

Synthesis of Nanocrystalline ZrO₂ in Near- and Supercritical Water

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SUMMARY

Fully crystalline ZrO₂ nanoparticles have been synthesized in near- and supercritical water, using a continuous flow-reactor. The average particle size can be controlled within 3-8 nm with a standard deviation of 2 nm depending on temperature and pressure. Products synthesized at near-critical conditions gives particles with a diameter of 2-4 nm, whereas under supercritical conditions the size increases to 4-8 nm. The nanoparticles have been extensively characterised with PXRD, TEM and SAXS with excellent mutual agreement on size and size distribution parameters. The SAXS analysis revealed polydisperse spherical nanoparticles.

INTRODUCTION

Zirconia systems have been studied intensively, as they have proved themselves to be of great use e.g. in sensor applications or as solid-state electrolytes in fuel cells [1]. Monoclinic zirconia is also used for catalyst purposes, as opacifiers in ceramics or as pigments [2]. For these applications small particle sizes and narrow, well-defined size distributions are needed. This can be obtained by synthesis in supercritical fluids, which furthermore enables manipulation of particle sizes and size distributions [3, 4]. In the present study pure zirconia nanocrystals were synthesized in near- and supercritical water employing a new synthesis facility. Cabanas *et al* recently have carried out similar experiments [5]. However, unlike Cabanas *et al.* the synthesized nanopowders were analysed by SAXS, which is relatively rarely used in supercritical investigations of nanoparticles.

EXPERIMENTAL

The continuous synthesis apparatus used in this study is shown on Figure 1. The pressure was in all experiment held at 230 bar, slightly above the critical pressure for water. The temperature was set at 300, 375 and 450 °C. As precursor an aqueous solution of zirconium acetate, Zr(ac)₄, supplied by Aldrich was used.

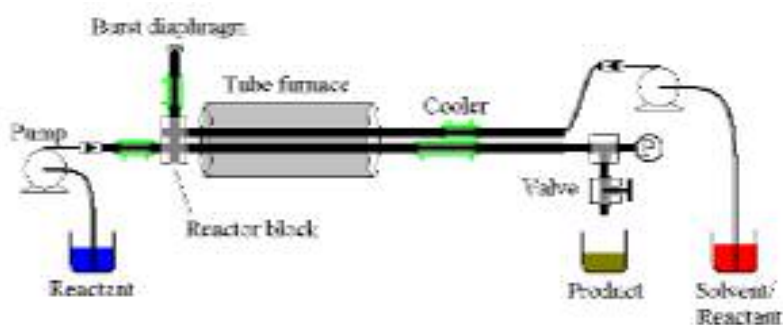


Figure 1. Principle sketch of the continuous synthesis apparatus

The synthesis products were analysed by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). The PXRD data were

measured on a STOE powder diffractometer at Department of Chemistry, University of Aarhus. A Ge(111) single crystal monochromator was used to produce $\text{CuK}_{\alpha 1}$ radiation, which was detected with a 40° position sensitive detector. The resulting diffractograms are shown in Figure 2 and it is seen that two phases are present. One of them is the monoclinic phase, whereas the other can be either the tetragonal or the cubic zirconia phase. The two latter phases have very similar X-ray patterns and the slight differences are masked by the broadness of the peaks. In the following it is assumed that it is the tetragonal phase that has been produced. The assumption is based on the research done by Garvie [6], as well as the literature in general, which almost exclusively reports on the production of tetragonal zirconia from hydrothermal syntheses. The width of the peaks were analysed by the Debye-Scherrer equation [7][8], which indicated particle sizes in the range of 4-6 nm.

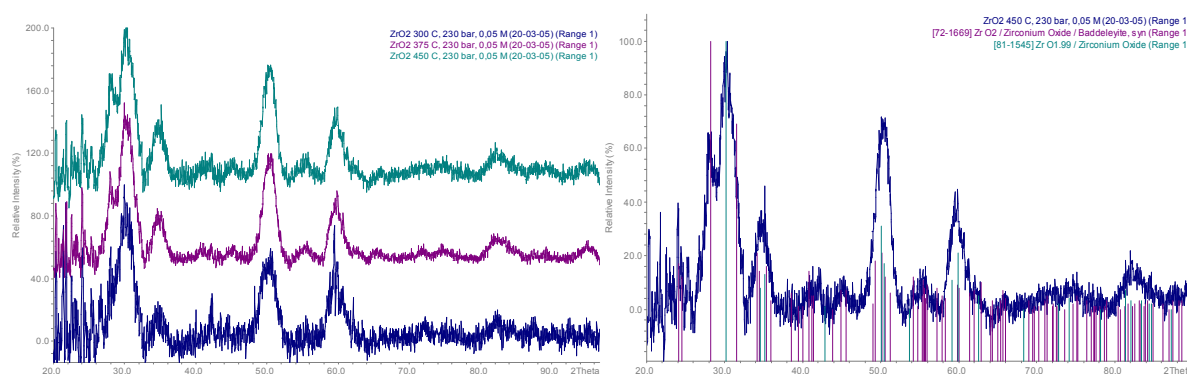


Figure 2. (a) XRD patterns of ZrO_2 synthesized at 230 bar and 300 °C (blue curve), 375 °C (purple curve) and 450 °C (turquoise curve). (b) XRD patterns of ZrO_2 synthesized at 230 bar, 450 °C with peak files of monoclinic ZrO_2 (purple) and tetragonal ZrO_2 (turquoise) inserted.

