Microwave synthesis of ZrO_2 and Yttria stabilized ZrO_2 particles from aqueous precursor solutions

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ABSTRACT

Zirconia and Yttrium stabilized zirconia are well-known ceramic materials. Scaling down the dimension of these ceramics can result in a faster sintering process at lower temperatures. Microwave synthesis of nano-structured particles is a very attractive synthesis route because of the short synthesis time and low reaction temperature. This allows a fast screening of the influence of different parameters such as time, temperature and pressure on the final size and crystal phase of the particles. In this study Zr and Zr/Y aqueous precursors are mixed with a variety of complexing agents or surfactants in different ratios. The reason is twofold: (1) we aim for a stable precursor solution which is established by lowering the free ion concentration and (2) we want to see the influence of the complexing agents on the growth of the particles and the formation of crystalline phases. Particle sizes of these particle vary from 40 -200 nm. The crystallinity is confirmed by X-ray diffraction. The stabilization of these particles and possible exchange of the ligands is examined with NMR measurements (1D - proton combined with 2D NOESY) and is compared with TGA-DTA analysis of the isolated particles.

INTRODUCTION

Ceramics are by definition a combination of metallic and non-metallic elements which gain their specific properties by a high temperature treatment. The temperatures necessary for crystallization and formation of the desired phases can be very high resulting in an high energy consumption [1]. In the light of green chemistry and environmental and energy friendly processes a lot of effort has been put in the research towards novel synthesis and preparation routes that overcome this temperature barrier. Well established solid state reactions for formation of ceramic use the shake-and-bake method in order to homogenize the precursor mixture and the increase the inter-granular contacts. Solution chemistry routes avoid those intensive milling and mixing steps and ensure a homogeneity of the precursor to the atomic level [2, 3]. Off course, precipitation has to be prevented at all times to avoid non-stochiometric precursor solutions. Solution chemistry routes allow beside the formation of bulk ceramics, the deposition of ceramic thin films by dip-coating, spin-coating, spray-coating or even ink-jet printing [4-7].

In all the above mentioned systems there is still a need for a high temperature treatment for the formation of the desired crystalline phase. In this work we focus on the synthesis of ceramic nanoparticles from solution precursors. These particles should be as crystalline as possible so that a much lower temperature treatment is necessary to convert the wet phase into a crystalline bulk or thin film material. This will open a new branch of applications such as the

deposition of ceramic thin films on polymers. Multiple approaches for the synthesis of nanoparticles from bottom-up have already been published such as: hot-injection, precipitation, peptization, ultrasonic treatment, solvothermal and hydrothermal treatment, microwave assisted solvothermal and hydrothermal treatment and many more [8-13]. In this paper the microwave assisted hydrothermal synthesis of well established ceramics as zirconia (ZrO_2) and yttria-stabilized-zirconia (YSZ) particles is described. Cubic zirconia is only stable above a temperature of 2000°C. Cooling down induced a phase transition to the monoclinic phase and subsequently cracks in the material. Due to these cracks and the different crystal lattice, pure zirconia inhibits the use for many applications. The cubic crystal structure can be retained at room temperature by addition of yttria. YSZ ensures the use for various applications such as thermal barrier coating in engines, SOFC, ceramic knifes, tooth crowns etc. The conventional method to synthesize nano-particulate YSZ is by a hydrothermal process. The long reaction times and high temperatures have practical and economical disadvantages. Microwave assisted hydrothermal synthesis can sometimes lower the reaction temperature but certainly scale-down the reaction times form hours to minutes. In this work the possibility of microwaves is tested for ZrO_2 and YSZ and the influence of different complexing agents of the formation of crystalline phases and particle growth are explored.

EXPERIMENT

ZrO_2 precursor

Zirconium oxynitrate hydrate ($ZrO(NO_3)_2.nH_2O$, Sigma Aldrich) is dissolved in distilled water (0.33 mol/L). The solution is kept in an ultrasonic bath until the salts are completely dissolved. 2.4 w% PEG 1000 (Alfa Aesar) is added to the solution to avoid agglomeration of ZrO_2 on the wall of the vessels. After µ-wave synthesis and purification, citric acid (Carl Roth) and ethanolamine (Sigma Aldrich) are added to stabilize the particles at a neutral pH level.

