ESRF

Experiment title: ***In situ*** **XAS study of the tunability of ZrO_2 based nanomaterial polymorphs in sub- and supercritical fluid conditions**

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Report:

During this beamtime we have *in situ* investigated the ZrO_2 particles formation in solvothermal conditions ($30 \leq T \leq 400$°C and $p = 250$ bar) using X ray absorption spectroscopy (XAS) measurements. There, the objective was to evaluate our capability to control the type of produced polymorphs (cubic, tetragonal or monoclinic), only playing with experimental parameters such as temperature, precursor concentration and use of surfactants. To do so we decided to use Zr(IV) propoxide precursors to carry out a sol gel like synthesis. From experience, we know that directly adding water to the reaction medium will provoke a massive precipitation which will be too fast (few seconds) to properly track the different steps with XAS measurements. To avoid this effect, the idea was to start with pure ethanol as solvent and use the water generated *in situ*, through ethanol dehydration in solvothermal conditions, to initiate the reaction. Based on this principle, the adjustment of the pressure and temperature enables to fine tune the amount of water released into the media and thus the reaction kinetics. Technically, such experiment could only be carried out at the FAME beamline which provides a dedicated HP/HT cell developed in house by D. Testemale and J.-L. Hazemann (Néel Institute, CNRS).

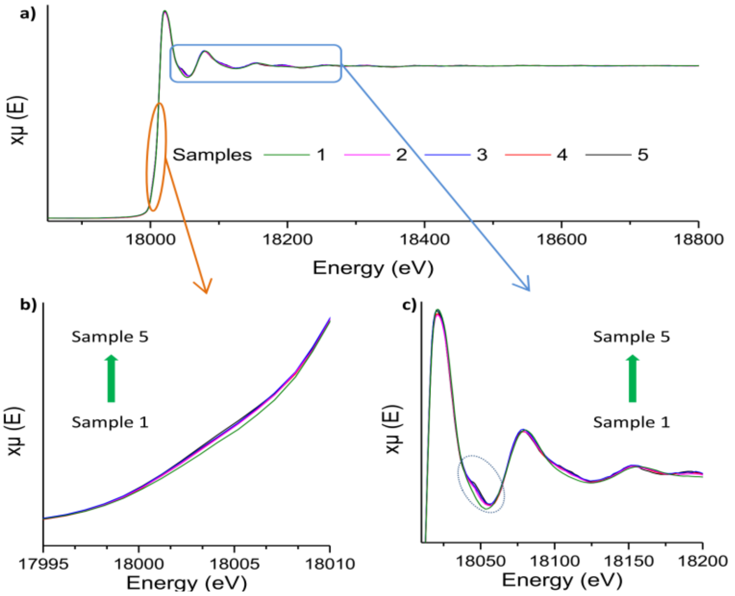

Figure 1. a) XAS transmission spectra of the five starndards: sample 1 pure tetragonal phase and sample 2 to 5 mixture of tetragonal and monoclinic phases with a gradual contribution of the monoclinic one, b) zoom in the XANES part and c) zoom in the EXAFS one.

Prior to the *in situ* characterizations, the first step was to measure standards. To do so, five different samples were produced beforehand, at the ICMCB Lab., with our solvothermal reactor and *ex situ* characterized with X-ray diffraction. The first sample was purely tetragonal and the other ones presented a gradual increase of monoclinic phase. Only by looking at the normalyzed transmission spectra (Figure 1a), it was possible to identify two areas of interest evidencing the growing contribution of a monoclinic phase; one in the XANES part (Figure 1b) and the second in the EXAFS (Figure 1c) one (Li *et al*. Physical Review B, 48, (1999) 10063-10073). In the XANES part, locally, the spectra are gradually shifted upward with the increase of monoclinic polymorph. In the EXAFS part, two phenomena have to be noticed; (i) similarly to XANES, locally, the spectra are gradually shifted upward, (ii) moreover, we can clearly identify a zone around 18.05 keV where the XAS spectrum of the tetragonal polymorph is different than the ones with a monoclinic contribution. These measurements will be further investigated to determine the local environment of Zr (neighbours, coordination number, geometry, etc.) for each standard. The obtained results will then be included as complementary information in a pending publication on ZrO_2 particle synthesis within these conditions.

