Preparation of ZrO_2 fine particles by CVD process: Thermal decomposition of zirconium *tert*-butoxide vapor

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Zirconia powder has many applications: wear parts, engine and machine components, mill media, refractory materials, ceramic pigments, fuel cells, lasers, and capacitors [1]. The particles of the powders have been produced and studied by various techniques such as sol/gel [2], pyrolysis [3, 4], and spray pyrolysis [5, 6]. The most frequently used sol/gel technique is concentrated on the commercial production of micron-sized zirconia powders. Demands for an ideal zirconia powder are high purity, large surface area, and monodisperse and nonagglomerated particles. For zirconia particle generation the metal salts, chlorides, and alkoxides have been used as precursors. A widely used and investigated precursor material for the pyrolysis is zirconium *tert*-butoxide (ZTBO) [3, 4]. This precursor has been used to produce zirconia particles by pyrolysis at high temperatures [3] and it can also be used to produce particles by hydrothermal reactions [7]. In this work we have studied zirconia particle production in the moderate temperature range (400–500 °C) by pyrolysis and hydrolysis of ZTBO in a tube flow reactor.

The tube flow reactor technique has been described in previous studies for titania, alumina and silica particle production [8–10]. The experiments were carried out using the apparatus shown in Fig. 1. Particles were prepared in an externally heated tube flow reactor of

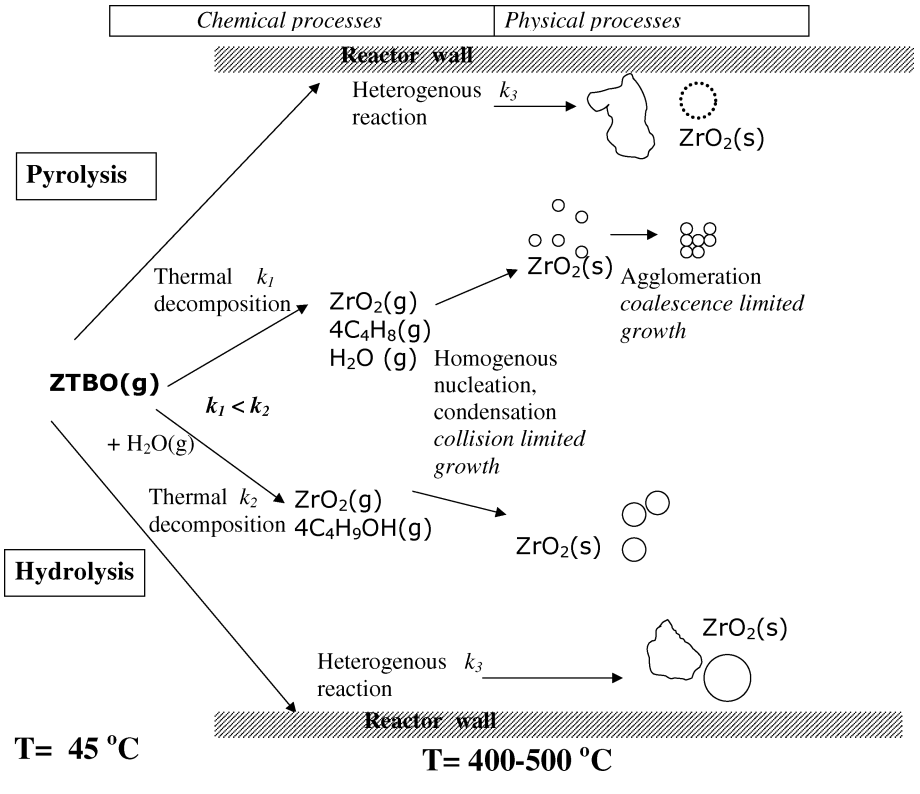

Figure 1 Scheme of the apparatus. (1) deoxidizer, (2) dryer, (3) electrostatic precipitator, (D) diluter, (F) filter, (H) humidity sensor, (M) electronic mass flowmeter, (P) pressure reducing valve, (S) saturator, (TC) temperature controller.

