Low Temperature Synthesis of Nanosized Metal Oxides by a Supercritical Seed Enhanced Crystallization process (SSEC)

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Summary

A novel low temperature method for the production of homogenous nanosized crystalline materials has been developed. The method is based on a Supercritical Seed Enhanced Crystallization (SSEC) process and has been shown to lower the crystallization temperature for several metal oxides significantly. The novel method is flexible and allows production of homogenous nanocrystalline powders with controlled properties from a wide range of metal oxides. The produced nanopowders have an average particle size of 5-10 nm with a very narrow size distribution. The crystallinity and particle size can be altered by adjusting the process parameters. The novel method allows direct production of dry crystalline nanopowders without the need for additional treatment. The process time is short (0.5 to 4.0 hrs.).

Introduction

The production of nanosized materials is of great interest in both industries as well as in academic research. Despite progress in scaling up and reducing costs, nanoparticles remain relatively expensive materials and the price depends on the production volume, material type, powder characteristics, manufacturing method, and post synthesis processing treatment [1]. The applications for nanosized metal oxides nanoparticles span a wide range of different areas such as UV-protection, plastics, cosmetics, solar cells, dental composites, and photocatalysis. Particle size, specific surface area, crystal phase, crystallinity, and surface properties are considered as key parameters for success in these applications.

In the SSEC process a sol-gel reaction is taking place in a supercritical environment in the proximity of a seeding material [2]. The sol-gel reaction starts with the hydrolysis of the precursor, normally a metal alkoxide ($M(OR)_n$), when it comes into contact with water. The hydrolysis continues simultaneously with the condensation of the hydrolyzed monomers leading to formation of a three dimensional metal oxide network [3]:

$$M(OR)_n + mH_2O \rightarrow M(OR)_{n-m}(OH)_m + mROH$$

$$M(OR)_{n-m}(OH)_m + RO\text{-}M(OR)_{n-m-1}(OH)_m \rightarrow (OR)_{n-m}M\text{-}O\text{-}M(OR)_{n-m-1}(OH)_m + ROH$$

A filling material is introduced in the process to enable the production and collection of nanosized crystalline particles. The filling material acts as seed or catalyst as well as a reservoir for collecting the nanoparticles. The filling material enables homogenous seeding of primary nuclei resulting in a nanosized powder with narrow size distribution.

Supercritical CO_2 is used as solvent in the SSEC process. Using supercritical fluids as solvents in sol-gel processes rather than the traditional alcohols, a significantly lower particle size in the nanometer range can be obtained. This is believed to be due to the higher reaction rate obtained in supercritical media [4].
Producing nanosized metal-oxides by the SSEC process the crystallization temperature is lowered significantly and a reduction of the process time is obtained. Furthermore, the nanopowders produced from the SSEC process do not need a succeeding calcination, which normally causes a reduction in the specific surface area.

In this paper it will be shown that the SSEC process is a promising method for synthesizing nanosized metal-oxides with controllable particle size, crystal phase, and degree of crystallinity without having to resort to costly post-reaction processing.

Materials and Methods

The experimental set-up used in this study is shown on Figure 1 together with a schematic representation of the process.

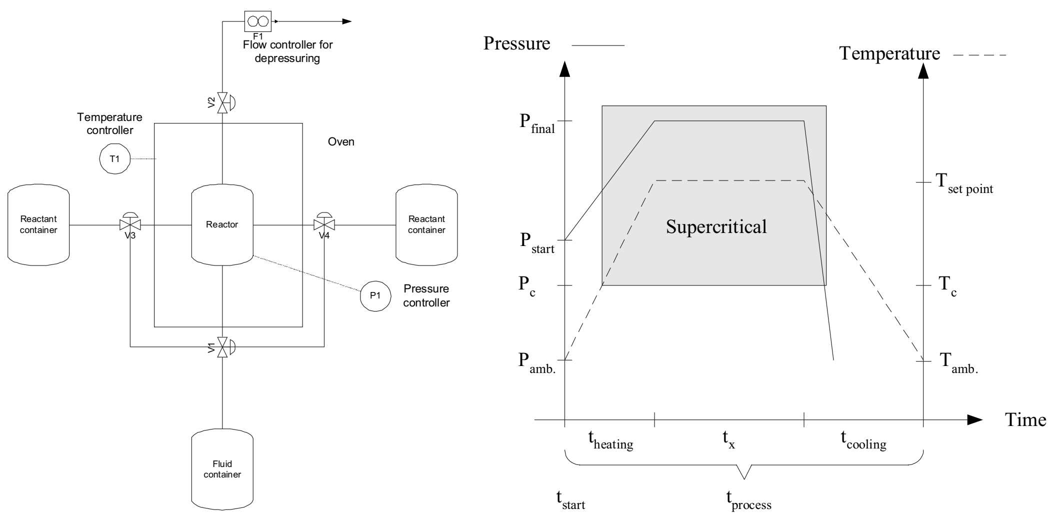

Figure 1 Experimental set-up and schematic representation of the SSEC process.

The central part of the experimental set-up is the reactor which is placed in a pressure safe oven. The experimental set-up can operate in the range from 0-680 bar and from 25-200 ºC. The process is occurring in a supercritical environment, which for CO_2 means above 31 ºC and 74 bar, which schematically is shown on Figure 1.
The produced powders are characterized by XRD to determine the crystal phase, the absolute crystallinity, and the crystallite size distribution. SAXS is used to determine the particle size distribution of the produced powders. The hard sphere model with an interparticle interference effect is used to model the SAXS data. The characterization methods are described in more details in [5-7].