After measuring the standards it is then possible to start the *in situ* measurements using the HP/HT cell of the FAME beamline. In the case of this study, the cell was a glassy carbon tube in which we put ≈ 0.1 mL of precursor solution and fit pistons in both ends. The cell is then placed in a stainless steel autoclave pressurized with helium and heated with a furnace. When the pressure increases inside the autoclave, the pistons move to compress the solution inside the tube. **The first experiment** consisted in looking at the temperature impact on ZrO_2 nanoparticles synthesis with experimental conditions similar to the ones used at the lab; meaning a Zr concentration of 0.033 mol.L^{-1} and a pressure of 250 bar. The temperature was first adjusted a 30°C and three XAS spectra, both in transmission and fluorescence, were measured. Then the temperature was increased step by step at 100, 150 and 200°C. Please note that for all these temperatures, three measurements were performed and averaged. As we can see in Figure 2, the absorption, which is related to both the Zr concentration and the solvent density, decreases with the increase of temperature. Measuring the variations of edge steps and taking into account the variation of solvent density with pressure and temperature, we can estimate the variation of Zr concentration and thus a reaction yield for a given temperature. Indeed, when ZrO_2 particles form, they sediment, thus we only analyse the remaining unreacted Zr in solution. Moreover, by zooming into the XANES part, it is also possible to notice a variation within the edge profile, which is directly related to the zirconium environment. There, at low temperature, we can clearly see the contribution of two peaks at the maximum of absorption. Increasing the temperature these two peaks tend to merge into a single one. This observation deserves a deeper investigation to conclude anything from it but this could be a sign a greater order (lower defects) and thus better crystallization at higher temperature. For this experiment the temperature was further increased to 250, 300, 350 and 400°C. Doing this we increased the amount of generated water into the media, speeding up the reaction kinetics to a point where they were too fast compared to the measurement time, making spectra difficult to interpret. **In the second experiment** we decided to investigate the influence of Zr precursor concentration on the produced polymorph. To do so, we reproduced the same experiment increasing the Zr concentration up to 0.132 mol.L^{-1}. The third, fourth and fifth experiments consisted in investigating the influence of surfactant on the produced polymorph. **For the third experiment** we selected the hexanoic acid and followed a surfactant to precursor molar ratio of 2:1. The starting Zr concentration was again 0.033 mol.L^{-1}, the hexanoic acid 0.066 mol.L^{-1}, the pressure was set at 250 bar and, as previously, the temperature was increased step by step from 30°C up to 200°C. **The Fourth experiment** was similar to the third one except that the hexanoic acid was replaced with trioctyl phosphine. **The fifth and last experiment** was also similar to the third one, we also used hexanoic acid, except that the starting Zr concentration was increased at 0.132 mol.L^{-1} and the hexanoic acid one at 0.264 mol.L^{-1}. For all these experiments we will follow the same strategy than the one briefly presented in the case of the first experiment. Please note that with such *in situ* setup it is possible to collect the sample afterwards giving us the capability of doing complementary *ex situ* characterizations such as infrared or Raman spectroscopy, transmission electron microscopy, etc. to confirm our conclusion based on *in situ* XAS results.

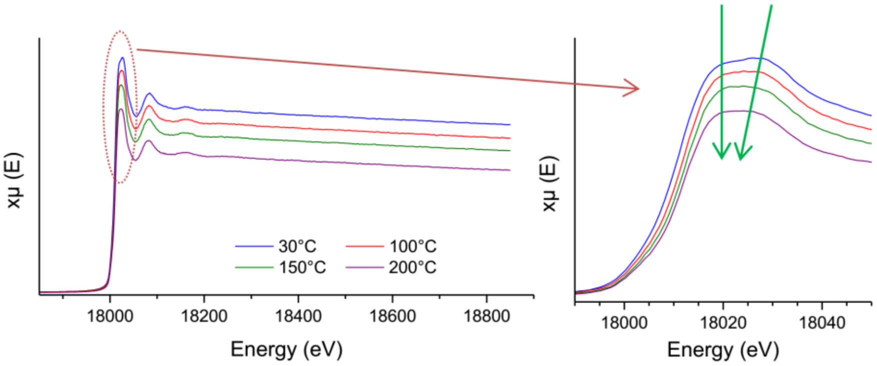

Figure 2. In situ XAS measurments during ZrO_2 particles synthesis at 250 bar with a step by step increase of temperature from 30°C up to 200°C.

To conclude, this beamtime was very fruitful, both standards and *in situ* measurements will bring crucial informations to better understand the formation of the ZrO_2 particles in solvothermal conditions. The only limitation is to compromise between acquisition time and reaction kinetics which prevented us to make precise measurements for temperatures high than 200°C. There the synthesis and thus precipitation were to fast and ultimately we lost the signal since no more Zr precursor was remaining into the solution.