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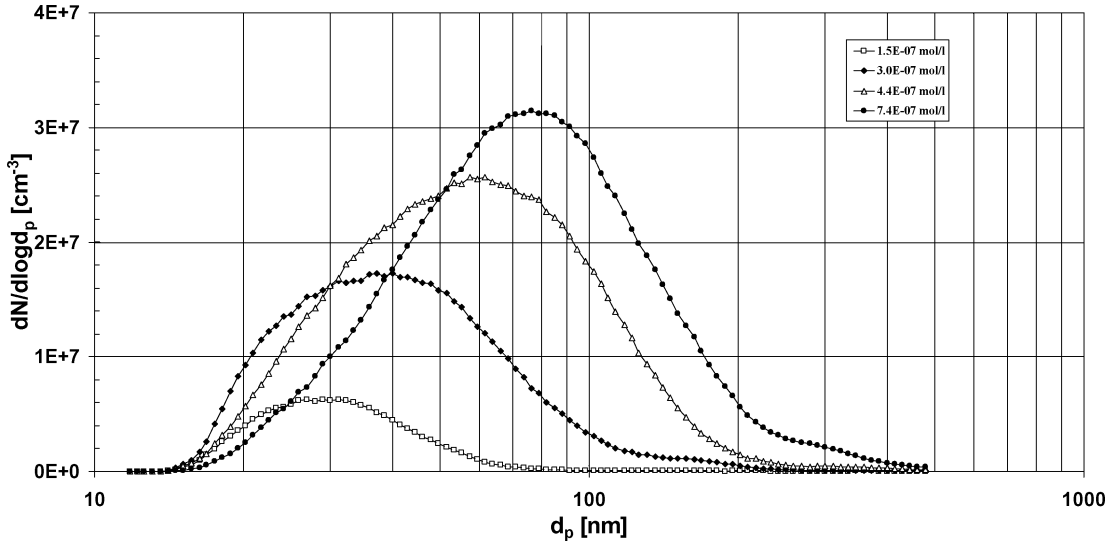

Figure 2 Influence of the ZTBO concentration (c_{ZTBO}) on the particle size distributions for the particles prepared by pyrolysis at $T_R = 500\,^{\circ}C$ and $Q_R = 600$ ml/min.

length 55 cm inside diameter 27 mm. The dry and particle-free nitrogen, used as carrier gas, was saturated by ZTBO vapor in an externally heated saturator. Saturator temperature was fixed to 45 °C. Precursor concentration in the reactor was controlled by the flow rate through the saturator. Saturated carrier gas was diluted by another stream of nitrogen and fed axially into the center of the reactor through an inlet section nozzle ($L = 250$ mm, $D_I = 17$ mm) surrounded by a coaxial stream of nitrogen. For hydrothermal reaction the stream of diluting nitrogen was saturated by water vapor at laboratory temperature. At the reactor outlet the stream of aerosol was cooled and diluted by another stream of nitrogen. The dilution ratio was kept at 1/2. Samples of particles were collected by point-to-plate electrostatic precipitator onto carbon coated Cu grids.

Particle size distribution was measured by scanning mobility particle sizer (SMPS, TSI model 3934C, or TSI model 3936L). Particle morphology was analyzed by scanning/transmission electron microscopy (SEM/TEM, JEOL-2000FX or JEOL 2010), composition by energy dispersive spectroscopy (EDS, Noran Vantage), and crystallinity by selected area electron diffraction (SAED).

Both the pyrolysis and hydrolysis of ZTBO were studied. Dependence of particle production on precursor concentration (c_{ZTBO}) and reactor temperature (T_R) was studied. The reactor flow (Q_R) in our experiments was 600 ml/min. The central flow (Q_{CF}), which goes through the inlet section nozzle, was defined as part of the reactor flow (Q_R in volume %) and it was 60%.

The influence of the ZTBO concentration (c_{ZTBO}) on the particle size distributions in the case of pyrolysis was tested at reactor temperature 500 °C, as shown in Fig. 2. Both the number concentration and mean particle size increase with increasing ZTBO concentration. The mean particle size increases from 20 nm at c_{ZTBO} 1.5×10^{-7} mol/l, to 40 nm at c_{ZTBO} 3.0×10^{-7} mol/l, 55 nm at c_{ZTBO} 4.4×10^{-7} mol/l, and 75 nm at c_{ZTBO} 7.4×10^{-7} mol/l.

