ESRF

Experiment title:

Investigation of early reaction steps towards high purity anatase nanoparticles

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SC-4458

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6

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Report:

The following report summarizes various results from the in-situ synthesis of TiO_2 nanoparticles. The initial idea was based on the time-resolved study of the formation of anatase particles at ambient temperatures. The reaction was carried out in its published form in order to link those results to the particles synthesized and characterized in the literature. This dataset of the pure synthesis acts as reference regarding the kinetics and emerging structures in the course of the synthesis. From there, several variations to the synthesis were introduced. In the first experiments reactants which represent weak organic ligands to the metal cations were added in low concentrations to the reaction. Other parameters such as temperature and concentrations were kept identical to the standard recipe. Depending on the additive and the temperature of the single experiment, measurement durations ranged between 1h to 3h.

Time resolved PDF data put forward in Fig. 1 emphasise the effect of additives to the reaction. 1,5-Diphenyl-1,3,5-pentatrione (Pent) as one of the chosen ligands is generating an decelerating and peak broadening effect compared to the pure reaction at 90°C.

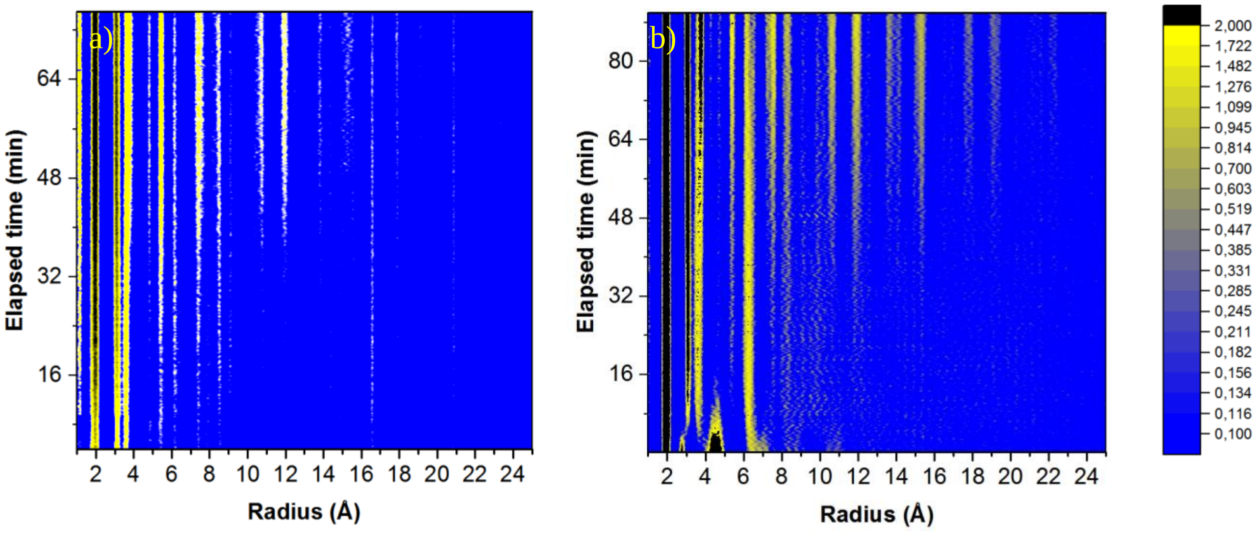

Fig. 1. Temporal evolution of d-PDFs for a) pure synthesis over 1.3h (left) b) Pent additive over 1.5h (right)

As apparent in the data, particles form ab initio just after the reactant mixing process with the time resolution of the nucleation and growth stage being fabulous. First polycondensations towards single chains of Ti-octahedra are mainly observed until the 25 minutes mark. Afterwards, in midst of constant aging condition, the three dimensionally more complex particles are formed. The early clusters formed with Pent deviate from those of the pure synthesis which is most obvious with the emerging 6.5 Å signal and the missing chain peak at 16 Å. The very broad peaks are explained by the much slower ordering of the particles and corresponding fits confirm SAXS data of smaller particles being created. The anticipated effect of the ligand can be attributed to a chelating effect of Pent. Yet, due to the reversible interaction of the ligand to the Ti^{4+} cation, particles can progressively grow towards anatase.

Since Ti(IV) possesses a high scattering cross section, signal to noise ratio after background corrections were excellent. Modelling initially with powder data enabled us to confirm the presence of edge connected octahedron chains in solution. Concomitantly with other characterisation methods we describe multicore cluster formation and their growth in the regarded time frame towards particles of 4 nm size.

