

Synthesis and Characterisation of Monodisperse Zirconia Particles

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Monodisperse spherical ZrO₂ particles were prepared by controlled hydrolysis of zirconium tetraalkoxide in alcoholic solution. Ageing the reaction solution at 60 °C for 4 h yields particles with sizes in the range between 200 and 2000 nm. The influence of various ions and surfactants on the final product was investigated. Stable suspensions of coated, monodisperse, zirconia particles were prepared by hydrolysis and subsequent polymerisation of tetraethoxysilane in an alkaline ethanol solution. Thermal analysis revealed that the weight loss of bound water occurred below 400 °C and is about 35 %. The phase transition from amorphous zirconia to

the tetragonal phase proceeded at approximately 450 °C, the transition to the monoclinic phase began at about 600 °C and was completed at about 800 °C. The crystallinity of the powders was investigated by X-ray diffraction. Electrophoretic measurements were carried out to determine the charges on the particle surface. Elementary analyses were used for further investigations. On the basis of the results obtained, the mechanism of particle formation was discussed.

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Introduction

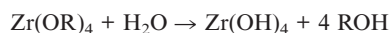
Mesoscale spheres of metal oxides, like zirconia particles, are of particular interest for applications as ceramics. To advance the sintering kinetics, i.e. to obtain shorter sintering times and lower sintering temperatures, elimination of agglomerates and control of the particle size distribution is required. Controlled hydrolysis of metal alkoxides seems to be a promising method for obtaining particles with well-defined sintering properties during the powder synthesis. Zirconia particles are widely used as high-performance ceramics, catalysts or in cosmetics. New applications for zirconia powders are high-temperature fuel cells, lambda probes or bioceramics such as dental prostheses.^[1]

The preparation of zirconia powders was described in a number of publications.^[2–6] Sada et al.^[3] reported the preparation of zirconia particles by hydrolysis of zirconium tetrabutoxide in 1-propanol. The average diameter of particles obtained range from 140 to 380 nm. A decrease in the particle size with increasing reaction ratio was observed. Kato et al.^[2] prepared various sizes of particles by the seeded-growth method. Mizutani et al.^[5] reported the influence of chain length and branching, and the molecular structure of the alcoholic solvent on the hydrolysis behaviour of zirconium tetrabutoxide. The goal of our research was to establish a controlled and reproducible synthesis of zirconia particles with a narrow size distribution and of various sizes. Additionally, we investigated the influence of ions and polymers and of different ratios of precursors on the synthesis of zirconia particles. In order to change the surface proper-

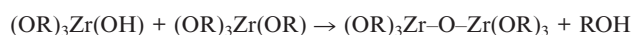
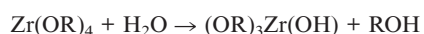
ties of the zirconia particles and to make the particles visible for confocal scanning laser microscopy (CSLM), the particles were coated with a silica shell into which dye molecules could be incorporated.

Results and Discussion

Zirconia particles with a narrow size distribution were obtained in a precipitation reaction from zirconium alkoxide and water in an alcoholic solution. Depending on the reaction conditions, particles in the range between 200 and 2000 nm were obtained (Figure 1). The scanning electron micrographs reveal the perfectly uniform shape and high monodispersity of our particles (Figure 2 and Figure 3). The synthesis proceeds in two steps. During the first step, the hydrolysis, zirconium hydroxide molecules and primary particles are generated. In the second step, the primary particles aggregate (see Figure 1).^[5]



The zirconia particles are formed by a stepwise hydrolysis of zirconium tetraalkoxides, as described above, and polymerisation of hydrolysed zirconium alkoxide.^[3] In addition to hydrous zirconia, hydrated polymeric species with a number of Zr–O–Zr bridges are formed. A macromolecular oxide network is then obtained through hydrolysis and condensation.^[2,10]