The particles produced by pyrolysis have various morphologies. In Fig. 3, the particles produced at c_{ZTBO} 4.4×10^{-7} mol/l and reactor temperature 400 °C are shown. At 500 °C the morphology scheme was the same (Fig. 4). There were very large nonspherical particles (<500 nm), darker spherical particles (<100 nm), and agglomerates of very small primary particles (∼15 nm), see Figs 3 and 4. Comparing the particle size measurements by SMPS and those from TEM photos (Fig. 4) we can conclude that the results of main mode of the SMPS distribution (Fig. 2) are the sizes of agglomerates of primary particles. The primary particle size evaluated from the TEM pictures varied in the range from 10 nm to 20 nm (Fig. 4).

Particle composition and crystallinity were studied at reactor temperatures 400 and 500 °C in the case of pyrolysis. At 400 °C SAED showed that the small spherical primary particles and the nonspherical large particles consist of face centered cubic (FCC) ZrO_2 (Fig. 3). The result of EDS analysis in both cases indicated the Zr/O ratio of 1/2. However, the circled spherical black particle consists of Zr/O in ratio 1/1 (EDS). Also the electron diffraction pattern indicated FCC ZrO as shown in Fig. 3. At 500 °C all EDS analyses gave the Zr/O ratio 1/2 and also all obtained electron diffraction patterns indicated FCC ZrO_2. Electron diffraction patterns of small particles were rather weak, see Fig. 4, which signalizes that small particles were crystalline only partially. The influence of reactor temperature on particle size distributions has also been studied at temperatures 400 °C and 500 °C. The particle size and number concentration decreased when temperature increased as shown in Fig. 5.

In the case of hydrolysis the stream of diluting nitrogen at the reactor inlet was saturated by water vapor at laboratory temperature. The mean particle size measured by SMPS was now at about 50 nm at c_{ZTBO} 4.4×10^{-7} mol/l and reactor temperature 500 °C, which compares with primary particle size from the TEM photo (Fig. 6). The measured particle size by SMPS was observed now to be the primary particle size and not the