YSZ precursor

Zirconium oxynitrate hydrate ($ZrO(NO_3)_2.nH_2O$, Sigma Aldrich) and yttrium nitrate ($Y(NO_3)_3.nH_2O$, Alfa Aesar, 99.9%) are dissolved in distilled water. The solution is kept in an ultrasonic bath until the salts are completely dissolved. Ethylenediaminetetraacetic acid (EDTA, Alfa Aesar, 99%) or nitrilotriacetic acid (NTA, Alfa Aesar, 99%) are used as complexing agents. EDTA is used in a 1:1.5 ratio (metal:ligand) whereas NTA in a 1:2 is used. Both solutions (salts and complexing agent) are heated till 60° C before the complexing agent is added drop wise to solution of the salts. Finally, the pH of the mixtures is adjusted by addition of ethanolamine (Sigma Aldrich, ≥99.9%). In some experiments a pH range is explored. The pH is lowered by formic acid (VWR, 100%) or ethanolamine is added for more alkaline solutions. The final concentration equals 0.033 mol/L.

Microwave assisted hydrothermal synthesis

2 mL of the above prepared precursors are put in to capped 10 mL vessels and are treated by microwave (Discovery, CEM) at temperatures between 110 °C – 180 °C for 2 till 10 minutes. The particles are purified by destabilization with an ethyl acetate/ethanol mixture. They are separated by centrifugation and redispersed in an aqueous solution of citric acid and ethanol amine.

Characterization

The particle sizes and particle size distribution are examined by dynamic light scattering (Zetasizer Nano ZS, Malvern). The crystallinity and the crystal phases were determined with X-ray diffraction (Thermo Scientific ARL X'tra diffractometer) followed by Rietveld refinement (TOPAS Academic). Differential and thermogravimetric analysis (DTA, TGA) (STA449F3 Jupiter, Netzsch) are used to examine the decomposition behavior. X-ray fluorescence (XRF) (Rigaku, Nex CG) is used to analyze the amounts of yttrium and zirconium in the YSZ samples. NMR experiments (1D proton, 2D proton and 2D NOESY, Bruker DRX 500 MHz AVANCE) were performed to identify the presence of stabilization groups fixed to the particles.

## DISCUSSION

ZrO_2 particles

Not all solutions remained stable after microwave assisted hydrothermal treatment. The samples treated at higher temperature and longer times showed precipitation afterwards that could not be redissolved. Figure 1 shows the results of the analysis of the destabilized and dried particles after µ-wave treatment. With increasing temperature the hydrodynamic diameter of the particles shifts from 40 to 60 nm (Figure 1a). The polydispersity is rather broad. X-ray analysis was performed to see whether any crystallinity could be obtained at this low temperatures. As can be seen in Figure 1b, broad reflections are obtained caused by the small crystallite sizes. Monoclinic and to a lesser extend tetragonal zirconia phase could be identified with an average crystallite size of 5 nm. No remarkable changes could be noticed upon variation in temperature and time. The diffraction pattern of the precursor treated at 180 °C for 10 min shows much more crystalline materials but the solution was not stable after µ-wave treatment and precipitation could be seen. No exact percentage of the amorphous phase could been calculated as no internal standard was added to the powders. The particles measured in solution are thus clearly agglomerates of smaller crystallites.
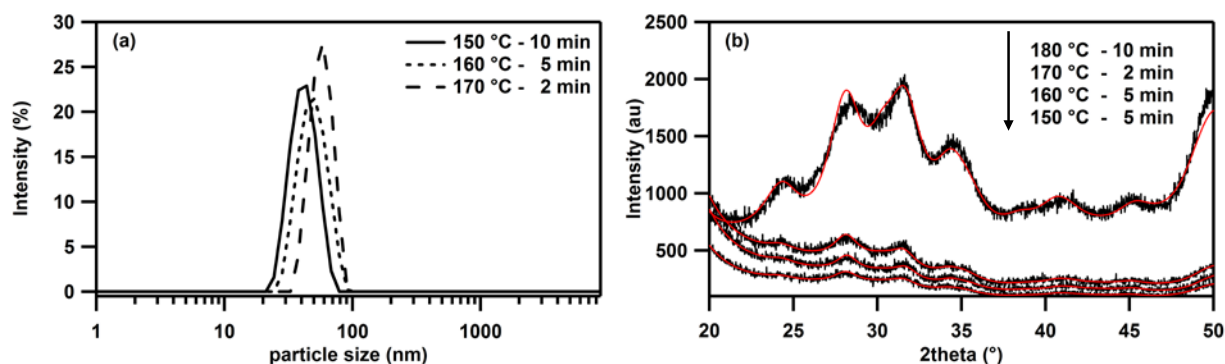
Figure 1: (a) DLS results of the µ-wave treated ZrO_2 precursor at various conditions – (b) X-Ray diffraction pattern of the destabilized and dried particles. The red lines indicate the calculated X-ray pattern by Rietveld analysis.