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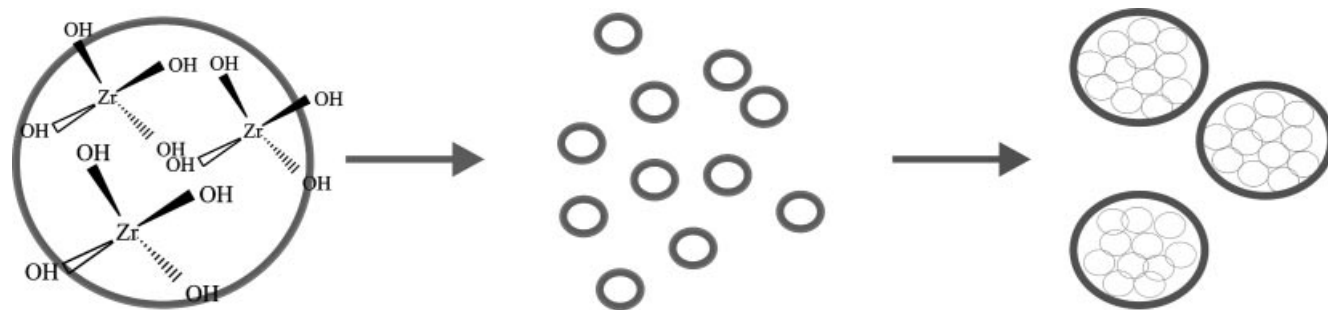


Figure 1. Primary particles formed by the hydrolysis of the metal alkoxide coalesce fast and grow into spheres. Residual primary particles do not form secondary particles but promote the growth of the spheres.

Variation of Precursors and Their Concentrations

To obtain spherical and monodisperse zirconia particles, various zirconium tetraalkoxides and alcohol solvents were tested. Among zirconium tetraethoxide, tetrapropoxide and tetrabutoxide, the best results were obtained with zirconium tetrabutoxide. When ethanol, 1-propanol and 1-butanol were tested as solvents, particularly uniform and monodisperse particles were obtained with ethanol for a wide range of precursor concentrations. 1-Propanol and 1-butanol provided only narrow ranges of concentration where spherical and monodispersed particles were obtained. In the case of ethanol, the induction time for the formation of particles optimally fell between 1 and 5 min. When the induction time was shorter than the optimum, hydrolysis occurred

more quickly, and the nuclei formed polydisperse aggregates. In the case of a prolonged induction period, nucleus formation and particle growth proceeded simultaneously and polydisperse particles were formed.^[5] An ethanol volume of 100 mL, mixed with 0.2–0.6 mL of Millipore water, aqueous salt or polymer solution, followed by the addition of 3.25–5.00 mL of zirconium tetrabutoxide was found to be the best condition for obtaining uniformly spherical and monodisperse zirconia particles.

The uniformity in size and spherical shape of the resulting particles decreased as the initial amount of water became higher than 0.6 mL or lower than 0.2 mL. The higher the water concentration in the reaction solution, the faster the hydrolysis, and the smaller the particles obtained (Figure 2). For zirconia particles synthesised with NaCl, the

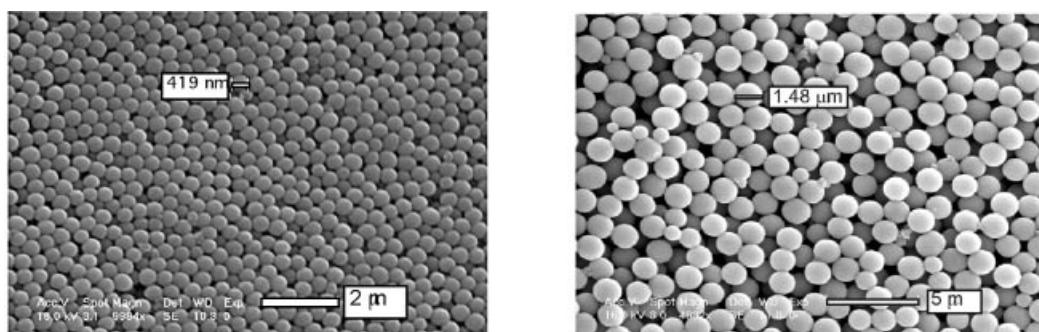


Figure 2. Zirconia particles synthesised with 0.40 mL (l) and 0.20 mL (r) of a 0.1 M NaCl solution, with addition of 3.25 mL $\text{Zr}(\text{O}i\text{Bu})_4$ in 100 mL ethanol.

