Preliminary Report on High Energy Synchrotron SAXS/WAXS *In Situ* Study of the Formation of Titania Nanoparticles in a Supercritical Synthesis

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Abstract
Understanding the dynamics of particle formation is important for the development and optimization of sol-gel syntheses. In this study particles of anatase TiO_2 are produced by a modified sol-gel reaction (SSEC) in a supercritical media. The final products are highly crystalline anatase particles with a narrow size distribution and sizes in the nanorange.
To investigate the dynamics of the process time resolved *in situ* SAXS/WAXS of the formation of the TiO_2 particles in a new custom designed pressure cell was performed. To penetrate the reactor windows, X-rays with very high energy and high intensity must be used. The signal to noise ratio is a serious challenge and only few synchrotron facilities in the world can be utilized for this purpose. Raw data examples are presented from a single synthesis as an experiment proof of principle.

INTRODUCTION

Sol-gel chemistry is widely used in the production of metal oxides, because of the low temperature needed, the purity of precursors, the mild chemical conditions and the easy doping with other metals or functionalization with organic ligands [1]. Supercritical fluids have during the last two decades been studied as solvent in sol-gel processes [2]. Using supercritical solvents crystaline materials can be produced at much lower temperatures and with significantly shorter reaction times than conventional sol-gel processes. Furthermore, both porous and nanocrystalline products can be obtained and the properties can be tuned by varying process parameters such as temperature, pressure, and concentration [3-5]. The sol-gel process is generally a hydrolysis followed by condensation. Understanding the reactions involved is complicated and the ability to study the reaction as it occurs is thus very attractive. By using *in situ* SAXS/WAXS simultaneously, it is possible to monitor the particle formation as well as the crystallization as a function of time.

In situ studies of sol-gel reactions in supercritical CO_2 (sc-CO_2) have so far not been accomplished due to the high pressure limitation. To withstand the pressure thick windows are needed, which will absorb radiation. By using X-rays with much higher energy ($E > 80$ keV) than conventionally used, the transmission becomes acceptable if the incoming X-ray intensity is high enough. For these reasons *in situ* supercritical experiments can only be performed at a few synchrotron facilities in the world.

I - MATERIALS AND METHODS

The hydrolysis and condensation of titanium tetraisopropoxide (TTIP) and water in sc-CO_2 forming titania nanoparticles with polypropylene fiber as seeding material was studied [3-5].

To study the reaction at supercritical conditions a specially designed reaction chamber with windows of borosilicate was built. The reaction chamber is a 30 mL view cell with a max pressure of 680 bar and a max temperature of 200 ºC. The *in situ* set-up allows precise control of the heating rate, final temperature, and pressure. The *in situ* experiment was performed at the Advanced Photon Source (APS) at Argonne National Laboratory. In the experiment a beam with an energy of 80 keV (λ = 0.1535 Å) was optimized to a beam width of approximately 50μm at the position of the sample. Each window had a thickness of ½ inch in order to withstand the pressure. By using the high energy X-rays only 30% of the intensity was absorbed in each window (μ = 0.015 mm^{-1}).

Standard experiment:

In a standard experiment the chamber is loaded with polypropylene fiber, TTIP, and deionised water. The water is injected in the bottom of the chamber and TTIP in front of the chamber windows. This approach ensures that mixing of TTIP and water does not occur before the chamber is pressurized with CO_2. The chamber is pressurized to 100 bar in a few minutes and the temperature is raised to 100 ^{o}C a rate of 2-3 ^{o}C/min. The data collection is initiated, when the chamber is pressurizing, allowing the study of the effect of the density increase and the initial hydrolysis. Both the WAXS and the SAXS detector are CCD detectors and these are both exposed for 20 s followed by 30 s of data collection leading to a time resolution of 50 s.

II – RESULTS AND DISCUSSION

The raw data recorded as a proof of the success of the experiment is shown in Figure 1. The analysis of data is ongoing and will be published later.

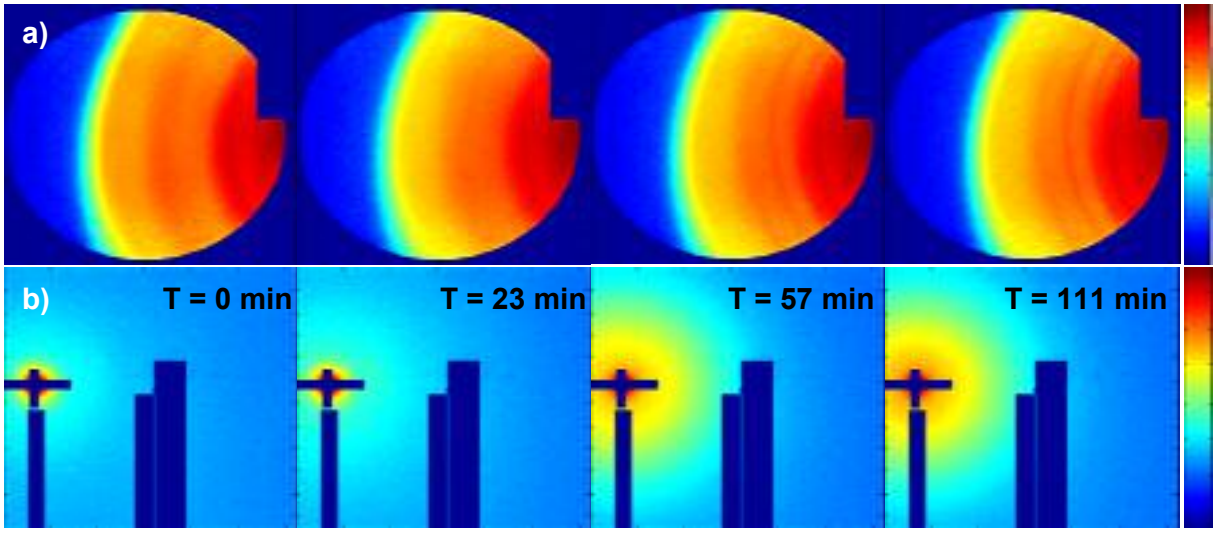

Figure 1: 2D *in situ* images from a) SAXS and b) WAXS during an experiment. The rectangular bars are inserted to zero the beamstop area and areas with detector bleeding.

From both the *in situ* SAXS and *in situ* WAXS images a scattering development is observed. The crystalline features from WAXS are stronger after data reduction and subtraction of background and diffuse scattering allowing size analysis. Furthermore, a change in scattering intensity with changing process condition was observed.

CONCLUSION

Very hard X-rays with high intensity produced at third generation synchrotron sources make it possible to do simultaneous SAXS and WAXS *in situ* studies of supercritical processes. This opens up great possibilities for future investigations of the formation of nanoparticles in supercritical syntheses.

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