TGA-DTA analysis is performed on the synthesized solutions during the different steps of the purification. Each sample is dried at 60 °C before TGA-DTA analysis. TGA-DTA analysis of a sample after washing with ethanol (Figure 2a) shows a weight loss of approximately 30 % that can be attributed to loss of water, ethanol and PEG that is associated with the particles. After this washing procedure, the particles are redispersed in an aqueous citric acid solution (0.33 mol/L). Figure 2b (thick lines) clearly shows that a lot of organic material is burned off during this procedure even at higher temperatures in comparison with the previous sample. Only 10 % oxide

material was remained afterwards. The suspension of particles in the citric acid solution are destabilized, separated by centrifugation and washed several times. TGA-DTA analysis of this sample (Figure 2b thin lines) shows the same decomposition behavior as before washing but now a substantial amount of citric acid is removed. Nevertheless, even after a few washing steps citric acid is remained in the sample or on the surface of the particles. NMR 1D and 2D spectra are used to see whether organic groups are attached to the surface of the particle in order to stabilize the particles and to identify the nature of this organic groups.
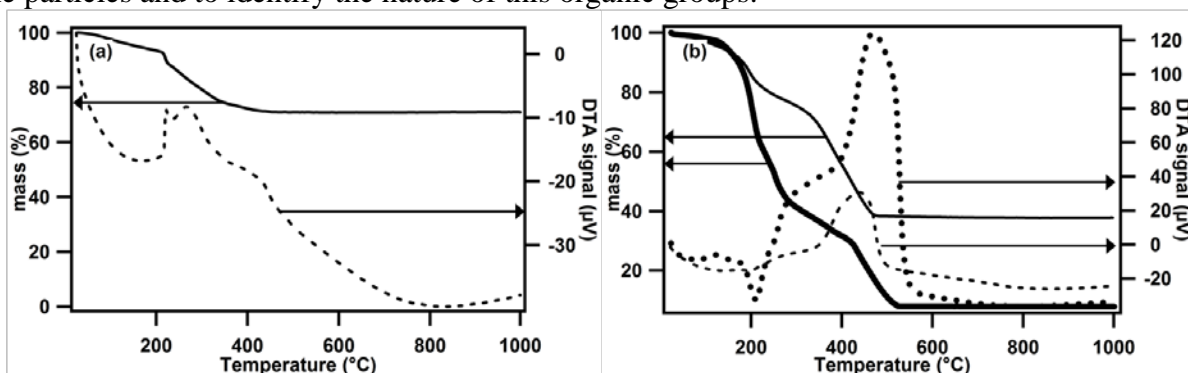
Figure 2: (a) TGA-DTA curve of particles after first washing step. Full line: TGA signal – Dashed line: DTA signal - (b) TGA-DTA curve of particles after first washing step and after addition of citric acid (thick lines) and after an additional washing step (thin lines).

The 1D-NMR spectra show the presence of PEG, citric acid and ethanolamine in the suspension. Nevertheless, this gives no proof for the fact that these groups are actually attached to the surface of the particles. A strong negative nOe cross coupling in the 2D-NOESY spectrum can confirm the presence of the group at the surface of the particles [14]. This can be seen for the ethanolamine groups The non-symmetric signals for citric acid are also caused by interface interactions. The interaction is rather fast most likely due to an exchange with other ethanolamine and citric acid groups in solution. No such behavior could be noticed for the PEG systems.
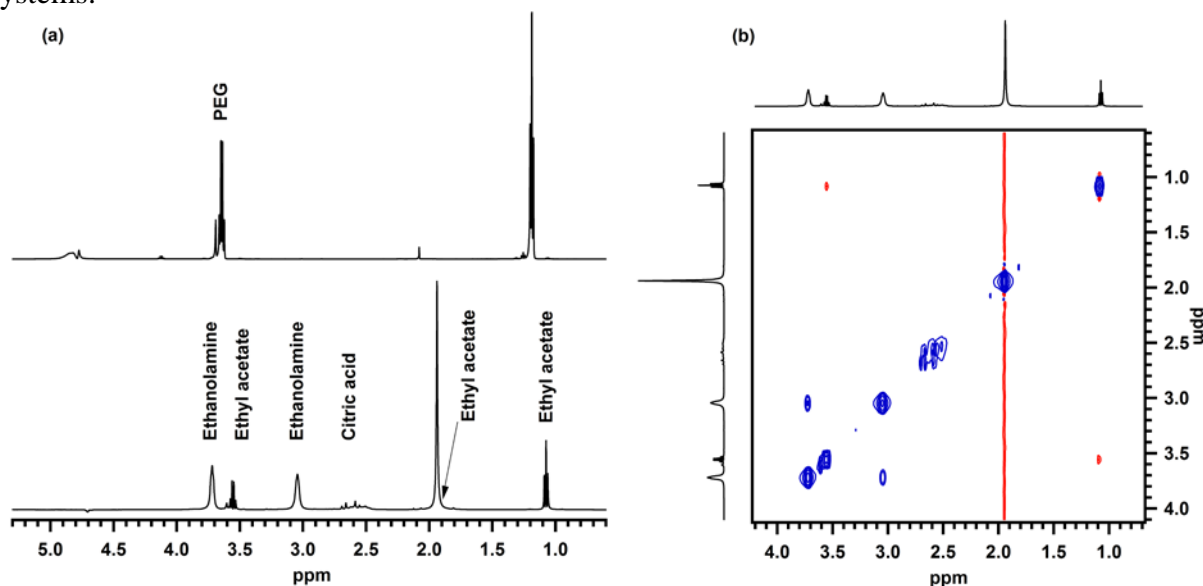
Figure 3: (a) 1D NMR spectra at room temperature, 500 MHz. The upper spectrum corresponds to a suspension directly after μ-wave synthesis. The lower spectrum shows a sample after addition of citric acid and ethanolamine - (b) 2D NOESY NMR spectrum at room temperature, 500 MHz.

