ROUTES TO DEAGGLOMERATED NANOPOWDER BY CHEMICAL SYNTHESIS

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ABSTRACT

The concept of tailored interfaces has been applied to the synthesis of nano-scaled Y_2O_3/ZrO_2 powders. The microemulsion technique as well as the thermodynamically controlled growth reaction have been utilized for this purpose. Both methods yielded agglomerate free amorphous powders with particles sizes of 8 nm and 15 nm, respectively. Cubic zirconia was obtained by calcination between 300 and 400 °C and crystallite coarsening was not observed. The calcined powders could be redispersed by treating them with tertiary amines in aqueous solutions.

INTRODUCTION

The utilization of nano-scaled ceramic powders for the production of advanced ceramic materials requires high quality with respect to chemical purity, crystallinity, homogeneity, controlled state of agglomeration (soft) and particle size distribution as well as low production costs. Comparing already described synthesis methods [1-7], one can conclude, that only a few techniques can fullfil these prerequirements. One of the most promising routes are wet chemical methods because these processes start from molecular precursors and, consequently have to undergo a growth reaction and pass a nanosized state. However, these nanosized particulate systems tend to minimize their surface free energy either by growing to larger particles or agglomeration. In order to utilize chemical processes for the synthesis of nanosized powders, these reactions have to be avoided by controlling the thermodynamics of the interfaces within the reacting system. One approach is the w/o microemulsion techniques limiting the reaction volume to a nanometer scale and to use these so-called nano-scaled reactors as vehicles for particle synthesis [8-11].

An alternative is to modify the surface of growing particles during the precipitation process in a way that growth reaction can take place but a "growing together" (agglomeration) is prevented. The use of surface active compounds seems to be suitable for this purpose. In this case, the surface free energy is reduced to an appropriate level by the interaction of the surface modifier with the generated particle surface. Thus the enthalpy of the system is influenced by the coupling reaction of the modifier with the surface functional groups.

This type of surface modification can provide steric repulsive forces between particles preventing agglomeration by van der Waals forces. As a model for the investigation, yttria-stabilized zirconia (Y_2O_3/ZrO_2) has been selected to prove the feasibility of the above described hypothesis. Since the redispersibility of nano-scaled powders is one of the main objectives the results of microemulsion and controlled growth preparation techniques have to be compared with respect to this.

State of the art concerning microemulsion techniques already shows, that nano-scaled powders can be prepared, whereas controlled growth techniques are at their infancy. Therefore, the microemulsion techniques has been optimized with respect to reduce the emulsifier concentration and to end up with more simple systems compared to the multicomponent systems [10, 11]. The question arises whether it is possible to use the HLB-theory with only one type of molecule.

EXPERIMENTAL

Microemulsions were prepared by mixing cyclohexane, tetraethylenglycoldodecylether (Brij 30®, ICI, HLB = 9.7) and an aqueous solution of 4,4 wt. % $ZrO(NO_3)_2$ and 1 wt.-% $Y(NO_3)_3$ (9 mole-% Y_2O_3 with respect fo ZrO_2). For the preparation of the particles a cyclohexane/Brij 30 volume ratio of 7.8 was used. Particles were precipitated inside the aqueous droplets by bubbling ammonia through the emulsion. For isolation of the powder, water and cyclohexane were removed by destillation and the residual was washed with $CHCl_3$ and dried at 60 °C. For the growth reactions, a solution of zircon-n-propoxide in ethanol containing 5 mole % of $Y(NO_3)_3$ with respect to Zr was added dropwise to an aqueous emulsion of surface modifying agents (about 2-6 wt.%) and ammonia. For all experiments, the mass ratio of the precursor solution to the aqueous solution was 1. As emulsifier system a mixture of Emulsogen OG® (Hoechst), Tween 80® (ICI) and octanol was used. The precipitates were isolated by filtration, washed several times with ethanol and dried at 60 °C. The dried powders were calcined in a ventilated laboratory furnace in air at 400 °C for 3 hours. For redispersion, the calcined powders were treated with tertiary amines in aqueous solutions under reflux. After centrifugation of the refluxed dispersion, the supernatant clear solution contained the redipersed particles. The as prepared as well as the calcined powders were characterized by TEM, HRSEM and X-ray diffraction. The state of agglomeration was investigated by redispersing experiments. The particle size distribution of the suspension was determined by PCS.

