

Near- and supercritical hydrothermal flow synthesis of CeO₂ nanoparticles

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Abstract

The continuous hydrothermal synthesis is a promising way to synthesize metal oxide nanoparticles. This process exploits the strong variations in the thermo-physical properties of water around its critical point and is based on the mixing of a cold aqueous metal salt solution with hot compressed water. Since a large variety of metal oxide nanoparticles (e.g. CeO₂, Fe₂O₃, ZrO₂) with outstanding properties can be synthesized an apparatus was built up, tested and put into operation. The long-term stability of different process parameters, i.e. pressure, temperature and mass flow rate, was proved. First primary experimental results obtained with Ce(NO₃)₃ as precursor for the synthesis of CeO₂ particles were reported.

Introduction

The amount of nanoparticles with features like a small particle size and a narrow size distribution is continuously increasing [1]. Near- and supercritical water (scH₂O) is an attractive nontoxic medium for the synthesis of metal oxide nanoparticles ($d < 10$ nm). Among others, these nanoparticles play an important role in areas such as electronics, diagnostics, therapeutics, and bio-separation. Usually the synthesis of metal oxide nanoparticles is complex and time consuming, e.g. with sol-gel processes [2]. A promising alternative to conventional processes is the continuous hydrothermal synthesis (CHTS). This method is based on the mixing of a cold aqueous metal salt solution with hot compressed water. Figure 1 shows simplified the basic principles of the CHTS process.

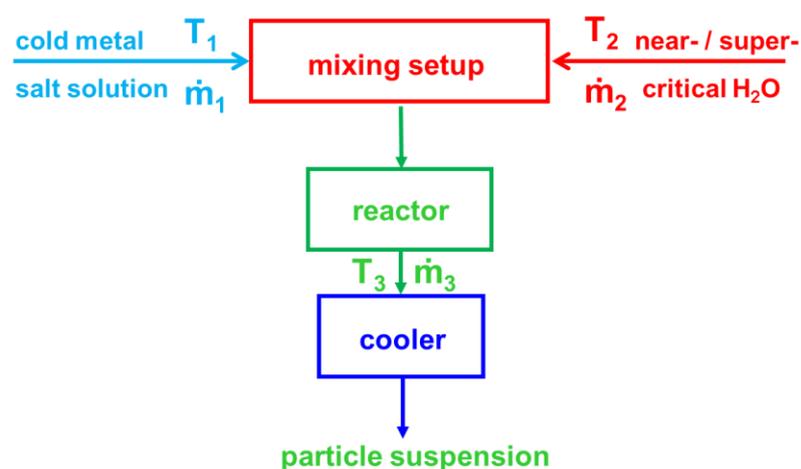


Figure 1: Basic principles of the CHTS process [3]

This process exploits the strong variations in the properties of water around the critical point ($T_c = 647.1$ K, $p_c = 22.1$ MPa). High diffusion rates and low viscosities, mass transfer properties similar to those of gases, densities and therewith solvating capabilities close to liquids together with the complete miscibility with a large number of substances, makes

scH₂O to an excellent process medium [see e.g. 4-7]. The strong influence of temperature on these properties is illustrated in Figure 2. Together with the density, the dielectric constant shows drastic changes around the critical temperature. At ambient temperature H₂O has a high density and thus high ability to solve inorganic salts. By rising the temperature to supercritical conditions, this ability decreases due to the strong decrease of the density and dielectric constant from around 80 at ambient conditions to 2 in the supercritical region. Thus, the solubility of inorganic salts is strongly reduced above the critical point compared to ambient conditions. A further property that decreases strongly with increasing temperature is the viscosity. At supercritical conditions, the viscosity is approximately two orders of magnitude lower than that of water under ambient conditions. Such an improved fluidity is attractive for chemical reactions because mass transfer and diffusion-controlled chemical reactions are considerable enhanced.