YSZ particles

Particle sizes (Figure 4a and 4b) vary from 80-90 nm for the NTA system to 100-190 nm for the EDTA system. The polydispersity is more in the EDTA systems as stronger complexes are formed which limits the particle growth. This variation of the complexing agent limits the temperatures that can be used in the μ-wave set-up. As the complex stability constant for Zr-EDTA complexes is $10^{29.4}$ and Zr-$(NTA)_2$ is $10^{20.9}$ [15], it can be understood that higher temperatures will be necessary to break down the strong complex in order to allow the particles to grow.
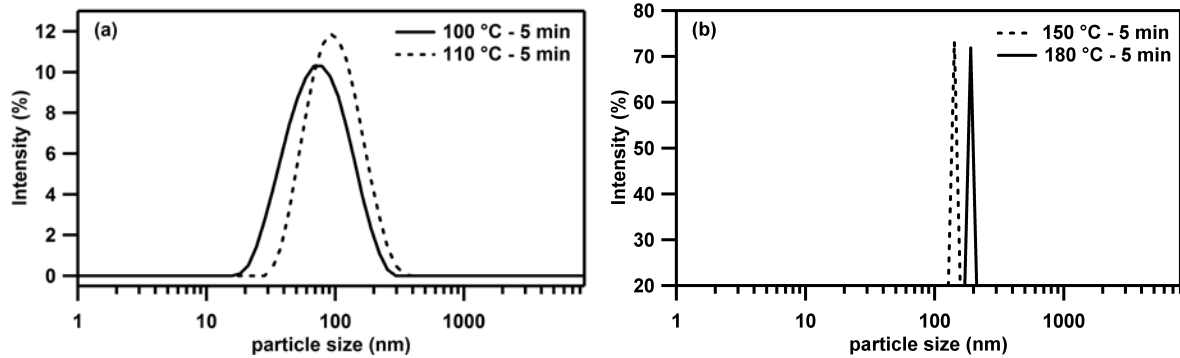

Figure 4: (a) DLS results of the μ-wave treated YSZ NTA - precursor at various conditions – (b) DLS results of the μ-wave treated YSZ EDTA - precursor at various conditions.