RESULTS AND DISCUSSION

W/O Microemulsion Technique

The formation of w/o emulsions requires the use of emulsifiers which reduce the interfacial tension of the two immiscible liquids. As shown in [10,11], a suitable mixture of emulsifiers can be selected following the concept of HLB (Hydrophilic-Lipophilic-Balance)-numbers and taking the chemical structures of the emulsifier and of the oil phase into account. Microemulsions are obtained for HLB-numbers between 9 and 10, from which nanosized Y_2O_3/ZrO_2 have successfully been synthesized. However, this process is accompanied by a high amount of emulsifiers (20 vol %) and a relatively low water content (10 - 12 vol %), which limits the powder yield (around 4-5 g/l) [11].

These results can be attributed to a non-optimized compensation of the different surface tensions of the water- and the oilphase and indicate some structure incompatibility of the used emulsifiers. From this point of view, the development of a microemulsion systems with low emulsifiers concentration and higher water content can be expected for emulsifiers having gradient transition properties from hydrophilic to lipophilic within one molecule and a HLB number of about 10.

This approach has been tested for the synthesis of Y_2O_3/ZrO_2 with tetraethylenglycoldodecylether (Brij 30, HLB = 9.7) selected as a suitable emulsifier because of its chemical structure $(CH_3-(CH_2-)_{10}CH_2-O-(CH_2-CH_2-O-)_4H)$.

Systematic experiments, using aqueous salt solutions of $ZrO(NO_3)_2$ and $Y(NO_3)_3$ with an overall salt concentration between 0.2 and 0.4 mol/l have been carried out. The upper value represents the limit of the solubility of $ZrO(NO_3)_2$ in water. For thermodynamically stable microemulsions, temperature is expected to have an influence on the stability conditions and for this reason the temperature was introduced as an important parameter of the variation parameters.

A strong temperature dependence of the maximum water loading of the emulsion was observed (fig. 1). It was found, that stable microemulsions are formed within cyclohexane/Brij 30 ratios ranging from 4.5 to 11 with salt solution concentrations between 5 and 25 vol.-%.
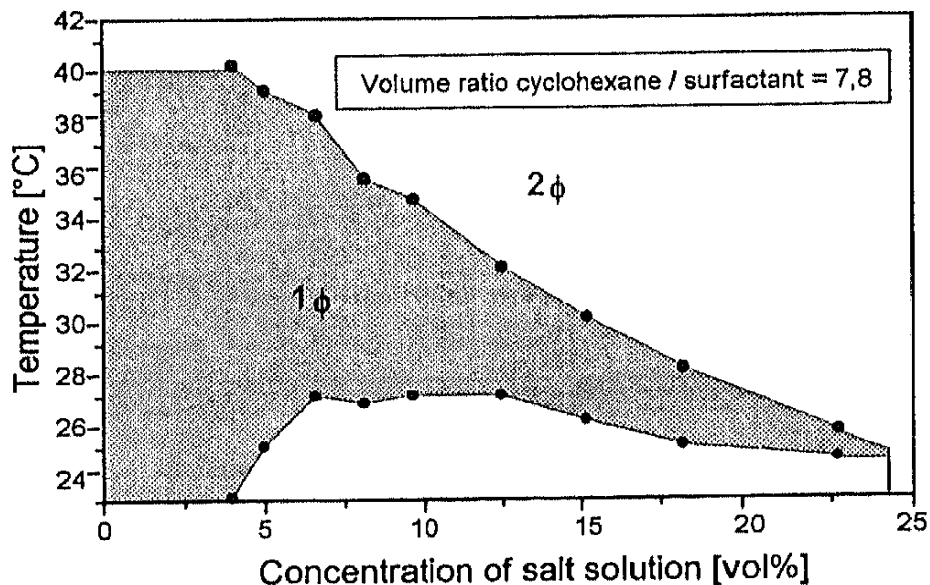

Fig. 1: Influence of temperature on the salt solution content in the w/o microemulsion for a constant cyclohexane/Brij 30 volume ratio of 7.8.