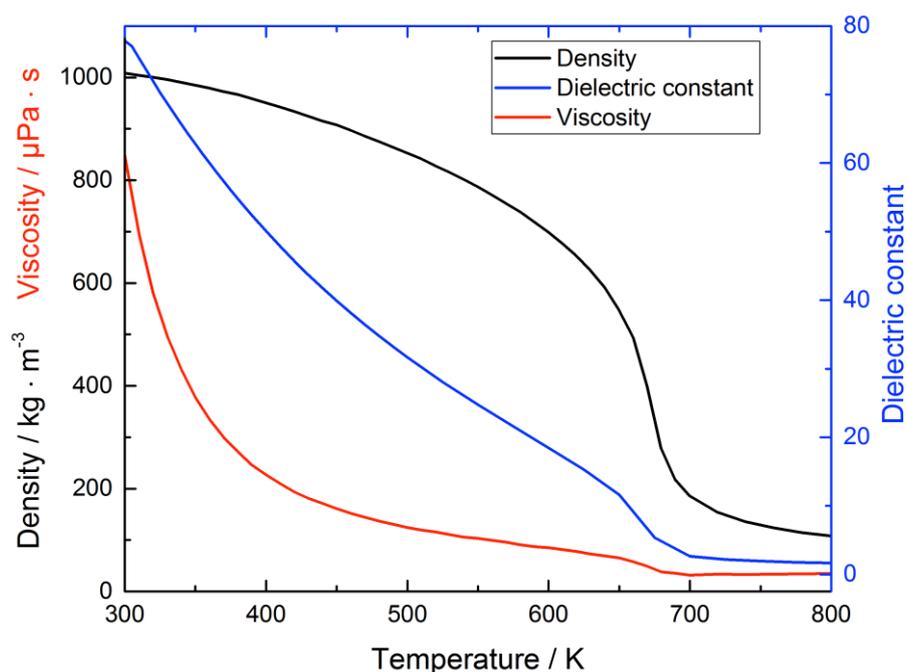
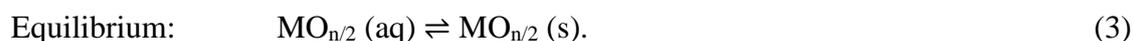
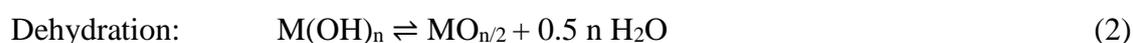


Figure 2: Changes in density ρ , viscosity η and dielectric constant ϵ versus temperature at 25 MPa [3]

It has been suggested in literature (e.g. [1-3]) that the synthesis of the metal oxides occurs in three consecutive (equilibrium) steps:



In Eq. (3) refer (s) and (aq) to the crystalline solid oxide and the aqueous species. In a first step the metal ions of the aqueous metal salt solution are hydrolyzed and form a metal hydroxide. Thereafter the metal hydroxide is converted into a metal oxide. Thereby it is worthy to notice that the degree of hydrolysis depends on the cation as well as on the pH value and temperature of the solution. As a consequence, at supercritical temperatures, the solubility of inorganic salts is strongly reduced compared to ambient conditions. This causes a high supersaturation and the fast precipitation of metal oxide nanoparticles.

For the design of inorganic materials with desired product properties i.e. size, morphology, structure, and composition, it is essential to control the following process parameters: solvent nature, reagent nature and concentration, reactor technology, residence time in the reactor,

additives and, as already said, pressure and temperature. Therefore, it is important to investigate the influence of starting material, mixing ratio and fluid velocity on the size distribution of both, primary particles and particle agglomerates, as well as on the colloidal stability of the dispersions.

Materials and Methods

For studying the metal oxide nanoparticle synthesis, particle growth and especially reaction kinetics, an apparatus for CHTS was designed and built up as shown in Figure 3. Two HPLC pumps enable to realize process pressures up to 40 MPa while temperatures up to 720 K can be reached. The cold aqueous metal salt solution \dot{m}_1 is mixed with the near or scH₂O stream \dot{m}_2 in a heated T-shaped mixer surrounded by an insulation housing. The rapid heating causes the initialization of the chemical reaction and the suspension is instantly cooled down by a water-cooled high-pressure heat exchanger. Before depressurizing, realized by a back-pressure regulator at the outlet, the nanoparticle suspension is filtered by an inline filter with a mesh of 10 μm . Two coriolis mass flow meter are used to measure the mass flow rate of the cold metal salt solution and hot water stream. Thus, the total mass flow rate \dot{m}_3 can be calculated by summation of the individual mass flow rates.