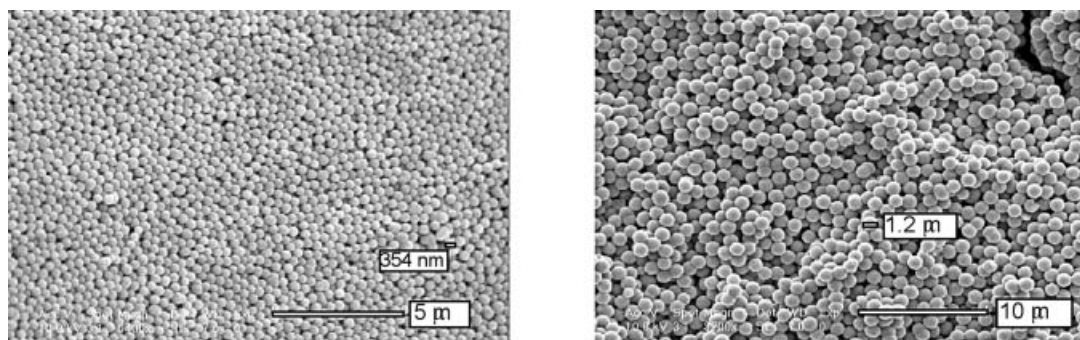


Figure 3. Zirconia particles synthesised with 3.25 mL (l) and 5.00 mL (r) of $\text{Zr}(\text{O}i\text{Bu})_4$, with addition of 0.40 mL of a 0.1 M NaCl solution in 100 mL ethanol.

particle sizes decreased from 1500 to 400 nm when the amount of water in the solution increased from 0.2 to 0.4 mL per 100 mL ethanol. Analogous results were observed for particles synthesised with polymers such as Lutensol ON 50 (Table 1). With a large amount of water, the induction time of hydrolysis was very short; the hydrolysis was fast enough to generate a lot of primary particles. Because of the high density of primary particles, these particles agglomerated in an uncontrolled manner and became polydisperse. No precipitate was observed when the amount of water was below 0.1 mL. The average size increased depending on the initial concentration of $\text{Zr}(\text{OBU})_4$. The sizes of the particles synthesised with Lutensol ON 50 increased from 300 to 1200 nm when the amount of zirconium tetrabutoxide increased from 1.25 to 5 mL per 100 mL ethanol (Figure 3, Table 2).

Table 1. Sizes of zirconia particles synthesised with various amounts of 0.1 M Lutensol ON 50 solution with addition of 5.00 mL zirconium butoxide in 100 mL ethanol.

Lutensol ON 50 (0.1 M solution in H_2O , mp) [mL]	Particle size [nm]
0.20	no precipitation
0.40	$1200 \pm 10\%$
0.50	$1000 \pm 10\%$
0.60	$900 \pm 10\%$
0.80	600–800
1.00	400–600

Table 2. Sizes of zirconia particles synthesised with various amounts of zirconium butoxide with addition of 0.40 mL of a 0.1 M NaCl solution in 100 mL ethanol.

