

# Nanoparticle Formation in Supercritical Fluids – The World’s First Real Time In-situ Investigation

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## ABSTRACT

In this study the world’s first real time in-situ simultaneous small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) characterization of supercritical nanoparticle formation was performed. In previous supercritical studies the reaction is treated as a ‘black box’ and the final product has been used to understand the process. In this study we open up the black box and directly reveal the mechanism behind sol-gel reactions in supercritical CO<sub>2</sub>. The brilliance of the APS source and the design of the supercritical reaction chambers played a critical role in successfully exploring the key parameters in the formation of high quality nanoparticles in supercritical fluids. By the current set-up the supercritical sol-gel nanoparticle formation can be controlled and altered by changing the process parameters. This means that the particle properties can be tailor-made by fine-tuning the process parameters.

**Keywords:** supercritical, nanoparticles, in-situ, sol-gel.

## 1 INTRODUCTION

Nanomaterials and nanoparticles are gaining a lot of public and research attention. A special interest is being devoted to developing new synthesis and characterizing methods to investigate the changes observed going from bulk material to nanoparticles.

The sol-gel technique is the most broadly applied wet chemical process and it can be used for the production of nanosized materials in the form of particles or coatings for a wide range of materials. However, conventional sol-gel techniques have a number of drawbacks such as long reaction times and post treatment processing. For example, drying and calcination are required to obtain a crystalline material which represents a considerable increase in energy consumption. In addition to high energy usage, the post

heat treatment reduces the specific surface area by up to 80% due to sintering and particle growth.

We have addressed the problems related to the conventional sol-gel techniques by using supercritical CO<sub>2</sub> as the reaction media [1], [2]. Supercritical fluids are superior solvents due to gas like mass transfer properties and liquid like densities. Thereby the kinetics of the sol-gel processes can often be enhanced by more than an order of magnitude compared to the traditional alcohols.

In this study the world’s first real time in-situ simultaneous small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) characterization of supercritical nanoparticle formation was performed [3]. In previous supercritical studies the reaction is treated as a ‘black box’ (Figure 1) and the final product has been used to understand the process. In this study we open up the black box and directly reveal the mechanism behind sol-gel reactions in supercritical CO<sub>2</sub> (Figure 2).

### Normal Supercritical Nanoparticle Studies

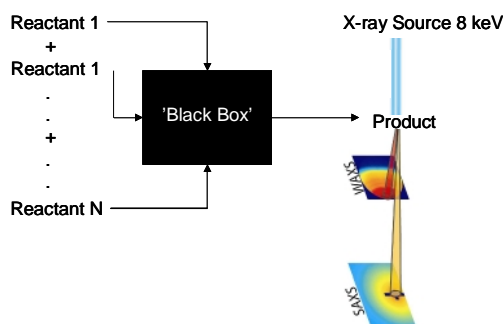


Figure 1. Normal set-up for supercritical nanoparticle study.

The brilliance of the APS source and the design of the supercritical reaction chambers played a critical role in

successfully exploring the key parameters in the formation of high quality nanoparticles in supercritical fluids. By the current set-up the supercritical sol-gel nanoparticle formation can be controlled and altered by changing the process parameters. This means that the particle properties can be tailor-made by fine-tuning the process parameters. Furthermore, a general crystallization temperature was determined at unprecedented low temperatures. Optimization of the processes showed that a solid nanocrystalline product can be obtained at very short process times.

### In-Situ Supercritical Nanoparticle Study

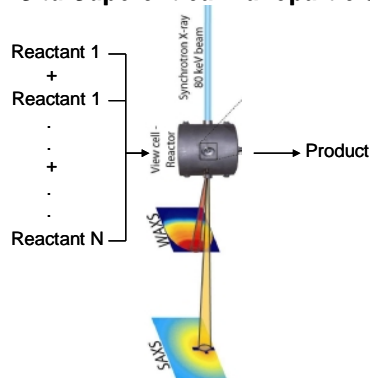


Figure 2. In-situ set-up for real time supercritical nanoparticle study.

## 2 EXPERIMENTAL DETAILS

The design of the in-situ set-up is made from prior knowledge from supercritical particle formation [1], [4]. Furthermore, the design is made with the requirement to investigate the process in-situ by synchrotron radiation and with focus on high flexibility. The main constrains are the thickness of the windows, the window size (width), the rapid reaction time, and the large heating and cooling time due to the experimental conditions. The in-situ set-up is shown in Figure 3.

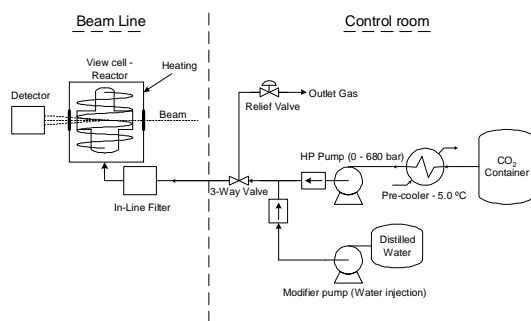
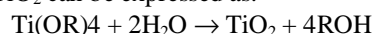


Figure 3. The in-situ set-up.

The in-situ set-up is centered around the view cell reactor which is placed inside the hutch at the beam-line.