1Ø: one-phase interval (microemulsion); 2Ø: two-phase interval (thermodynamic instable)

From fig. 1, it can be seen that brine concentrations above 10 vol.-% are obtained in the temperature range between 25 and 35 °C. The maximum water loading of 23 vol.-% is obtained at 25 °C for the investigated emulsifier content. Compared to the microemulsions described in [10,11] the emulsifier concentration is significantly reduced (from 20 vol.-% to 8.8 vol.-%) with an simultaneously increased water content (from 12 vol.-% to 23 vol.-%). Using this microemulsion for the synthesis of Y_2O_3/ZrO_2 powders, a theoretical yield up to 12 g/l emulsion can be expected. In addition these results indicate that the HLB number of the used emulsifier changes with temperature and that a certain temperature or temperature interval exits where an optimum compatibility between emulsifier/oil and water phase is achieved allowing the preparation of w/o microemulsion with high water loading.

Growth Reaction

However, for a large scale production of nano-scaled particles the overall yield is still too low and needs further improvement. One approach is the thermodynamically controlled reaction from molecular precursor solutions, because the powder yield is only limited by the solubility product(s) of the precursor(s) in the desired solvent. In order to prevent agglomeration of the growing particles, a surface active compound should be integrated in the reaction system. The general feasibility of such a procedure has been tested for the synthesis of Y_2O_3/ZrO_2 using a model shown in fig. 2.
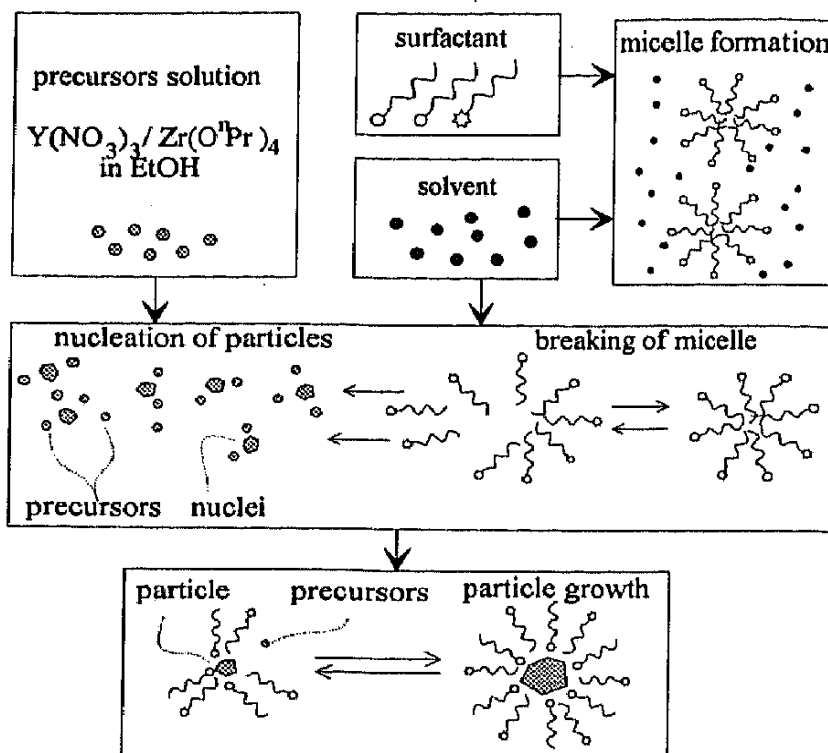
Fig 2: Model for the synthesis of nano-scaled particles by thermodynamically controlled growth reactions using emulsifiers as surfactants

The basic idea of the model is that above the critical micelle concentration surface active molecules (e.g. emulsifiers) spontaneously undergo selforganisation in a solvent forming micelles. The used emulsifier system consisting of Emulsogen®, Tween 80® and octanol forms a stable emulsion in an aqueous ammonia solution. When the alcoholic precursor solution is added to the basic solvent/surfactant system nucleation of Y_2O_3/ZrO_2-particles occurs by hydrolysis and condensation reactions of the metal alkoxides and a "rearrangement" of the emulsifier system takes place forming a coating around the growing particles since the surfactant molecules obviously possess a high affinity to the particle surface ($\Delta G < 0$). The thin layer provides a repulsive interparticular force between the different particles and prevents an uncontrolled agglomeration. A further growth of the particles is possible by diffusion of Y_2O_3/ZrO_2 precursor molecules through the thin surfactant layer.