$\text{Zr}(\text{OBU})_4$ (80% solution in BuOH) [mL]	Particle size [nm]
1.25	$300 \pm 10\%$
2.50	$450 \pm 10\%$
3.25	$550 \pm 10\%$
2.75	$700 \pm 10\%$
4.25	$1000 \pm 10\%$
5.00	$1200 \pm 10\%$

Variation of Salts and Polymers

The stability of dispersion depends inter alia on the magnitude of the electric charge of the particles. Oxide surfaces in an aqueous medium are generally charged positively under acidic conditions and negatively under basic conditions. Similar to the measurements carried out by Kato et al.,^[6] zeta potential values between 20 and 30 mV were detected in ethanol solution at pH 6 for our particles. For particles prepared with various salts, no significant differences were observed. In contrast, the zeta potential values obtained for titania particles synthesised with alkali halides increased from lithium chloride to caesium chloride, from 9 to 27 mV. The sizes and size distributions were very sensitive to the type of salt added.^[8] The influence of alkali halides on the particles was not as strong as in the case of titania. The smallest particles were obtained, however, by addition of

CsCl, the largest with LiCl (Table 3). Particles synthesised with pure Millipore water ranged between 300 and 1400 nm in size. We assume that interactions between the zirconium alkoxide, hydroxide and dioxide molecules and the salt ions are much weaker than those between the titanium compounds and salt ions.

Table 3. Sizes of zirconia particles synthesised with 0.40 mL of 0.1 M various salt or polymer solutions with addition of 3.25 mL zirconium butoxide in 100 mL ethanol.

Added salt or polymer	Particle size [nm]
CsCl	$200 \pm 10\%$
KCl	$350 \pm 10\%$
NaCl	$550 \pm 10\%$
LiCl	$700 \pm 10\%$
–	$1000 \pm 10\%$
Lutensol ON 50	$600 \pm 15\%$
Pluronic PE 6400	$2000 \pm 15\%$

The influence of polymers on the size and the size distribution of the colloidal particles was investigated in the next step. Two different types of polymers, diblock-copolymer Lutensol ON $[\text{RO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}]$ and triblock-copolymer Pluronic $[\text{PEO}_n\text{-PPO}_m\text{-PEO}_n]$, were used for steric stabilisation. Depending on the amounts of water and zirconium tetrabutoxide, it was possible to obtain particles of up to 1200 nm with Lutensol ON 50 and of up to 2000 nm with Pluronic PE 6400. The hydrophilic part of Lutensol ON is likely to interact with the nanoparticle surface, while the hydrophobic part extends into the medium, thus providing additional steric stabilisation. In the case of Pluronic PE, the presence of two hydrophilic parts can be assumed to lead to a coating of the nanoparticle surfaces. The stabilisation by Pluronic polymers is not as effective and resulted in a broader size distribution of the titania particles. The same effect, but not as strongly pronounced, was observed for zirconia particles. The monodispersity of zirconia particles synthesised with Lutensol ON 50 was higher than that of particles prepared with Pluronic PE 6400.

In order to determine whether polymer molecules were built into the colloidal particles during the aggregation process, we carried out elementary analyses of as-synthesised zirconia powders. Elementary analyses showed carbon values of under 2%, which originated probably from untreated butoxide groups. Therefore, we assume that the polymer was not (or only in very small amounts) built into the final particles during the aggregation process. In the case of titania particles, higher amounts of carbon were observed. The interaction between polymer molecules and titanium alkoxide, hydroxide or dioxide was much stronger, so that polymer molecules were built into the particles. This resulted in porous titania particles with a specific surface area of $a_s = 300 \text{ m}^2/\text{g}$ in average, determined by the Brunauer–Emmett–Teller method. For zirconia particles, the values for the specific surface area were always below $10 \text{ m}^2/\text{g}$. Apparently, interactions between zirconium compounds and

polymer molecules are too weak to prevent a compact aggregation of the primary particles.