The TEM pictures of the nanocrystals were taken with a Phillips CM20 transmission-electron microscope at Department of Physics and Astronomy working at 200 kV (data not shown). The resulting pictures revealed spherical particles, with particle sizes of a few nm. A certain level of agglomeration was seen to occur. The particle sizes were also estimated from SAXS data measured on a Bruker NanoSTAR at Department of Chemistry, University of Aarhus [9]. Measurements were done on aqueous suspensions of the synthesis products, inserted into small glass capillary tubes. After background subtraction, the data were fitted to a fractal model [10] with polydisperse primary particles [11]. The size distributions of the primary particles were described by a Schultz-Zimm function. The model provided good fits to the data in the entire range of the measured data. Numerous other models with polydisperse cylinders or ellipsoids [11] were tried; however, none of these models gave satisfactory fits. The distributions derived from the data fitting are shown in Figure 3.

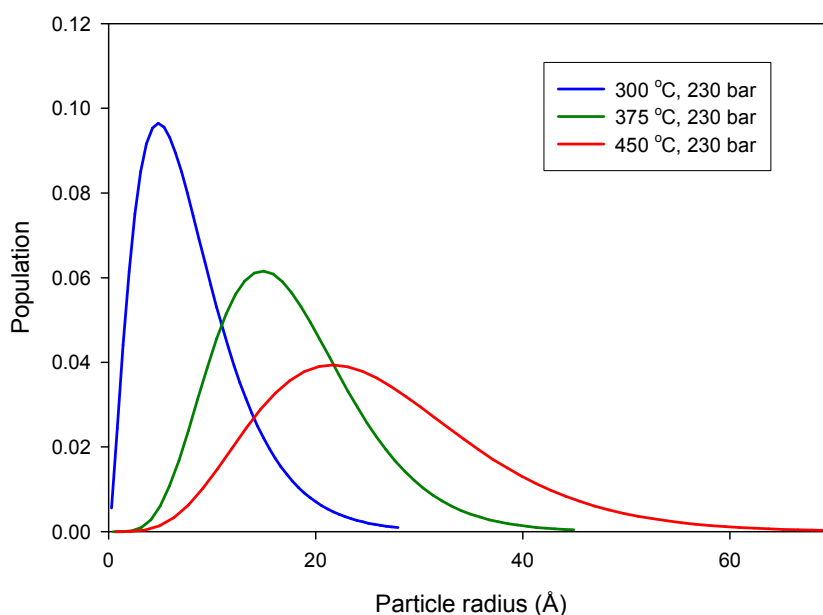


Figure 3. SAXS determined size distribution curves

The particle sizes obtained from PXRD, TEM and SAXS are shown in table 1.

Table 1

	Size XRD [nm]	Size (mean) SAXS [nm]	Size TEM [nm]
300 °C	4.8	1.66	2.6-3.6
375 °C	5.2	3.52	[no TEM]
450 °C	6.8	5.24	4.7-6.2

DISCUSSION

From the PXRD data the phase contents are seen to vary with increased synthesis temperature. Below the critical temperature the tetragonal phase is dominant, and at very high temperatures the monoclinic phase becomes dominant. No abrupt change is observed at intermediate temperatures, or at the critical point.

Comparing PXRD and SAXS data, the phase change is seen to follow a trend of increasing particle size. At low temperatures the particles are very small and tetragonal, at elevated temperatures they have grown into the monoclinic phase. The changes of the mean particle sizes may be expected from reaction kinetics. At elevated temperatures there are time for the nanocrystals to fuse and grow as the nucleation stage is completed faster than at lower temperatures.

In this experimental series the change in size distributions is continuous. However, in other experimental runs, irregularities in the immediate vicinity of the critical coordinates were observed. According to the present results, we have synthesized tetragonal ZrO₂ nanocrystals with diameters of a few nm. However, it has not been possible to synthesize pure tetragonal zirconia nanocrystals in supercritical water. This result is in line with the study of Bokhima *et al.* [12], who also obtained mixed phases using various hydrolysis catalysts. In that study the

average particle sizes ranged from 8 - 32 nm for the tetragonal phase and from 4 – 34 nm for the monoclinic phase. In other routes of synthesis tetragonal crystals of more than 100 nm have been obtained [13].

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