It is obvious that a successful process control i.e. the synthesis of particles with desired properties, requires steady state process conditions. Therefore, first of all after buildup and implementing of the CHTS apparatus studies on the stability of the process parameters i.e. system pressure, temperature (T_2 , T_3) and mass flow rate (\dot{m}_3) were performed.

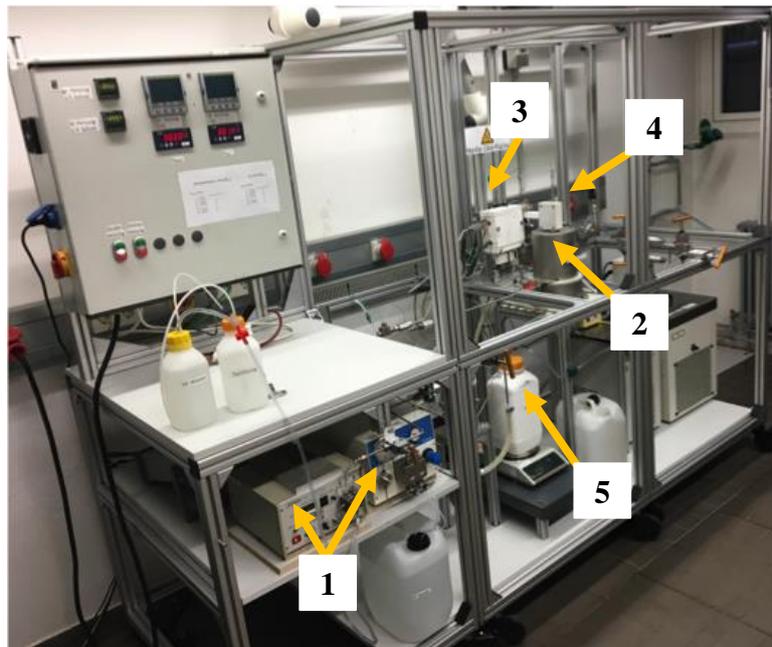


Figure 3: CHTS apparatus: 1 HPLC pumps, 2 heating unit, 3 isolated reactor, 4 cooler, 5 collection vessel

First Experimental Results

After the successful long time leakage tests of the CHTS apparatus, which were performed at different pressures, different stability tests were carried out. First of all, the temperature stability during mixing a hot and a cold water stream was proved. Figure 4 shows the results for an operating test which was performed at a pressure of 30 MPa and a temperature of $T_2 = 573 \text{ K}$. After heating up to the desired temperature and a waiting period of 50 min, T_2 is constant for the different mass flow rates investigated. Furthermore, Figure 4 shows clearly that increasing the mass flow rate leads to a decreased temperature fluctuation. From these results one can conclude that temperature and pressure stability can be ensured. In a next step, mixing tests were performed with different process temperatures, pressures and mass flow rates. These tests were necessary for characterizing the apparatus and the mixing behavior. In

this context, the mixing ratio a , which is defined as the ratio of the cold to the supercritical H_2O stream is an important process parameter. In the first experiments, a was varied between 0.05 and 0.4. The tests were carried out for a total mass flow rate \dot{m}_3 of 35 g min^{-1} , two different temperatures and pressures and the results are shown in Figure 5. It is obvious that the mixing temperature T_3 decreases with increasing mixing ratio which is caused by the increasing mass flow rate of the cold stream. This effect seems to be independent from the process pressure in the temperature and mass flow rate range investigated. The experiments were carried out twice and both lead to identical results.

