

Synthesis and characterisation of porous and non-porous monodisperse TiO₂ and ZrO₂ particles

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Abstract

Monodisperse spherical titania and zirconia particles of variable sizes are produced in a sol-gel synthesis from metal tetraalkoxides in alcohol with addition of a salt or a polymer solution. The influence of various precursor concentrations and the addition of different salt ions or polymer molecules on the size and on the size distribution of the final particles was investigated. The particles were characterised by electron microscopy, thermogravimetry, X-ray diffraction and electrophoresis. Nitrogen absorption measurements revealed that in the case of titania the addition of polymers yielded porous titania colloids.

Keywords: Sol-gel; Titania; Zirconia; Particles; Monodisperse

1. Introduction

Mesoscale spheres of metal oxide particles, like titania and zirconia particles, are of particular interest for applications as ceramics [1–7]. To advance the sintering kinetics, i.e. to obtain shorter sintering times and lower sintering temperatures, the elimination of agglomerates and the control of the particle size distribution is required. Controlled hydrolysis of metal alkoxides seems to be a promising method to obtain particles with well-defined sinter properties during the powder synthesis. Titania and zirconia particles have been widely used as high performance ceramics, catalysts or in cosmetics since several years [8]. New applications for zirconia powders are high temperature fuel cells, lambda probes or bioceramics like dental prostheses [9]. Titania particles are particularly interesting for optical applications, due to their high refractive index [10,11].

The goal of our research was the development of a controlled and reproducible synthesis of monodisperse titania and zirconia particles. We investigated the influence of various ions and polymers, and different ratios of precursor molecules on the synthesis of titania and zirconia particles. In order to change the surface properties of the particles and to make the particles visible for confocal scanning laser microscopy (CSLM), they were coated with silanes, and dye molecules.

2. Experimental

2.1. Synthesis of titania particles

Monodisperse spherical TiO₂ particles were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol [12]. An ethanol volume of 100 ml was mixed with 0.4–0.6 ml of aqueous salt or polymer solution, followed by addition of 1.7–2.0 ml titanium tetraethoxide at ambient temperature under inert gas atmosphere, and under stirring. 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 dispersion of TiO₂ beads. After a few minutes stirring was discontinued. After a period of two hours the reaction was finished and the spheres were collected on a Millipore filter and washed with ethanol.

2.2. Synthesis of zirconia particles

Ethanol, 1-propanol and 1-butanol were used as solvents in the synthesis of zirconia particles. Zirconium alkoxides like zirconium tetraethoxide, tetrapropoxide and tetrabutoxide were tested as precursors. Monodisperse spherical zirconia particles could be synthesised by a 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

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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 ZrO₂ 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.

2.3. Coating of titania and zirconia particles with silica

A silica shell was formed around the titania and zirconia particles by the following process: an ammonia solution (0.18 ml of a 25% NH₃ solution) was added to a suspension of titania or zirconia particles (100 mg) in ethanol (10 ml) under stirring. Subsequently, 0.2 ml of TEOS was added. To make the particles visible for CSLM 0.01 ml of APS-FITC (3-aminopropyltriethoxysilane fluorescein isothiocyanate) was added to the reaction solution. The reaction solution was stirred for 24 h. 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 [13]. The reactants were slowly stirred for 12 h in ethanol, water was excluded to prevent hydrolysis and condensation of the APS molecules. 1 ml of ethanol p.a. was used per 0.1 g of APS.

2.4. Methods of characterisation

The water content of the TiO₂ and ZrO₂ beads was determined thermogravimetrically using a Netzsch-thermoanalyzer STA 429 (O₂ atmosphere, 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 Cu K α ₁ radiation.

Scanning electron micrographs (SEM) were obtained on a Philips raster electron microscope (XL Series). Confocal scanning laser micrographs (CSLM) were obtained on a Zeiss Axiovert 200 with a Yokogawa confocal scanner.

Electrophoretic mobility was measured on a Zetasizer (Brookhaven). 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 on a Quantachrome Nova 3000. The samples were degassed at 475 K and 1 mPa for 12 h.

3. Results and discussion: titania particles

Titania particles with narrow size distribution were obtained in a precipitation reaction starting from titanium tetraethoxide and water in an ethanol solution. Depending on the reaction conditions, particles in the range between 500 and 3000 nm were obtained.

X-ray powder diffraction patterns showed that the as-synthesised TiO₂ particles were amorphous. DTA measurements show three peaks, the first one at about 250 °C and the second one at 450 °C corresponded to the release of water while the third one at 480 °C indicates a phase transition to anatase. For the phase transition to rutile no DTA peak could be observed, since this phase transition extended from 600 to 1000 °C.