X-ray Diffraction and Thermal Analysis

X-ray diffraction patterns showed that the as-prepared ZrO_2 powders were amorphous. The DTA plot of ZrO_2 particles synthesised with salts showed a very broad exothermic peak from 30 to 360 °C due to dehydration (Figure 4). For samples synthesised with polymers, a sharp exothermic peak was observed, probably corresponding to the spontaneous thermal decomposition of untreated alkoxy groups. Bound water and untreated alkoxy groups, lost below 400 °C, make up 40% of the total weight. That means, the synthesised zirconia particles, after storing for 7 d in an oven at 100 °C, contain 4 mol water and hydroxide groups per mol of zirconium dioxide. The total formula can be specified as $\text{ZrO}_x(\text{OH})_{2-x}n\text{H}_2\text{O}$ with $(x + n = 4)$. The amount of untreated alkoxy groups should be very low. Elementary analysis exhibited carbon values of under 2%.

For particles synthesised with polymers, the transformation into the tetragonal phase proceeded by heating to 450 °C, and for particles synthesised with addition of salts, to 510 °C. The transition to the monoclinic phase (Baddeleyite) occurred between 600 and 800 °C. A shift to higher transition temperatures was observed for zirconia particles prepared with addition of salt (Figure 4 and Figure 5). High-temperature X-ray diffraction patterns support these results.

X-ray diffraction provided evidence for the existence of small crystalline domains of approximately 5 to 10 nm, so that the particle growth seems to be controlled by the aggregation of primary nuclei (Figure 1). The sizes of crystalline domains were calculated with the Scherrer Formula. The TEM picture clearly showed the rough surface of a zirconia

particle and supports the aggregation growth mechanism for the formation of our colloids (Figure 6). The same growth mechanism was found for the titanium dioxide particles synthesised by a hydrolysis process with titanium alkoxide in ethanol.^[8] Bogush and Zukowski proposed nucleation followed by aggregation as a model that would confer monodispersity of precipitates.^[9] The model is based on the premise that nucleation proceeds for a substantial fraction of the reaction period and that nuclei, as well as small clusters of nuclei, aggregate faster with large particles than they do with each other. Mizutani et al.^[5] also described the aggregation model as the best suitable model for the growth of zirconia particles. They specified that the primary particles are formed by the hydrolysis of alkoxides during the induction time. In the second step, these particles aggregate to form larger particles. The growth can be followed by light scattering and hence reduction of light intensity transmitting through the solution, according to the Tyndall phenomenon. Kato et al.^[2,6] investigated the initial growth step of zirconia particles. They observed the growth of nuclei to primary particles of about 10–20 nm by electron microscopy. In the next step, the aggregation to larger particles proceeded because of excess surface energy because of a small radius. Furthermore, they assumed that residual primary particles do not form secondary particles but promote the growth of the spheres. The aggregation mechanism was also described by Sada et al.^[3] to be best suitable for the growth of zirconia particles. These authors summarised, according to the reaction kinetics, that if the reaction is very slow, the particle growth takes place through polycondensation of nuclei on the particle surface. In fast reactions, an aggregation process of nuclei grown to primary particles takes place. The clarification of the formation mechanism of hydroxide particles is not trivial, inter alia due to the amorphous state of the precipitated solids. On the basis of