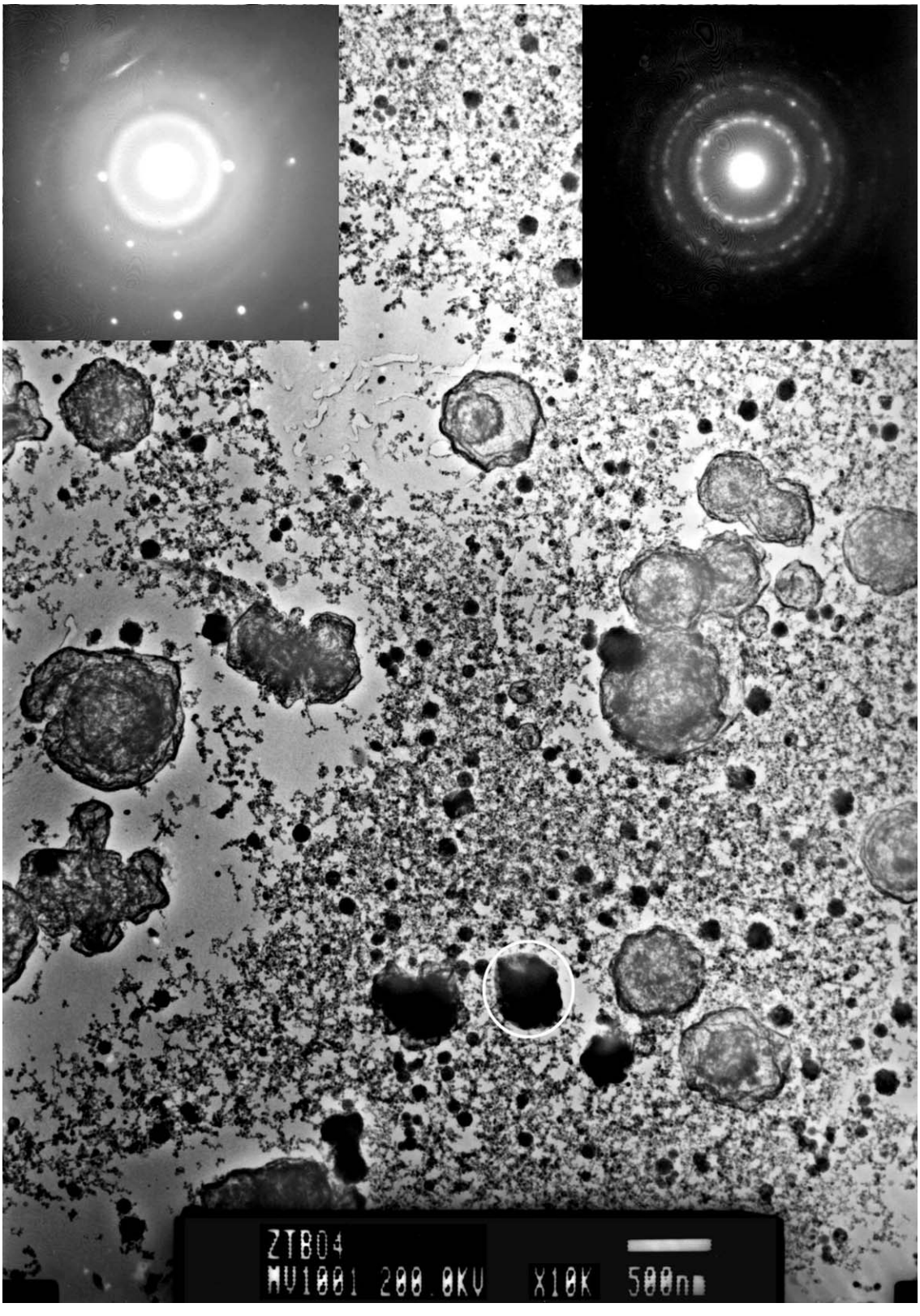

Figure 3 TEM photo (BF) and diffraction patterns of the sample of zirconia particles prepared by pyrolysis at $T_R = 400\,^{\circ}C$, $c_{ZTBO} = 4.4 \times 10^{-7}$ mol/l and $Q_R = 600$ ml/min. Left side diffraction pattern is from circled particle and right side from primary sized particles.

agglomerate size as in the case of pyrolysis. The total number concentration of the particles was much lower than in the case of pyrolysis. The particles have also manifold morphology as shown in Fig. 6. There were large nonspherical and spherical particles and also small spherical ones. These small particles were not as agglomerated as in the case of pyrolysis. The electron diffraction patterns of particles from hydrolysis at 500 °C are also shown in Fig. 6. The larger spherical and nonspherical particles were clearly FCC ZrO_2. The pattern of small particles was not so obvious but there were still some dots to prove some amount of crystalline phase. Zr/O ratio from EDS analysis for all particles in Fig. 6 was 1/2. The influence of reactor temperature on particle size distributions is shown in Fig. 7. Also in the case of hydrolysis the particle size is lower at higher