3.1. The addition of salt

The concentration of all reactants was varied. 100 ml ethanol, 1.70 ml Ti(OC₂H₅)₄, 0.40 ml of 0.1 M aqueous salt or polymer solution were found to be optimal. Variations in the concentration of ethanol, water or Ti(OC₂H₅)₄ showed no significant effect on the size of the particles but on the size distribution. The size and the size distribution were very sensitive to the type of salt that was added (Table 1).

With alkali halides, we observed that the particle size decreased with increasing ionic strength in the reaction solution. Beads with diameters of about 2500 nm were obtained with lithium chloride, whereas the use of cesium chloride yielded 200 nm particles. No size changes were obtained when the halide anions were changed; approximately the same results were obtained for alkali bromides and iodides.

The electrophoresis results (Table 1) exhibited that an increased positive zeta potential led to a reduction in particle size. With very high ionic strength, i.e. with high salt concentration, no particle formation was observed. Probably, in this case the ions bind most of the water molecules in the hydration shell, so that not enough water molecules exist for the generation of titania.

Bogush and Zukoski likewise reported that changes in the ionic strength affect the formation of titania particles [14–16]. They described the growth mechanism of particles in an aggregation model, which implies that the colloidal particles are formed by aggregation of small particles with a size of 5–20 nm (primary particles). They suggested, furthermore, that the formation of primary particles proceeds independently of the existing particles and that the absolute size of the final particles is determined by the size and the aggregation tendencies of the primary particles.

Table 1
Sizes and zeta potentials of titania particles depending on the addition of different salt solutions under following conditions

Salt	Salt concentration in the reaction solution (M)	Particle size (nm)	Zeta potential (mV)
LiCl	4×10^{-4}	700–2500	9
NaCl	4×10^{-4}	800 \pm 7%	16
KCl	2×10^{-4}	500–900	20
KCl	4×10^{-4}	300 \pm 5%	22
KCl	8×10^{-4}	50 \pm 20%	27
KCl	16×10^{-4}	No particles	
CsCl	4×10^{-4}	200 \pm 20%	25

Reaction time: 120 min; 100 ml EtOH, 1.70 ml Ti(OEt)₄, 0.40 ml of 0.1 M salt solution.

Table 2
Size of titania particles depending on the addition of different polymer solution under following conditions

Polymer	Formula	Particle size (nm)
Lutensol ON 50	$\text{RO}(\text{CH}_2\text{CH}_2\text{O})_5\text{H}$ $R < \text{C}_8\text{H}_{17}$, fatty alcohol	$1000 \pm 3\%$
Lutensol AN 7	$\text{RO}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ $R = \text{C}_{12}\text{C}_{14}$, fatty alcohol	$900 \pm 5\%$
Lutensol AT 11	$\text{RO}(\text{CH}_2\text{CH}_2\text{O})_{11}\text{H}$ $R = \text{C}_{16}\text{C}_{18}$, fatty alcohol	$800 \pm 5\%$
PluronicPE4300	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_y(\text{CH}_2\text{CHO})_z\text{H}$ Molar mass: 1750 g/mol PPO=30%	$600 \pm 20\%$
Pluronic PE 6400	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_y(\text{CH}_2\text{CHO})_z\text{H}$ Molar mass: 2900 g/mol PPO=40%	600–1300

Reaction time: 120 min; 100 ml EtOH, 1.70 ml $\text{Ti}(\text{OEt})_4$, 0.40 ml of 0.1 M polymer solution.

Since the as-synthesized titania particles are amorphous, the size of the primary particles is difficult to determine. The AFM demonstrated that the surface of the final particles is rough: the height variation amounts to about 5 nm. This result indicates that the final particles consist of primary particles with a diameter of about 10 nm.

3.2. Addition of polymer

The influence of polymers (Table 2) on the size and size distribution of the colloidal particles was investigated in the next step. Two different types of polymers, diblock-copolymers Lutensol ($\text{RO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$) and triblock-copolymers Pluronic ($\text{PEO}_n\text{-PPO}_m\text{-PEO}_n$), were used for steric stabilisation. The polymers could stabilise the primary particles in different ways: The hydrophilic part of Lutensol interacts with the nanoparticle surface while the hydrophobic part extends into the medium providing additional steric stabilization. In case of Pluronic, the presence of two hydrophilic parts leads to a coating of the nanoparticle surfaces.

