Preparation of CeO_2 nanoparticles by continuous hydrothermal synthesis: experimental and modeling results

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The development of novel chemical processes that allow controlling the particle size, size distribution and morphology of catalytic active nanostructures enables new possibilities for energy-related applications and automotive emission control. Among others, Ceria (CeO_2) is one of the most promising materials for environmental and energy related applications. For example, CeO_2 can be used as the active component of the catalyst or as the substrate of noble metal catalysts for the CO and propane oxidation [1]. Furthermore, reducing the CeO_2 particle size to the nanoscale has a significant influence on the catalytic behavior [2,3]. A promising method to synthesize nano sized particles with well-defined properties is the Continuous Hydro-Thermal Synthesis (CHTS) that is based on the mixing of a cold aqueous metal salt solution with hot compressed water [4,5]. However, a deeper understanding of the relationship between synthesis conditions (e.g. temperature, pressure, mass flow rate and type of salt) and the obtained product properties (i.e. catalytic activity and selectivity) is currently not yet available.

Therefore, our investigations are focused on: a) Experimental studies of the influence of various process parameters such as reaction pressure (25, 30 MPa) and temperature (523, 573, 673 K), salt concentration (0.005 - 0.15 mol dm^{-3}) and type ($Ce(NO_3)_3$, $Ce_2(SO_4)_3$)), and mass flow rate (35, 45, 55 g min^{-1}) on size, size distribution and shape of the synthesized CeO_2 nanoparticles. b) Three-dimensional computational fluid dynamics (CFD) simulations for typical process conditions. Thereby, the temperature and velocity field in a tubular flow reactor were calculated using the software Analysis System (ANSYS) which is based on the finite-volume-method (FVM) for the discretization of equations of fluid dynamics. Based on this, residence time distribution (RTD) curves are calculated for different process conditions and compared with experimental particle size distributions.

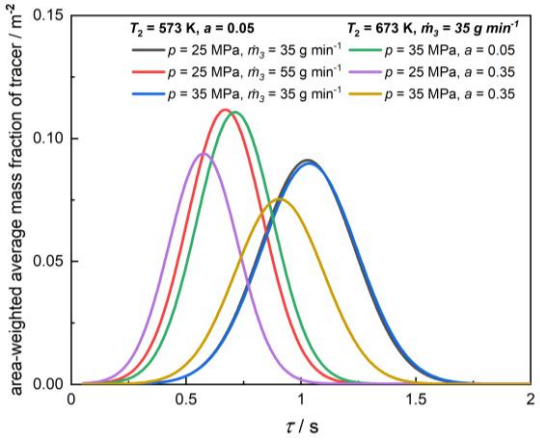

Figure 1: p = 25 & 35 MPa, T_3 = 573 & 673 K, m_3 = 35 & 55 g min^{-1}, a = 0.05 & 0.35.

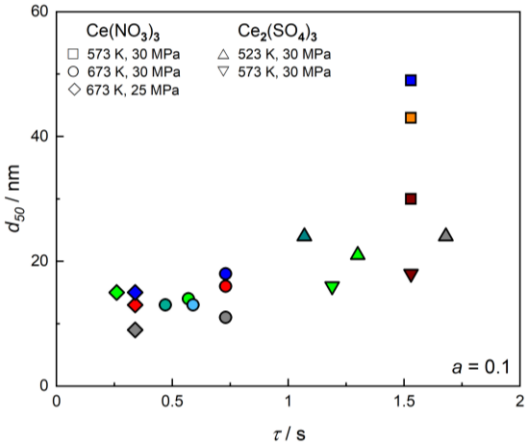

Figure 2: Mean particle size (d_{50}) versus residence time at different process conditions.

First, this talk will give a short introduction into the basic principles of the CHTS process. Based on this, selected experimental and modeling results from our research group will be presented and discussed in detail. In summary, the obtained results can be summarized as follows:

1) Deviation between experimental and calculated mixing temperature is less than 4%.

2) Decreasing the pressure, increasing the temperature or total mass flow rate leads to smaller particles while increasing salt concentration results in larger particles as shown in Figure 1.

3) CeO_2 particles in the range from 11 - 49 nm can be synthesized as shown in Figure 2.

References:

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