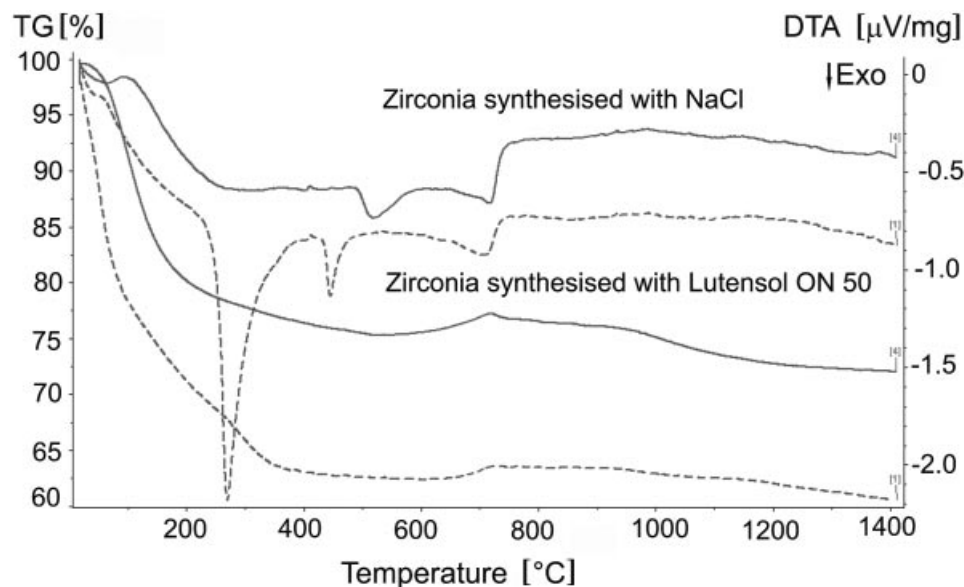


Figure 4. Thermal analysis of zirconia particles synthesised with addition of polymer molecules and with addition of salt ions.

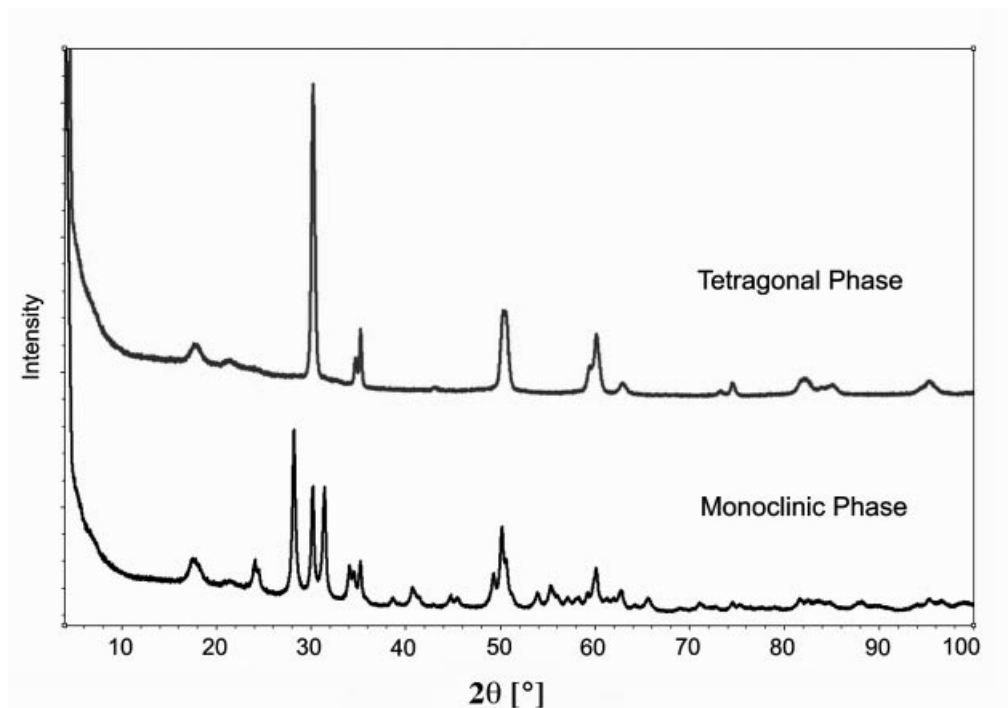


Figure 5. X-ray diffraction patterns of crystalline zirconia particles.

our results and on the literature, we assumed that the aggregation model describes the formation of our zirconia particles very well.