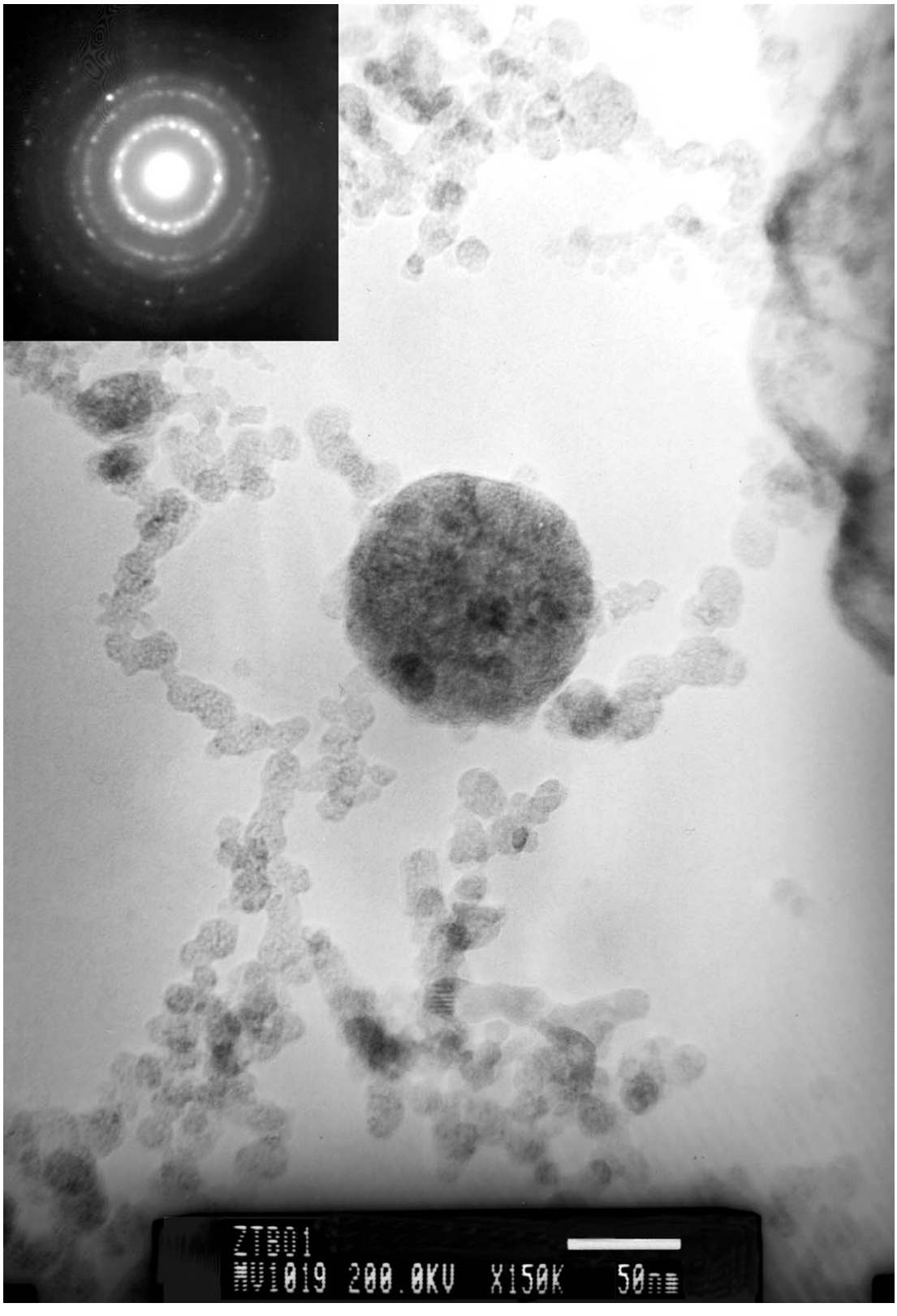

Figure 4 TEM photo (BF) and diffraction pattern of the sample of zirconia particles prepared by pyrolysis at $T_R = 500\,^{\circ}C$, $c_{ZTBO} = 4.4 \times 10^{-7}$ mol/l and $Q_R = 600$ ml/min.

temperature while number concentration is almost the same at both temperatures.

The particle growth with increasing precursor concentration is an expected result [3, 8–10, 12]. The particle formation mechanisms in tube flow reactor are illustrated in Fig. 8. The particle formation mechanism is closely connected to the chemical reaction rate. In the case of hydrolysis, the reaction rate (k_2 in Fig. 8) is supposed to be faster than for pyrolysis (k_1) [7], and particles grow to larger sizes. Small spherical particles are the result of homogenous reaction in the gas phase as was observed also in the study of Adachi *et al.* for zirconia particle synthesis [3]. In the case of pyrolysis, the particle growth mechanism seems to be collision limited (formation of small particles from 10 to 20 nm) and after that the formation of agglomerates seems to

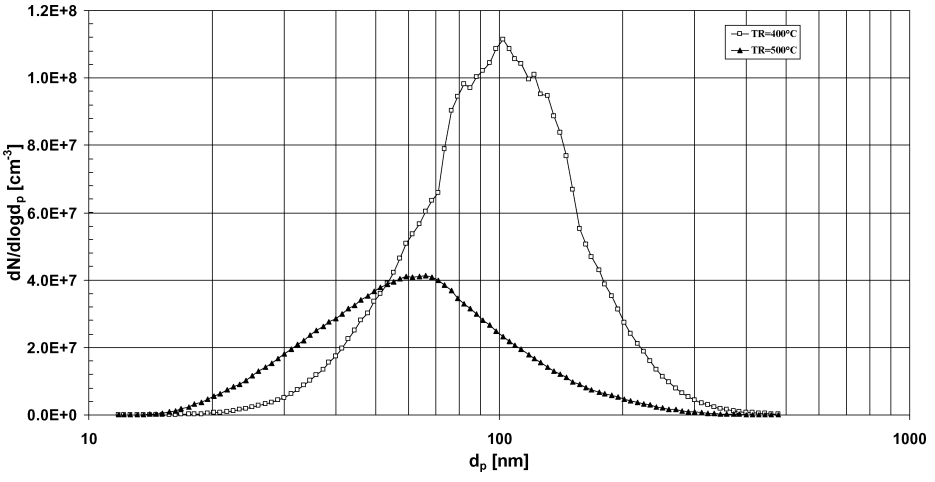

Figure 5 Influence of the reactor temperature (T_R) on the particle size distributions for the particles prepared by pyrolysis at $c_{ZTBO} = 4.4 \times 10^{-7}$ mol/l and $Q_R = 600$ ml/min.