As shown in Fig. 1, highly monodisperse particles are obtained in the presence of Lutensol. The size of the colloids obtained increases with decreasing length of the hydrophobic part (Table 2), as expected from the increasing stabilisation of the primary particles by a surfactant with long hydrophobic chains. The length of the hydrophilic part, on the other hand, has no effect on the particle size. This part lies closely on the primary particle surface and causes no significant effect on particle stabilization. The stabilisation by Pluronic is not as effective as in the case of Lutensol. It results in a broad size distribution of the titania particles. The average size of the particles could be increased with increasing length of the Pluronic polymer.

In order to determine whether the polymer is built into the colloidal particles during the aggregation process, we carried out EDX measurements of the colloidal particles. They showed that these particles contained around 8% carbon. Therefore, we

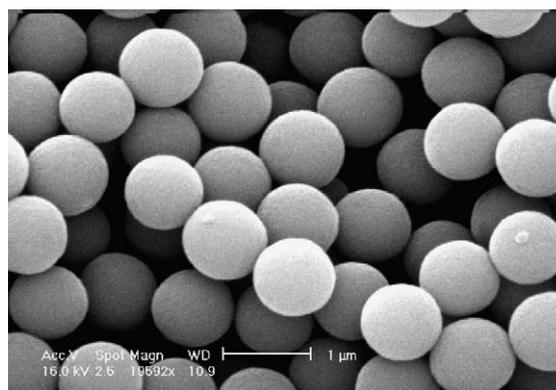


Fig. 1. SEM picture of the titania particles synthesised by addition of Lutensol.

assume that the polymer is built into the final particles during the aggregation process (Fig. 2). This aggregation model suggests that at the end of the reaction, the particles are porous and the porosity could be controlled by the polymer type. Nitrogen absorption measurements showed that the specific surface area (a_s), determined by the Brunauer–Emmett–Teller method, increased when the polymer is added to the reaction medium. Lutensol ON 50 yielded the largest porosity with $a_s = 300 \text{ m}^2/\text{g}$, presumably, because it requires the largest space around the particles and prevents the formation of compact particles. In contrast, the Pluronic polymer caused the formation of more compact aggregates and a_s decreases to $200 \text{ m}^2/\text{g}$. As the electrostatically stabilised colloids are formed without polymer, no porosity is expected and, indeed, the surface area decreased to $35 \text{ m}^2/\text{g}$.

4. Results and discussion: zirconia particles

Zirconia particles with narrow size distribution were obtained in a precipitation reaction from zirconium alkoxide and water

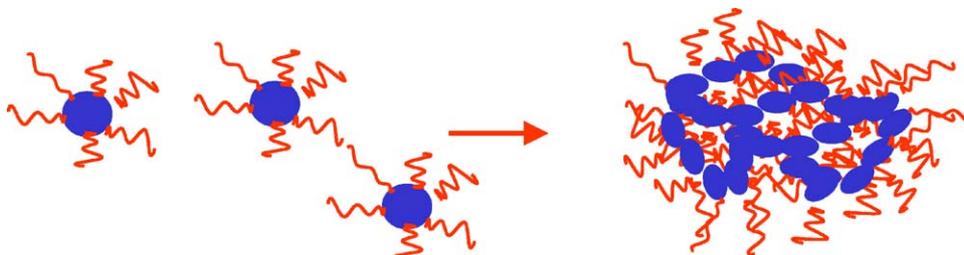


Fig. 2. Aggregation mechanism of sterically stabilised primary particles.

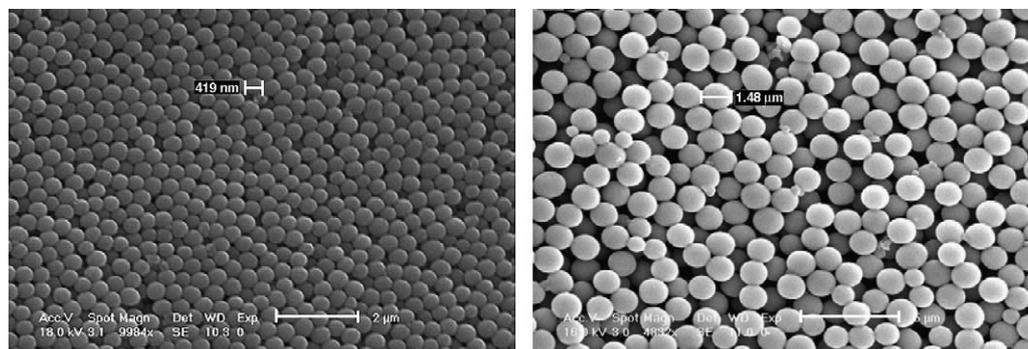


Fig. 3. Zirconia particles synthesised with 0.40 ml (l) and 0.20 ml (r) of 0.1 M NaCl solution, with addition of 3.25 ml Zr(OBu)₄ in 100 ml ethanol.