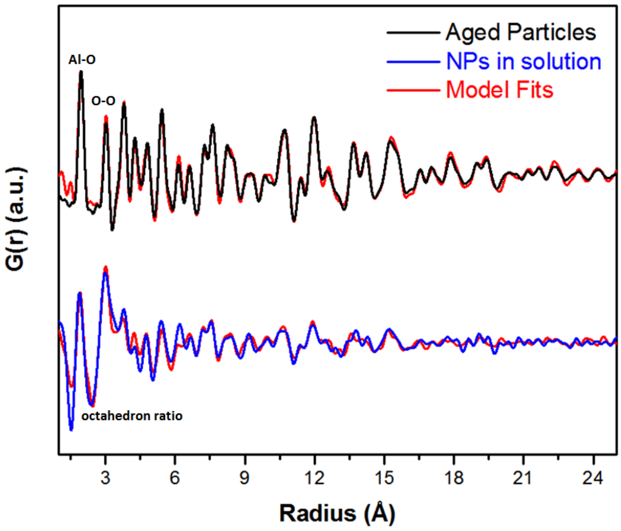

Fig. 2. Anatase at the end of the reaction (black) and at early stage of growth reaction (blue) and their corresponding fits of spherical anatase nanoparticles.

In a second set of experiments very low amounts of acetates (4 wt%), Zn^{2+} and Fe^{3+} respectively, were added to the reaction. The effects on the reaction progress are depicted in Fig. 3 (Zn^{2+} left, Fe^{3+} right). The synthesis with zinc as additive shows a more usual behaviour similar to the pure synthesis. Iron, however, seems to inhibit the reaction mechanism to a much stronger extend and exhibits characteristic anatase peaks around 30 minutes later into the reaction. Metals salt, which were initially thought to mainly act as acetate sources, participate in competing reactions and exhibit a tremendous effect even at low concentrations (precursor peak at 4.8 vanishes not seen in pure synthesis).

This behaviour is possibly explained by the existence of rather stable metatitanates (e.g. ilmenite) which may strongly interfere in the early stages of the reaction. Furthermore, internal cation transportation processes are eased in solution and described by various cation exchange mechanisms. Herein, additional studies are required to investigate whether the charge of those cations (and hence the coordination of the clusters) is the main driving force in the inhibition of particle formation.

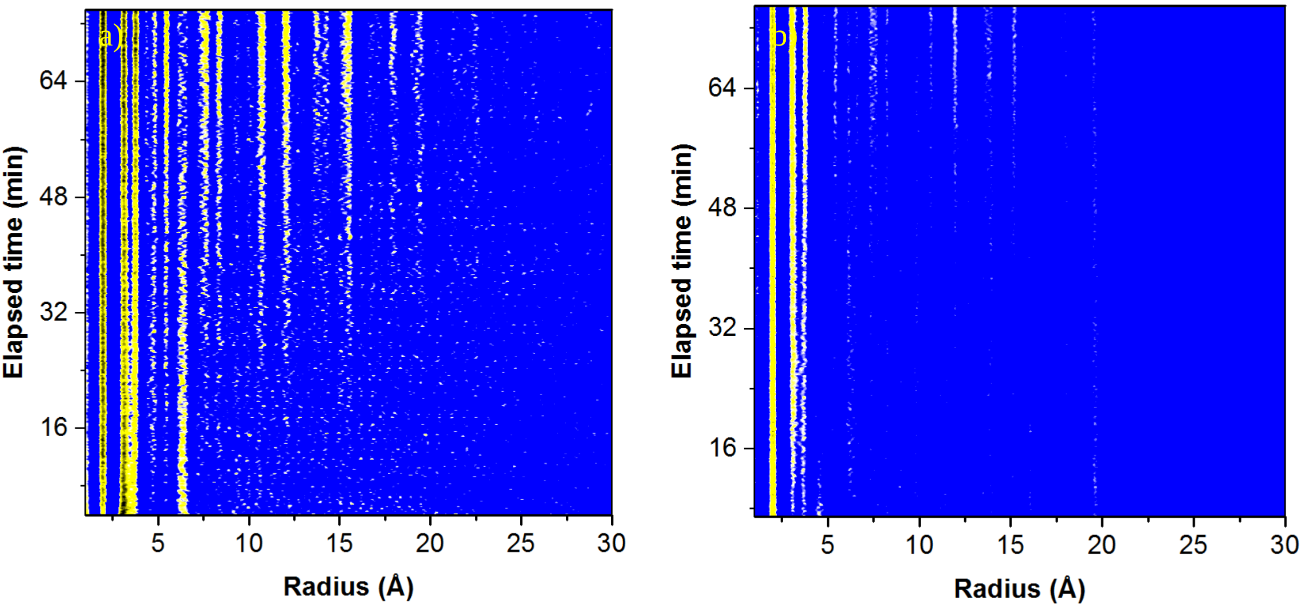

Fig. 3. Temporal evolution of d-PDFs over 1.3h for a) with ZnAc and b) FeAc as additive