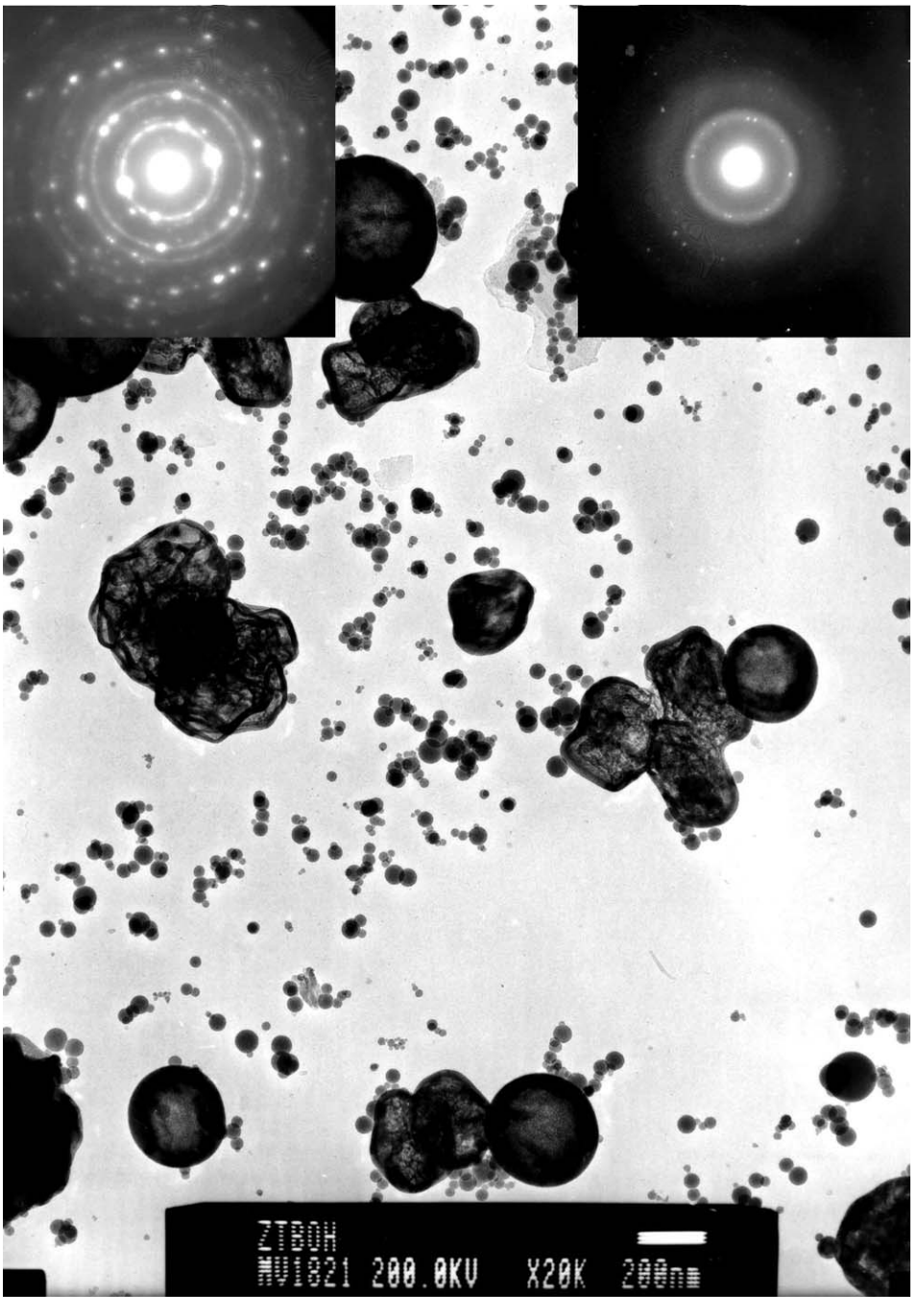

Figure 6 TEM photo (BF) and diffraction patterns of the sample of zirconia particles prepared by hydrolysis at $T_R = 500\,^{\circ}$C, $c_{ZTBO} = 4.4 \times 10^{-7}$ mol/l and $Q_R = 600$ ml/min. Left side diffraction pattern is from large spherical particle and right side from primary particles.