Powder Synthesis: Comparison of both techniques

In fig. 3, the preparation schemes for yttria-stabilized zirconia powders, the microemulsion techniques and the controlled growth route, are compared.

Using the optimized parameters of the microemulsion-process, Y_2O_3 / ZrO_2 powders with an average particle size of 8 nm can be prepared as a consequence of the small doplet size (20 -25 nm) using only 8,7 vol % Brij 30 as emulsifier. Yields of 12 g calcined powder per liter reaction volume can be obtained. In contrast using optimized preparation conditions for the growth reaction route, yields of 110 g powder per liter reaction volume are possible, clearly demonstrating the advantage of this technique.
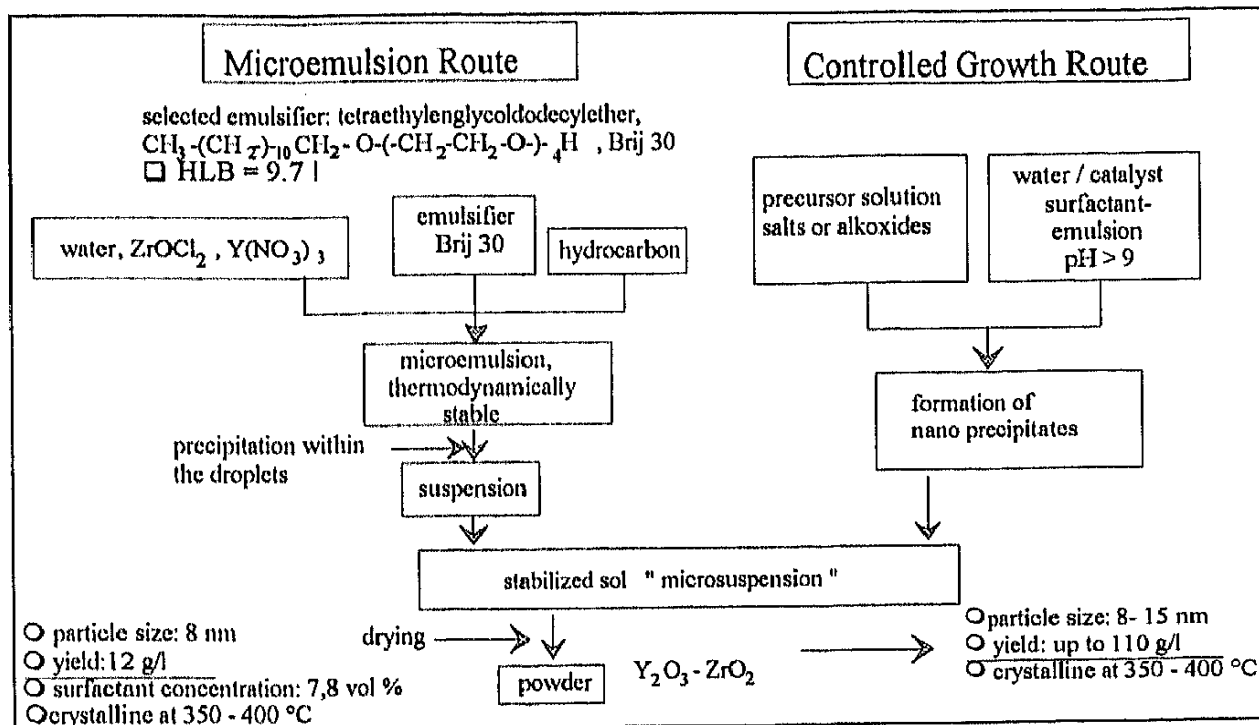
Microemulsion Route | **Controlled Growth Route**

selected emulsifier: tetraethylenglycoldodecylether,
$CH_3-(CH_2)_{10}CH_2-O-(-CH_2-CH_2-O-)_4H$, Brij 30
□ HLB = 9.7 |

water, $ZrOCl_2$, $Y(NO_3)_3$

emulsifier Brij 30

hydrocarbon

precursor solution salts or alkoxides

water / catalyst surfactant-emulsion pH > 9

microemulsion, thermodynamically stable

formation of nano precipitates

precipitation within the droplets

suspension

stabilized sol " microsuspension "