in an alcoholic solution. Depending on the reaction conditions, particles in the range between 200 and 2000 nm were obtained. The scanning electron micrographs reveal the perfectly uniform shape and high monodispersity of our particles (Fig. 3).

X-ray diffraction patterns show that the as-prepared ZrO₂ powders were amorphous and transformed into the tetragonal phase by heating to 450 °C for particles synthesised with polymers and to 510 °C for particles synthesised with addition of salts. The transition to the monoclinic phase (Baddeleyite) occurred between 600 and 800 °C, a shift to higher transition temperature was observed for zirconia particles prepared with addition of salt. High temperature X-ray diffraction patterns supports these results.

The DTA plot for ZrO₂ powders synthesised with salts showed a very broad exothermic peak from 30 to 360 °C due to dehydration. For samples synthesised with polymers a sharp exothermic peak, probable corresponding to the spontaneous thermal decomposition of untreated alkoxy groups, was observed. The bound water and untreated alkoxy groups were lost below 400 °C and amount up to 40%.

The zirconia particles are synthesised in a two steps process. During the first step, the hydrolysis, zirconium hydroxide molecules and primary particles are generated. In the second step the primary particles aggregate.

X-ray diffraction provided evidence for the existence of small crystalline domains of approx. 5–10 nm, so that the particle growth seems to be controlled by the aggregation of primary nuclei. The sizes of crystalline domains were calculated with the Scherrer formula. The same growth mechanism was found for the titanium dioxide particles synthesised in a hydrolysis process of titanium alkoxide in ethanol [12].

4.1. Variation of precursors and their concentrations

To obtain spherical and monodisperse zirconia particles, various zirconium alkoxides and alcohols as solvent were tested. In the range of zirconium ethoxide, propoxide and butoxide the best results were found for zirconium butoxide. Ethanol, 1-propanol and 1-butanol were tested as solvent, uniform and monodisperse particles in a wide range were obtained with ethanol. 1-Propanol and 1-butanol provide only narrow ranges,

where spherical and monodisperse particles were obtained. In the case of ethanol the induction time for the formation of particles optimally lay between 1 and 5 min. When the induction time was shorter than the optimum, hydrolysis occurs more quickly and the nuclei formed polydisperse aggregates. In the case of a prolonged induction period, the nucleus formation and particle growth could proceed simultaneously and polydisperse particles were formed [17]. 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 zirconium tetrabutoxide was found to be the best condition to obtain uniform 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 was, the faster the hydrolysis and smaller the obtained particles. For zirconia particles synthesised with NaCl the 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 like Lutensol ON 50 (Table 3).

Corresponding to 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 uncontrolled and became polydisperse. No precipitate was observed as the water amount was below 0.1 ml. The average size increased in dependence of the initial concentration of Zr(OBu)₄. The sizes

Table 3

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 ₂ O, mp (ml)	Particle size (nm)
0.20	No precipitation
0.40	1200 ± 10%
0.50	1000 ± 10%
0.60	900 ± 10%
0.80	600–800
1.00	400–600

Table 4

Sizes of zirconia particles synthesised with various amounts of zirconium butoxide with addition of 0.40 ml 0.1 M NaCl solution in 100 ml ethanol

Zr(OBu) ₄ 80% solution in BuOH (ml)	Particle size (nm)
1.25	300 ± 10%
2.50	450 ± 10%
3.25	550 ± 10%
2.75	700 ± 10%
4.25	1000 ± 10%
5.00	1200 ± 10%

of 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 (Table 4).

4.2. Variation of salts and polymers

The stability of a dispersion depends on the magnitude of the electric charge of the particles. Oxide surfaces in an aqueous medium are generally positively charged under acidic and, negatively charged 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. No significant differences were observed for particles prepared with various salts. 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 size and the size distribution were very sensitive to the type of salt that was added [12]. The influence of alkali halides on the particles was not as strong as in the case of titania. However, the smallest particles were obtained by the addition of CsCl, the largest with LiCl (Table 5). The particle sizes synthesised with pure Millipore water, ranged between 300 and 1400 nm. We assume, that the interactions between the zirconium alkoxide, hydroxide and dioxide molecules and salt ions are much weaker than those between titanium compounds and the salt ions.