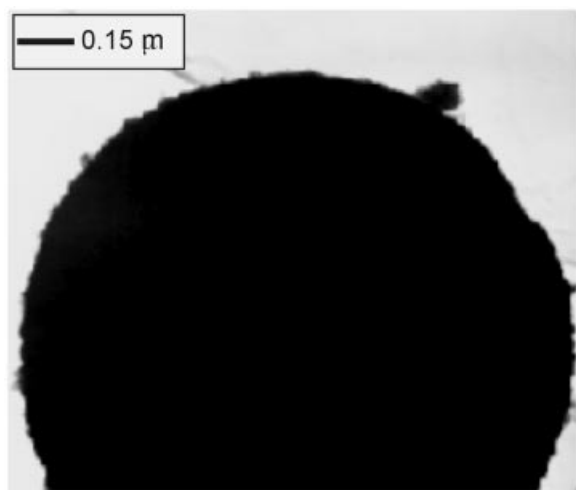


Figure 6. TEM picture illustrating the rough surface of a zirconia particle.

Silica-Coated Zirconia Particles

The surface properties of zirconia particles were controlled by coating with a silica layer. This was achieved by hydrolysis and condensation of TEOS in an ethanol/water/ammonia mixture. In the presence of ammonia as catalyst,

the TEOS molecules were able to form bonds with the hydroxide groups of zirconia (Figure 7). The thermal and elementary analyses provided evidence for the existence of hydroxide groups and water at the particle surface. The total formula of zirconia particles was specified as $\text{ZrO}_x \cdot (\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$. The coat was formed according to the silica particle synthesis developed by Stöber et al.^[11] Large zirconia spheres coated with fluorescent silica were visible in the CSLM. Therefore, fluorescein (APS-FITC) was added to the reaction solution. The dye molecules were incorporated into the shell. Figure 8 shows zirconia particles coated with a 50-nm thick shell of silica and APS-FITC in a one-step seeded growth process.

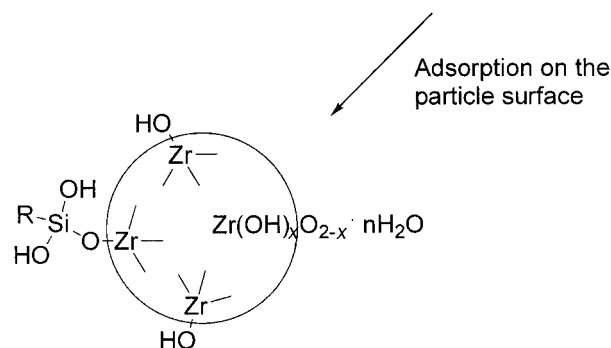
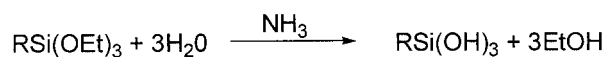


Figure 7. Coating of zirconia particles with TEOS.

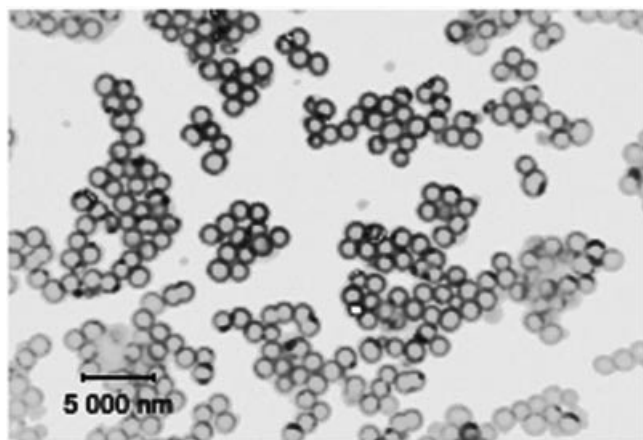


Figure 8. Confocal scanning laser micrograph of 1400 nm big zirconia particles coated with TEOS and fluorescein isothiocyanate acting as dye. The shell thickness is about 50 nm.