Results and Discussion

XRD and SAXS spectra obtained from SSEC synthesized TiO_2 are shown in Figure 2. The characterized powder was synthesized with titaniumisopropoxide as precursor and the experimental conditions were 100 bar and 100 ºC. These conditions will be referred to as standard or reference conditions.

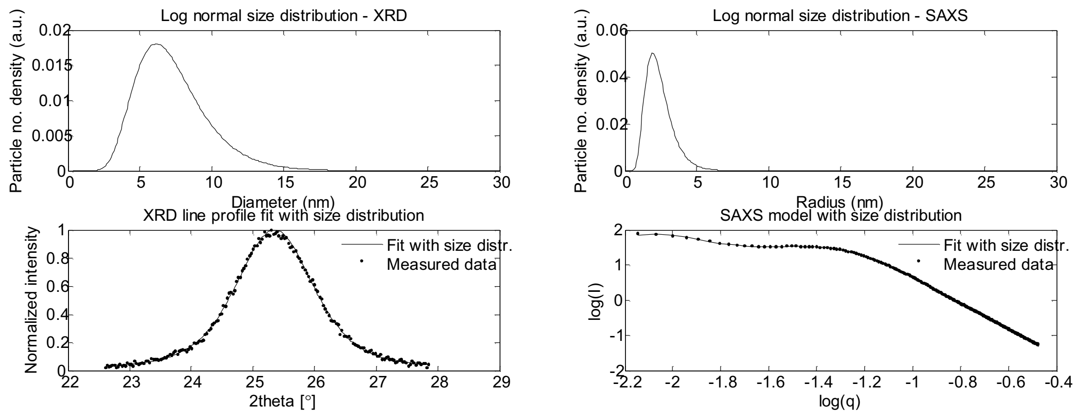

Figure 2 A: XRD spectrum of TiO_2 powder. B: SAXS spectrum of TiO_2 powder

The XRD spectrum in Figure 2A is a close up of the 100 % peak of anatase. Analyzing this peak by a size dependent XRD line profile model shows that TiO_2 prepared at reference conditions has an average crystallite size of 7 nm and a narrow size distribution. The prepared TiO_2 is a pure anatase phase with an absolute crystallinity of 63 % and the remaining part being amorphous titania. The absolute crystallinity is determined with respect to a 100 % crystalline CaF_2 reference.

SAXS analysis of the produced TiO_2 powder shows an average particle size of 4.4 nm. The SAXS analysis reveals that the powder is composed of nanosized primary particles aggregated in larger clusters, which is shown in the SAXS model by the interparticle interference effect.

The properties of the TiO_2 produced at reference conditions are in Table 1 compared to the commercial powder Degussa P25.

Table 1 Measured properties for TiO_2 powders.

	SSEC	Degussa P25
Average crystallite size	6.9 nm	25.7 nm
Average particle size	4.4 nm	18.8 nm
Average particle size (BET)	6.4 nm (236 m^2/g)	30 nm (50 m^2/g)
Crystallinity (anatase)	63 %	~ 100 %[a]

[a] Mixture of anatase (80 %) and rutile (20 %)

The SSEC produced TiO_2 has a pure anatase phase, while Degussa P25 also contains the rutile phase. The crystallite size and particle size of the SSEC produced powder is ~ 4 times smaller than for Degussa P25. Furthermore, in contrary to the normal sol-gel process the SSEC process allows for production of nanopowders without impurities such as residual alkoxy groups [8].

The SSEC process has proven suitable for synthesis of several crystalline metal oxides and hydroxides other than TiO_2. In Table 2 the properties of different metal oxides are shown together with two TiO_2 powders prepared at different temperatures.

Table 2 Measured particle properties for different metal oxides.

	TiO_2	TiO_2	ZrO_2	AlOOH	GeO_2
Temperature	45 ºC	100 ºC	185 ºC	175 ºC	185 ºC
Pressure	100 bar	100 bar	100 bar	100 bar	100 bar
Crystal phase	Amorphous	Anatase	Tetragonal	Boehmite	Tetragonal
Crystallinity	–	63 %	39 %	94 %	72 %
Average Crystallite Size	–	6.9 nm	6.1 nm	3.7 nm	13.2 nm

From Table 2 it can be observed that changing the temperature from 100 ºC to 45 ºC an amorphous titania is obtained with a particle size extracted from SAXS of 3.6 nm. Crystalline ZrO_2, AlOOH, and GeO_2 were synthesized at low temperatures with crystallite sizes in the nanorange. Fully amorphous ZrO_2, AlOOH, and GeO_2 are also obtained if the temperature is below the temperatures shown in Table 2.

Conclusion

The results presented in this paper show that nanocrystalline TiO_2, ZrO_2, AlOOH, and GeO_2 can be synthesized by the SSEC process. The crystallization temperatures were lowered significantly compared to traditional sol-gel processes. This alleviates the need for subsequent calcination. The produced homogenous powders consisted of nanocrystallites with an average particle size of approx. 5-10 nm and a very narrow size distribution.

Acknowledgement

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