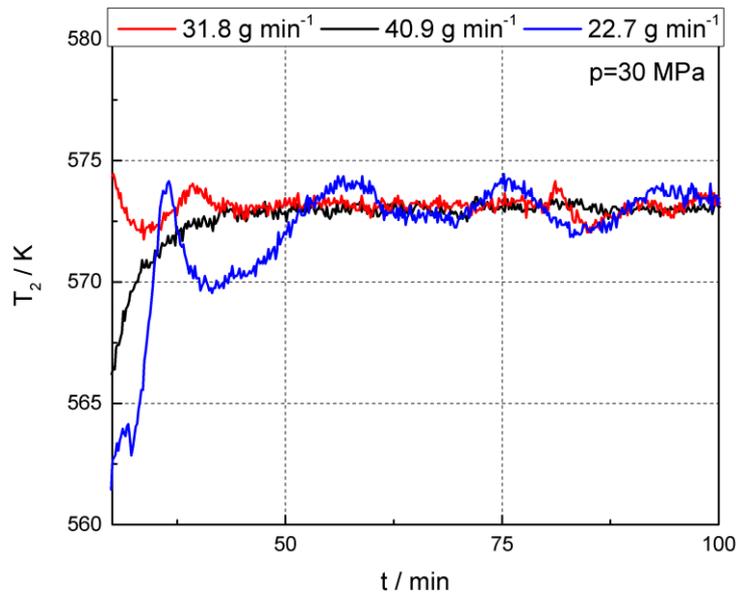


Figure 4: Temperature stability for T_2 for different mass flow rates as a function of time [9]

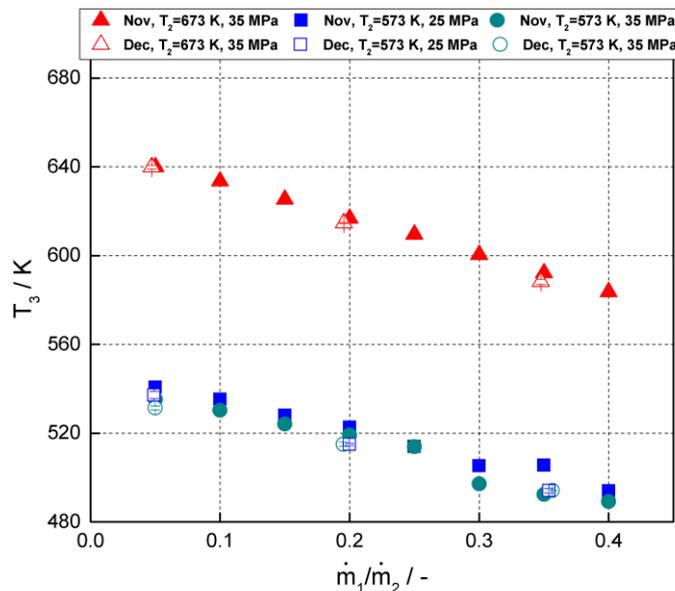


Figure 5: Mixing temperature T_3 for different process conditions as a function of the mixing ratio a [9]

In order to investigate the influence of the mixing ratio a on the mixing temperature T_3 further experiments with different mixing ratios were carried out at a pressure of 35 MPa and a total mass flow rate of 35 g min^{-1} . The results are shown below in Figure 6. As expected, the

temperatures T_1 and T_2 remain constant and T_3 decreases with increasing mixing ratio a . These results are an essential basis for the estimation of the mixing temperature T_3 , that is strongly influenced by the temperature T_2 , at different mixing ratios a .

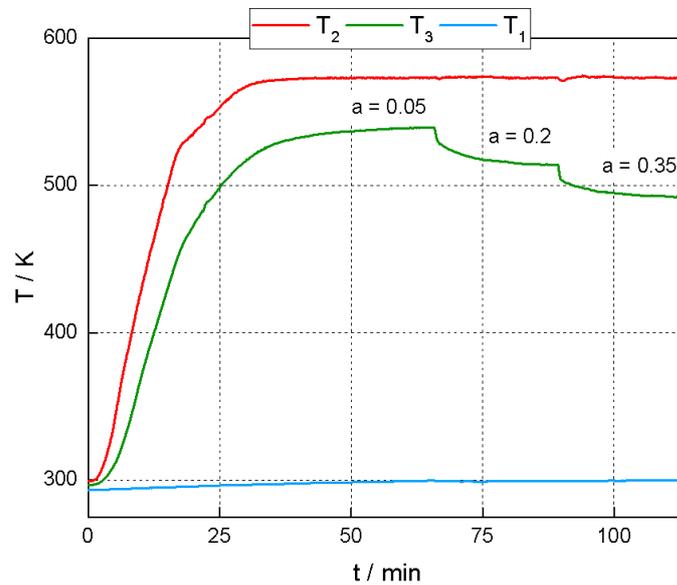


Figure 6: Process temperatures as a function of the time for different mixing ratios [9]

Summarising the results obtained from analyzing the particle free flow experiments, one can conclude that steady state flow condition could be ensured under the process conditions which are of interest for the CHTS process. Based on these promising result, additional experiments were performed with $\text{Ce}(\text{NO}_3)_3$ as precursor for the CHTS of CeO_2 particles and selected results are reported below.