○ particle size: 8 nm
○ yield: 12 g/l
○ surfactant concentration: 7,8 vol %
○ crystalline at 350 - 400 °C

drying ⟶ powder $Y_2O_3 - ZrO_2$

○ particle size: 8- 15 nm
○ yield: up to 110 g/l
○ crystalline at 350 - 400 °C

Fig. 3: Preparation scheme for the synthesis of nano-scaled Y_2O_3/ZrO_2 powders by w/o microemulsions and growth reactions.

X-ray diffraction measurements of both powders indicate an amorphous structure of the particles after precipitation. In order to obtain crystalline products, the powders had to be calcined at elevated temperature. This is the crucial step during the preparation procedure which has thoroughly be controlled because strong agglomerates can easily be formed by condensation reactions if the surface modifiers are removed before the particle surface is completely dehydroxylated. Therefore, in order to minimize the formation of strong agglomerates, powders were calcined at temperatures as low as possible but sufficient to complete crystallization. In fig. 4 the crystallisation behavior is displayed.
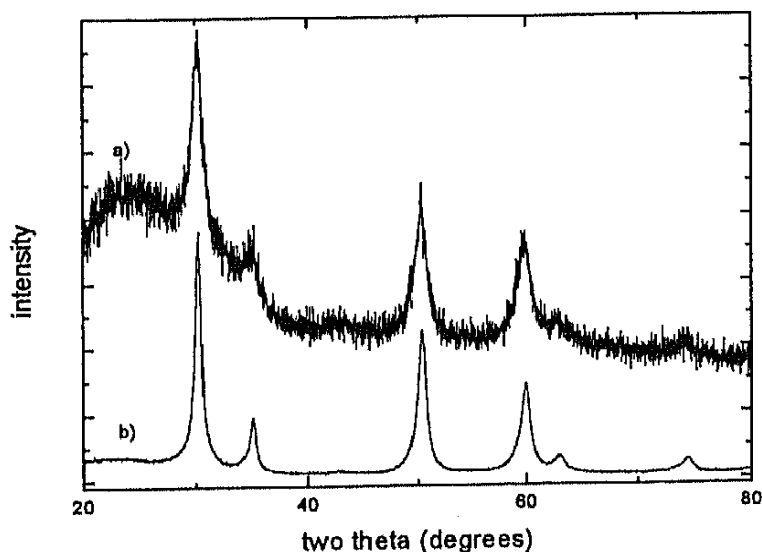
intensity

a)

b)

20   40   60   80

two theta (degrees)

Fig. 4: Crystallization behavior of nanosized Y_2O_3/ZrO_2 powders after calcination at 400 °C. a: microemulsion technique; b: growth reaction.