To withstand the high pressures (>200 bar), thick reactor windows are crucial, but these absorb the probing X-rays unless the energy is very high. For high-energy X-rays ( $E > 80\text{keV}$ ) transmission becomes acceptable even for one-inch thick borosilicate windows (70% transmission). However, the incoming X-ray intensity must still be sufficiently high to give a time resolution of minutes. The experiments were conducted at Beamline 1-ID at APS at Argonne National Laboratory, one of the few synchrotron beamlines in the world where a sufficient flux of high-energy X-rays is available.

The supercritical reaction studied is a modified supercritical sol-gel process, the SSEC process [1], [4]. The basic principle is a sol-gel reaction taking place in a supercritical environment. The sol-gel process starts with the hydrolysis of the precursor, normally a metal alkoxide, when it comes into contact with water. The hydrolysis continues simultaneously with the condensation of the hydrolyzed monomers, leading to the formation of a three-dimensional metal oxide network. The overall process for producing  $\text{TiO}_2$  can be expressed as:



Previous study has shown that the SSEC process can lower the crystallization temperature significantly for producing the anatase phase of  $\text{TiO}_2$  compared to a normal sol-gel process. The crystallinity of the powder produced by the SSEC process was also shown to be dependent on the heating rate and the supercritical media as well as the final temperature and seeding material [1], [4].

## 3 RESULTS AND DISCUSSION

The real time in-situ experiments showed that the formation of nanoparticles is a four step mechanism [3]. First an induction period (A) characterized by a gelation period followed by a latent period (B) occurring from the first crystalline material was detected to a sudden change in the system. The latent period is followed by a fast precipitation of crystalline material (C) which goes into a slow growth period (D). In Figure (4) is the data from a standard experiment shown.

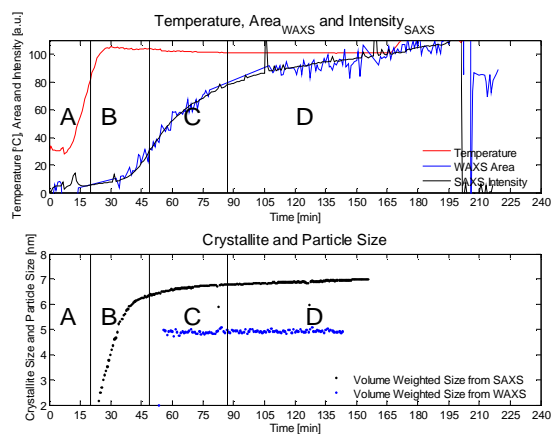


Figure 4. Upper) SAXS intensity vs. WAXS area as a function of time and temperature. Lower) Volume weighted sizes determined from SAXS and WAXS.

In the upper part of Figure 4 are the intensity at  $q = 0.028 \text{ \AA}^{-1}$  for the SAXS curves compared to the area under the anatase (200) peak as a function of time from 0 – 240 min which is shown together with the reactor temperature. In the lower part of Figure 4 are the extracted crystallite sizes obtained from Scherrers formula and the volume weighed primary particle sizes extracted from the SAXS curves are plotted [5].

The primary particle sizes,  $\sim 7.0 \text{ nm}$ , shown in Figure 4 are around 30-40 % larger than the crystallite size,  $\sim 5.0 \text{ nm}$ . The discrepancy between the primary particle size and the crystallite size is probably caused by the fact that the material consist of an amorphous fraction. The SAXS analysis used to extract the primary particle size can determine both the size for crystalline and amorphous material. Whereas the XRD analysis used to extract the crystallite size can only determine the size from crystalline material [5], [6]. So if the particles are composed of both crystalline and amorphous material the primary particle size becomes larger than the crystallite size.

The in-situ experiments showed that the supercritical nanoparticle process was a desupersaturation or precipitation of nanocrystalline material from a gel. The in-situ investigation also showed that the induction period in the supercritical process is mainly determined by the degree of supersaturation and the heating rate. The latent period was influenced by supersaturation and the final temperature and the time for the precipitation of nanocrystalline material was dominated by the final temperature. Crystalline  $\text{TiO}_2$  on the anatase phase was synthesized at an unprecedented low temperature. The in-situ study revealed that for the  $\text{TiO}_2$  system a general crystallization temperature, where the first traces of crystalline material was observed, was determined to  $87 \pm 5 \text{ }^\circ\text{C}$ . The in-situ study also showed that the process time going from the precursors to a final solid powder was obtainable within 30 min or less depending on the process parameters. The

process time was shown to be influenced by especially the heating rate, final temperature, and supersaturation.

## 4 CONCLUSION

Real time in-situ simultaneous wide angle and small-angle X-ray scattering (WAXS and SAXS) performed in this study revealed the mechanism for supercritical formation of nanoparticles. The investigated process was characterized by four distinct periods: an induction period, a latent period, a precipitation period, and a slow growth period. The four distinct periods were characterized to be influenced mainly by the heating rate, the final temperature, and the supersaturation.

The in-situ method presented in this paper makes it possible to follow nanoparticle formation in supercritical fluids. The present study showed that the supercritical sol-gel process parallels the characteristics of conventional sol-gel processes but at unprecedented low temperatures and in a new timescale. In supercritical fluids sol-gel processes occur in minutes rather than hours. This greatly improves the efficient fabrication of high-quality nanomaterials.

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