The effect of pH on the particle size for the EDTA system is shown in Figure 5a. The particles have the smallest sizes in the pH range 6-7. In this pH interval the EDTA structure mainly exists in its double and triple deprotonated form which facilitates the formation of stronger complexes in comparison with the protonated and single deprotonated species. The question remains if YSZ is formed or mixed ZrO_2 - Y_2O_3 phases. XRF analysis of the isolated particles show that the same ratios Zr: Y can be found as in the as-prepared solution. X-ray analysis of and EDTA stabilized sample cured at 180 °C for 5 min showed that besides the monoclinic (60 w%) and tetragonal (20 w%) phase 20 w% of cubic YSZ could be found. More detailed analysis about the homogeneity and yields need to be performed.
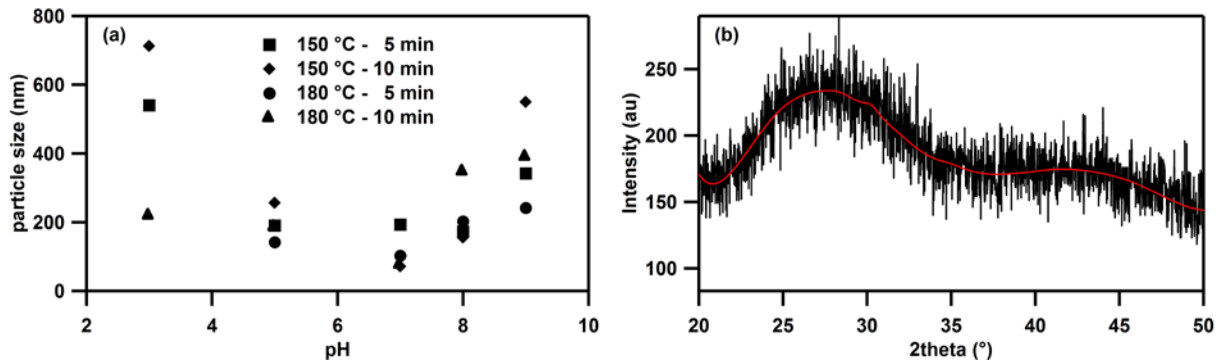

Figure 5: (a) DLS results of the μ-wave treated YSZ EDTA - precursor at various μ-wave conditions and with varied pH of the precursor solution - (b) X-Ray diffraction pattern of a YSZ –EDTA precursor pH 5 and treated at 180 °C for 5 min. The red line indicate the calculated X-ray pattern by Rietveld analysis.

CONCLUSIONS

Microwave assisted hydrothermal treatment has proven to be effective for the synthesis of nanoscaled (40-200nm) ZrO_2 and YSZ particles. The stabilization of zirconia particles in water can be established by addition of citric acid and ethanolamine. These species are present at the surface of the particles but are rapidly exchanged. The addition of complex agents during the microwave assisted hydrothermal synthesis allows a stable precursor solution but variation in the pH strongly affects the particle sizes. Upon deprotonation of the complexing agent, more stable complex are formed with smaller particles as result.

ACKNOWLEDGMENTS

REFERENCES

1. W.D. Callister, in Materials Science and Engineering: An Introduction, (Wiley & Sons, Danvers, 2000), p. 661.
2. C.J. Brinker and G.W. Scherer, in Hydrolysis and Condensation I Nonsilicates, (Academic press, San Diego, California, 1990), p. 20
3. J. Livage, New Journal of Chemistry **25**, 1 (2001).
4. J. Feys, P. Vermeir, P. Lommens, S.C. Hopkins, X. Granados, B.A. Glowacki, M. Bäcker, E. Reick, S. Ricart, B. Holzapfel, P. Van Der Voort and I. Van Driessche, J. Mater. Chem. **22**, 3717 (2012).
5. M. Arin, P. Lommens, N. Avci, S.C. Hopkins, K. De Buysser, I.M. Arabatzis, D. Poelman and I. Van Driessche, J. Eur. Ceram. Soc. **31**, 1067 (2011).
6. M. Arin, P. Lommens, S.C. Hopkins, G. Pollefeyt, J. Van der Eycken, S. Ricart, X. Granados, B.A. Glowacki and I. Van Driessche, Nanotechnology (2012).
7. V. Cloet, J. Feys, R. Huhne, S. Hoste and I. Van Driessche, J. Solid State Chem. **182**, 37 (2009).
8. T. Okubo and H. Nagamoto, J. Mater. Sci. **30**, 749 (1995).
9. H. Armendariz, M.A. Cortes, I. Hernandez, J. Navarrete and A. Vazquez, J. Mater. Chem. **13**, 143 (2003).
10. E. Gressel-Michel, D. Chaumont and D. Stuerga, J. Colloid Interface Sci. **285**, 674 (2005).
11. M.L. Moreira, G.P. Mambrini, D.P. Volanti, E.R. Leite, M.O. Orlandi, P.S. Pizani, V.R. Mastelaro, C.O. Paiva-Santos, E. Longo and J.A. Varela, Chem. Mat. **20**, 5381 (2008).
12. E.T. Thostenson and T.W. Chou, Compos. Pt. A-Appl. Sci. Manuf. **30**, 1055 (1999).
13. M. Zawadzki, Journal of Alloys and Compounds **454**, 347 (2008).
14. A. Hassinen, I. Moreels, C.D. Donega, J.C. Martins and Z. Hens, J. Phys. Chem. Lett. **1**, 2577
15. A.E. Martell and R.M. Smith, in Critical Stability Constants - Volume 3: Other Organic Ligands edited by Editor (Plenum Press, New York, 1977), p. Pages.