Conclusions

The controlled hydrolysis of alkoxides is a simple and powerful method to synthesise particles with well-defined sizes and narrow size distributions. Monodisperse, spherical ZrO_2 particles with sizes between 100 and 2000 nm were synthesised by hydrolysis. The size of the particles decreased with increasing reaction rate or with rising reaction temperature. Smaller particles were obtained with higher water concentration and larger particles with higher concentrations of zirconium butoxide. In contrast to the preparation of TiO_2 particles, in which salt ions and surfactant molecules were able to control the size of the particles and the porosity, the influence of such additives on the final zirconia particles is low. The surface properties of the zirconia particles were controlled by coating with a silica layer. The as-prepared powders were amorphous; a transition to crystalline forms was possible. The phase transition to the tetragonal phase occurred at about 450 °C, while the transition to the monoclinic phase began at 600 °C and was complete at about 800 °C.

Experimental Section

Materials: All reagents and solvents were used as received without further purification. Ethanol p.a., 1-propanol p.a., 1-butanol p.a. and alkali halide salts were purchased from Roth, zirconium alkoxides from Aldrich. Fluorescein isothiocyanate (FITC, isomer I) was purchased from Fluka, (3-aminopropyl)-triethoxysilane (APS) from Aldrich. Lutensol ON 50 and Pluronic PE 6400 were donated by BASF.

Synthesis of Zirconia Particles: In the synthesis of zirconia particles ethanol, 1-propanol and 1-butanol were used as solvents. Zirconium alkoxides like zirconium tetraethoxide, tetrapropoxide and tetrabutoxide were tested as precursors. Monodisperse spherical zirconia particles were synthesised by controlled hydrolysis of zirconium tetrabutoxide (80% solution in butanol) in ethanol. An ethanol volume of 100 mL was mixed with 0.2–0.6 mL of Millipore

water, aqueous salt or polymer solution, followed by the addition of 3.25–5.00 mL zirconium tetrabutoxide at 60 °C under inert gas atmosphere, using a magnetic stirrer. Reagents had to be mixed completely, so that nucleation occurred uniformly throughout the solution. Depending on the concentration, visible particle formation started after several seconds or minutes and gave a uniform suspension of ZrO_2 beads. After 4 h, the reaction was finished, and the spheres were collected on a Millipore filter and washed with ethanol, or separated by centrifugation.

Coating of Zirconia Particles with Silica: A silica shell was formed around the zirconia particles by the following process: An aqueous ammonia solution (0.18 mL of a 25% solution) was added to a suspension of zirconia particles (100 mg) in ethanol (10 mL) whilst stirring. Subsequently, TEOS (0.2 mL) was added. To make the particles visible for CSLM, APS-FITC (0.01 mL) was added to the reaction solution. The reaction solution was stirred for 24 h, and the resulting particles were separated by filtration.

APS-FITC was synthesised in the following way: The dye FITC was covalently attached to the coupling agent APS by an addition reaction of the amine group with the thioisocyanate group. The reactants were slowly stirred for 12 h in ethanol, water was excluded to prevent hydrolysis and polymerisation of the APS molecules. 1 mL of ethanol p.a. was used per 0.1 g of APS.^[7]

Characterisation of Zirconia Particles: The water content of the ZrO_2 beads was determined thermogravimetrically using a Netzsch-thermoanalyser STA 429 (under O_2 , heating rate 10 K/min), combining thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA). The crystallinity and phase-purity of the products were monitored by powder X-ray diffraction (XRD) using a Guinier-Huber camera 600 with $\text{Cu-K}_{\alpha 1}$ radiation. Scanning electron micrographs (SEM) were obtained with a Philips raster electron microscope (XL Series). Confocal scanning laser micrographs (CSLM) were obtained with a Zeiss Axiovert 200 with a Yokogawa confocal scanner. Electrophoretic mobility was measured with a Brookhaven Zetasizer. Particles were centrifuged out of suspension, and a small fraction of sedimented particles was resuspended in the supernatant again for use in mobility determinations. Nitrogen absorption isotherms were measured at 77 K with a Quantachrome Nova 3000 with samples which were degassed at 475 K and 1 mPa for 12 h.

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