intensity. b) PDFs of the data highlight the finite particle size and broad bond length variations which tend to narrow down with time.

In the background corrected data sets after 30 minutes of exposure the first broad Bragg peaks which are characteristic for boehmite appear at a Q of 9, 27, 33 and 44 nm^{-1} (Fig. 1a), respectively. The corresponding PDFs of the clusters which yield data up to about 9 Å confirm the crystalline size and the time dependent development. For fully aged boehmite particles, which are expected to reach sizes of around 3.2 x 2.2 x 1 nm, clear signals are measured up to 30 Å. In a first comparison to those data sets which yield more developed and crystalline AlOOH nanoparticles (which are omitted in this report), the present PDF peak positions are rather similar but the peaks shape is a lot broader. It appears that many sites of the $Al(OH)_6$ reactants have not yet condensed which explains the lack of a clear boehmite Al-Al distance of 2.9A. Instead we can still observe a very broad maximum at 2.6-3.4 Å indicating that a single condensation process is too fast to be monitored, the orientation and ordering processes of cluster, however, can be resolved by these kinds of measurements.
This measurement was carried out at low temperature to investigate a slow transformation of precursor to more crystalline nanoparticles. These reduced data sets represent the early stages of pure boehmite growth and is used as a reference to syntheses to which an organic ligand was added.
After having set up molecular models, fits to the PDF data will be carried out to facilitate statements on the structural features of the AlOOH precursor (e.g. either chainlike connected polynuclear clusters or 2D flat sheets of AlOOH).

Similar looking data sets were obtained by adding organic ligands (e.g. methyl sulfonic acid or DMLT) as surface coordinating and stabilizing agents prior to the reaction to the solution. Data thereof also indicate the occurrence of characteristic boehmite peaks, but very late in the synthesis. Moreover, 3 hours at higher temperature are required for peaks to appear.

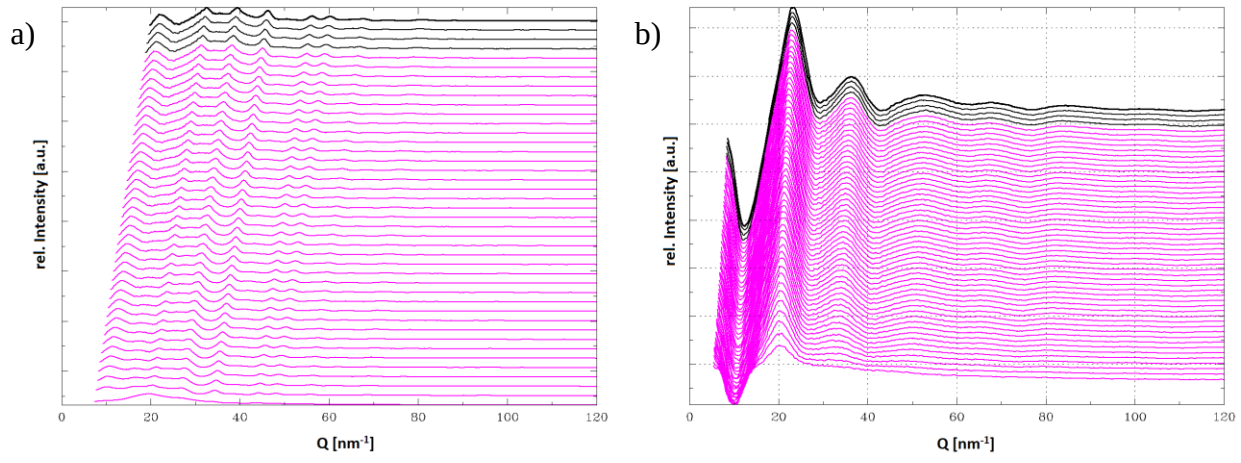

Fig. 2: In-situ synthesis of AlOOH nanoparticels with ligands after background substaction. There are obvious effects of a) carboxylic acid functionalised ligands which features a rather long period of amorphous precursor until the characteristic boehmite pattern slowly evolves b) hydroxyl group functionalised ligands which prevent any visible boehmite peak formation.

Therefore, an equilibrium of a ligand Al^{3+} complex formed by usual water exchange reactions to a condensed oxo-Al^{3+} species might prevail in solution. Until accurate background (which changes over time) corrections and a suitable precursor species is found, assumptions like that should be postponed. In the course of the investigation, however, it would be of great interest whether both, ligand addition at the beginning of the synthesis as co-reactant and ligand addition in later stages of the synthesis have similar effects on the reaction rate and product formation.

The investigation of a high temperature synthesis and therefore a drastic speedup of the reaction rate and appearing species is very challenging with the Perkin Elmer detector (4-5 sec detector readout time, double as much than the scan time itself). By the collected data however, we should manage to model at least one predominant precursor structure which is stable in solution at room temperature for a few minutes. We appreciate, that the new generation of area detectors (Cd-Te) has arrived at the ESRF which in the future will ease the acquisition of time resolved in-situ data.