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In situ Pair Distribution Function study of ZrO_2 nanocrystals formation in supercritical fluids

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Abstract

ZrO_2 is an extremely interesting model material to demonstrate the potential of *in situ* synchrotron Pair Distribution Function (PDF) studies to observe and thus control the formation of nanomaterials in supercritical fluid conditions. At the bulk state, ZrO_2 exhibits either of the following polymorphs: monoclinic (m-ZrO_2), thermodynamically stable up to 1170°C, tetragonal (t-ZrO_2) up to 2370°C and finally cubic (c-ZrO_2) above the latter temperature. Yet, as ZrO_2 particle size decreases towards the nanoscale, these well-defined boundaries dividing each domain become less evident. First insights have been given by B. Iversen *et al.* showing the stabilization of a mixture of polymorphs (monoclinic and tetragonal) at ambient conditions for particles exhibiting an average particle size of less than 5 nm [1].

The main goal of this presentation is to show the results of the *in situ* investigations of the impact of experimental parameters (temperature, nature and concentration of precursors, solvents, use of surfactants, etc.) on the ZrO_2 nanocrystals formation, and more precisely, the obtained polymorphs. This was achieved thanks to *in situ* synchrotron investigations using a fused silica capillary as reactor [2]. There, the fused silica capillary was filled with the precursor solution, pressurized with a high-pressure pump and heated with a flow of hot air. Meanwhile, every second, an X ray diffraction diagram was acquired to track in real time the ZrO_2 formation, from the molecular (non crystalline) organization in solution to the nanocrystals precipitation.

These results were combined to additional *ex situ* characterizations (DRX, FTIR, Raman, TEM, etc.) on powder produced in the lab to fully describe the formation mechanisms and demonstrate the tunability of the ZrO_2 nanocrystals synthesis in supercritical fluid conditions.

References

[1] J. Becker et al., Critical Size of Crystalline ZrO2 Nanoparticles Synthesized in Near- and Supercritical Water and Supercritical Isopropyl Alcohol, ACS Nano, 2008, 2, 1058-1068.

[2] J. Becker et al., Experimental setup for in situ X-ray SAXS-WAXS-PDF studies of the formation and growth of nanoparticles in near- and supercritical fluids, Journal of Applied Crystallography, 2010, 43, 729-736