In both cases, crystallization takes place between 300 and 400 °C and yttria-stabilized cubic zirconia is formed as it was expected from the chemical composition (9 mole % Y_2O_3). From the line broadening of the X-ray pattern an average crystallite size of 8 nm (microemulsion) and 16 nm (growth reaction) has been calculated. This could be confirmed by transmission electron microscopy (fig. 5).
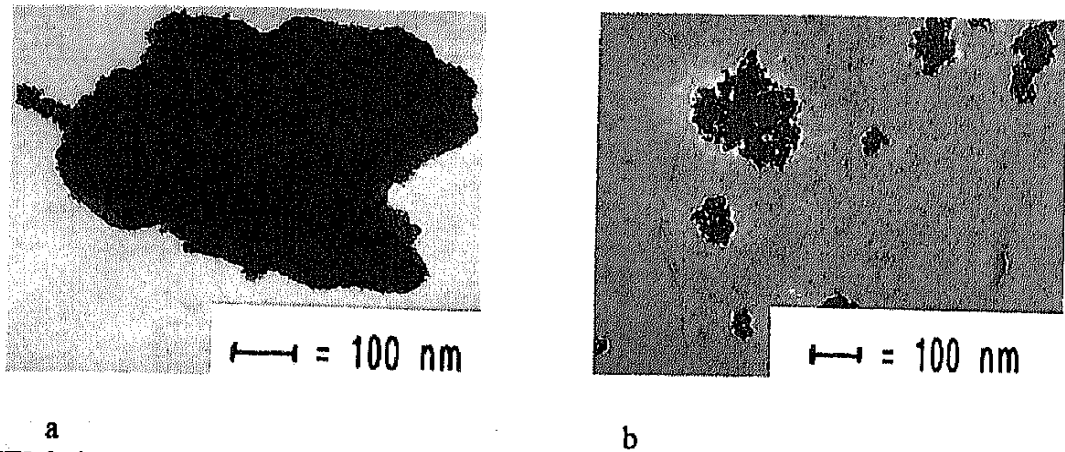

a   b

Fig. 5: TEM pictures of cubic Y_2O_3/ZrO_2 powders after calcination at 400 °C.
a: microemulsion; b: growth reaction.

As shown in fig. 5, the powders consist of primary particles of about 10 nm (a) and 15 to 20 nm (b) forming agglomerates of irregular shape and size. In order to estimate the state of agglomeration, redispersing experiments were performed. Calcined powders (400 °C) were treated with tertiary amines in aqueous solutions under reflux. Non-dispersed material was separated by centrifugation and the clear supernatant containing the dispersed nano particles was investigated by TEM (fig. 6).
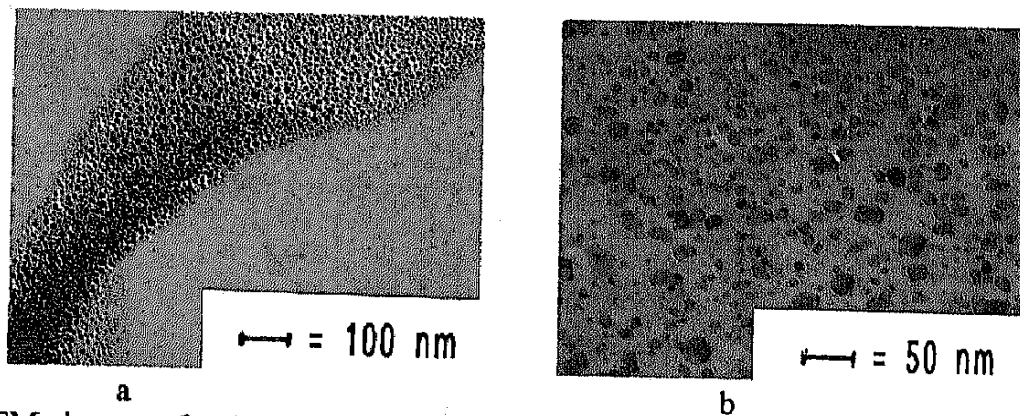

a   b

Fig. 6: TEM pictures of redispersed nano powder.
a: microemulsion; b: growth reaction.

The TEM pictures in fig. 6 show a good state of dispersion with particle sizes in the range of 3 to 20 nm. The redipersion yield in the first batch is only 10 wt.%, but the yield could be increased by removing the dispersed phase and by repeating the process with the undipersed phase. It seems that an equilibrium exists in the dispersing process which has to be investigated in detail. The particlesize of the not completely redispersed phase was determined by PCS. These measurements show agglomerate sizes between 40 and 100 nm which consist of nano-scaled primary particles as calculated from X-ray diffraction (fig. 5).

CONCLUSIONS

It has been shown that by using emulsifier systems two routes succesfully can be used to produce nano-scaled Y_2O_3/ZrO_2 powders. The two phase system (w/o-microemulsion) using a only one emulsifier leads to a reduced emulsifier concentration, whereas the one phase system (controlled growth), avoiding the organic phase, leads to an increase of the yield (110 g/l reaction volume) by the factor of 10. The crucial step is the redispersion process, which has to be improved.

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