In these experiments the precursor concentration varied between 0.005 and 0.15 mol l^{-1} while the other process parameters were constant: a pressure p of 30 MPa , a temperature T_3 of 673 K , a total mass flow rate of 35 g min^{-1} and a mixing ratio of 0.1 . The different suspensions obtained from these experiments are depicted in Figure 7 while a typical TEM picture is shown in Figure 8. Obviously, metaloxide nanoparticles were synthesized by CHTS because of the turbidity of the obtained suspension.



Figure 7: Suspensions obtained from different salt concentrations, 0.005 mol l^{-1} , 0.05 mol l^{-1} , 0.15 mol l^{-1} [9]

The intensity of the turbidity of the particle suspension increases with increasing salt concentration. The suspension with a concentration of 0.005 mol l^{-1} shows no turbidity whereas the suspensions with a salt concentration of 0.05 mol l^{-1} and of 0.15 mol l^{-1} show a strengthened turbidity. Obviously both, the size and the concentration of the synthesized particles in the suspension with the lowest salt concentration, are too low for causing a visible turbidity. In addition, the further results show that, in accordance with the classical nucleation theory, increasing the salt concentration leads to the formation of more particles. Thus, one would expect that a higher salt concentration would lead to larger particles. Furthermore, higher process temperatures would lead to higher supersaturations and higher reaction rates, which favors the formation of small nanoparticles. Among others, this point requires a more detailed examination and would be part of our ongoing experimental investigations in combination with numerical modeling of the complex mixing behavior.

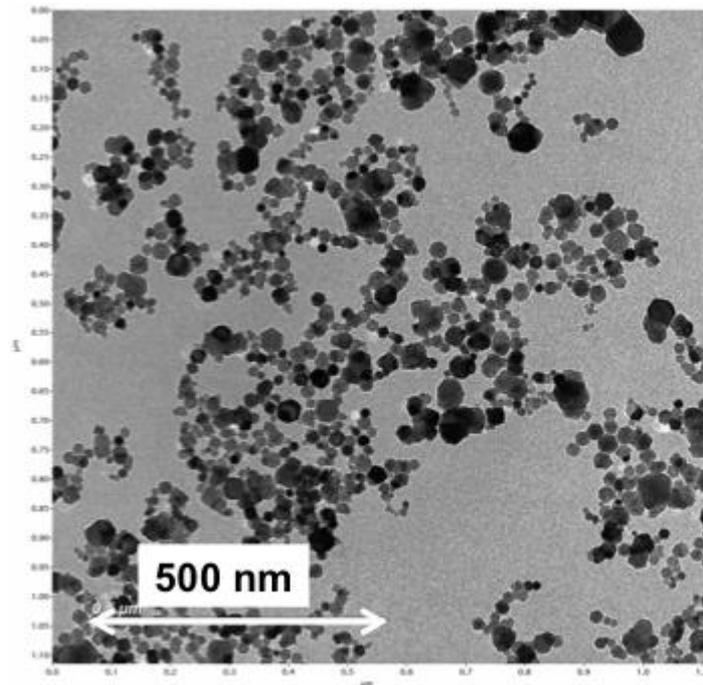


Figure 8: CeO_2 nanoparticles (ca. 20-40 nm) synthesized at $c_{\text{salt}} = 0.05 \text{ mol l}^{-1}$, $\dot{m}_3 = 35 \text{ g min}^{-1}$, $p = 30 \text{ MPa}$ and $T_3 = 673 \text{ K}$ [9]

Conclusion

An apparatus for the formation of metal oxide nanoparticles by CHTS was built up and put into operation. First preliminary tests, especially in terms of long-term stability of the process parameters were successfully performed. The tests showed that the constructed plant provides steady state process conditions for system pressure, temperature and mass flow rate. Mixing tests with a hot and a cold water stream demonstrated the impact of the cold water stream on the mixing temperature T_3 with increasing mixing ratio a . Further results showed that process conditions, especially T_3 and p , are constant during particle synthesis. The results of the first particle formation experiments showed, that in accordance with results published in literature, small uniform CeO_2 NPs with particles sizes between 20 and 40 nm could be synthesized by CHTS.

Acknowledgment

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