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-copolymers Lutensol (RO(CH₂CH₂O)_xH) and triblock-copolymers Pluronic (PEO_n-PPO_m-PEO_n), were used for steric stabilization. Depending on the amount of water and zirconium tetrabutoxide, it was possible to obtain particles up to 1200 nm with Lutensol ON 50 and up to 2000 nm with Pluronic PE 6400. The hydrophilic part of Lutensol is likely to interact with the nanoparticle surface while the hydrophobic part extends into the medium thus providing additional steric stabilization. In case of Pluronic, 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. It results in a broader size distribution of the titania particles. The same effect, however not as strongly pronounced, was observed for zirconia particles. The monodispersity of zirconia particles synthesised with Lutensol ON 50 was higher, than of particles prepared with Pluronic PE 6400.

In order to determine whether the polymer molecules were built into the colloidal particles during the aggregation process, we carried out elemental analysis of as-synthesised zirconia powders. Elemental analysis showed values under 2% for carbon, 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 porous titania particles with specific surface area of to $a_s = 300 \text{ m}^2/\text{g}$ in average, determined by the Brunauer–Emmett–Teller method. For zirconia particles the values for the specific surface area were always below $10 \text{ m}^2/\text{g}$. The interactions between zirconium compounds and polymer molecules are too weak to prevent a compact aggregation of the primary particles.

The interactions between zirconium compounds and polymer molecules are too weak to prevent a compact aggregation of the primary particles.

4.3. Silica coated titania and zirconia particles

The surface properties of titania and zirconia particles could be controlled by coating with a silica layer. This was achieved by hydrolysis and condensation of TEOS in an ethanol–water–ammonia mixture. The TEOS molecules were able, in the presence of ammonia, to form bonds with the hydroxide groups of titania and zirconia. Large spheres coated with fluorescent silica were visible in the CSLM, therefore fluores

Table 5

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 ± 10%
KCl	350 ± 10%
NaCl	550 ± 10%
LiCl	700 ± 10%
–	1000 ± 10%
Lutensol ON 50	600 ± 15%
Pluronic PE 6400	2000 ± 15%

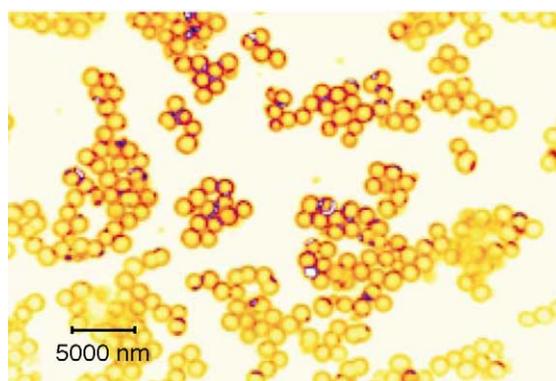


Fig. 4. Confocal scanning laser micrograph of 1400 nm big zirconia particles coated with TEOS and fluorescein isothiocyanate acting as dye. The shell thickness amounts about 100 nm.

cein (APS-FITC) was added to the reaction solution. The dye molecules were incorporated into the shell. Depending on the TEOS amount the shell thickness could be varied. Fig. 4 shows zirconia particles coated with a 100 nm thick shell of silica and APS-FITC in a one-step seeded growth process.

5. Conclusion

The controlled hydrolysis of alkoxides is a simple and powerful method to synthesise titania and zirconia particles with well-defined sizes and with narrow size distribution.

We have shown that size, porosity and monodispersity of colloidal titania particles can be controlled by careful choice of surfactants and of salts added during the synthesis. We obtained particles with narrow size distribution from 50 to 2500 nm in diameter of variable porosity. In particular, we have synthesized very monodisperse titania particles with diameters of 800 and 1000 nm in a reproducible way by using the diblock-copolymer Lutensol. This opens up the possibility to use titania particles in photonic applications.

In contrast to the preparation of TiO_2 particles, where salt ions and surfactant molecules were able to control the particle sizes and the porosity, the influence of such additives on fine zirconia particles is low. The particles' sizes of zirconia could be controlled by variation of the precursors' concentration. Monodisperse, spherical ZrO_2 particles with sizes in the range between 100 and 2000 nm were obtained. The surface properties of titania and zirconia particles could be controlled by coating with a silica layer.

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