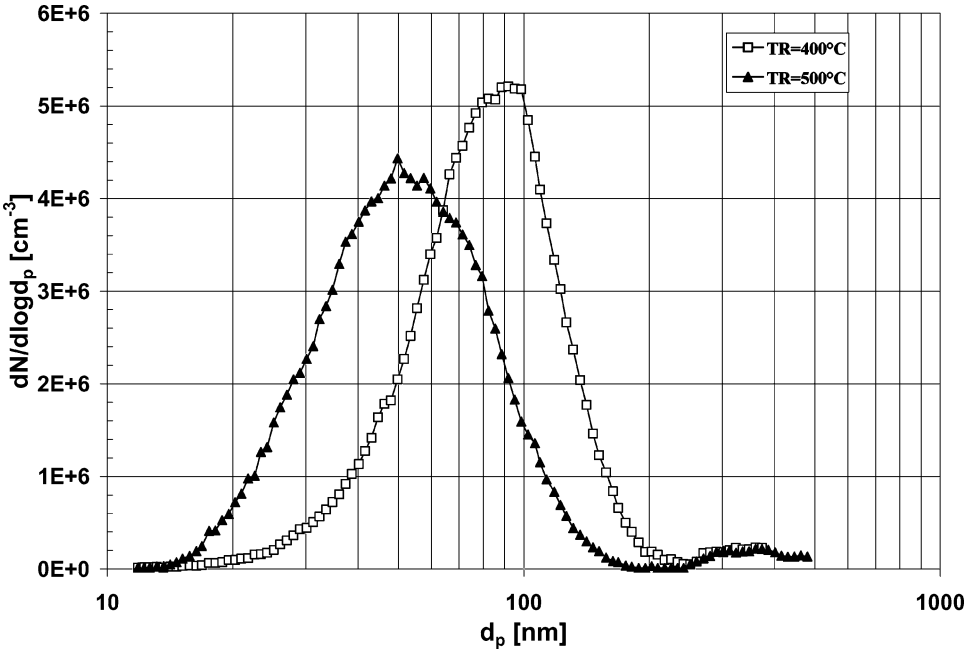

Figure 7 Influence of the reactor temperature (T_R) on the particle size distributions for the particles prepared by hydrolysis at $c_{ZTBO} = 4.4 \times 10^{-7}$ mol/l and $Q_R = 600$ ml/min.

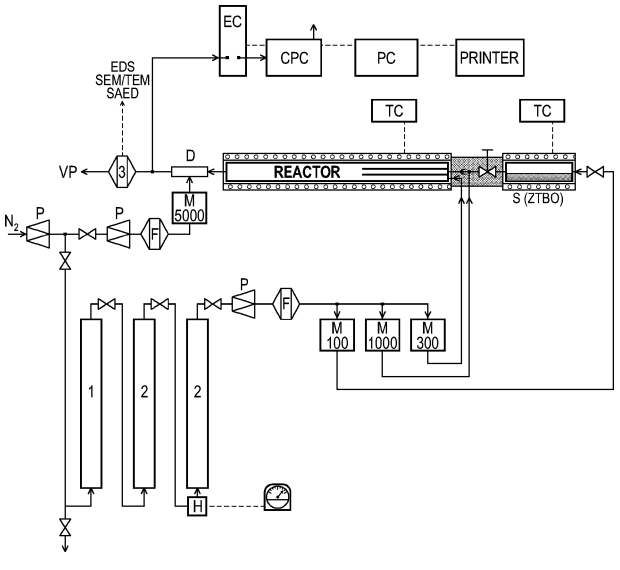

Figure 8 The assumed zirconia particle formation mechanism in tube flow reactor.

be limited by coalescence [12] as shown in Fig. 8. In the case of hydrolysis, particle growth could be mostly collision limited. The particle formation from gaseous zirconia to solid particles is very rapid. Therefore, the reaction rate (k_1, k_2) of the thermal decomposition is assumed to be the limiting step for the particle synthesis. Formation of large particles is supposed to be caused by heterogeneous reaction (Fig. 8) due to catalytic effect of the reactor glass surface on ZTBO decomposition [7]. Similar effect has been reported for the preparation of titania particles [8, 11]. Morphology of these large particles probably depends on the residence time in the hot zone of the reactor. Dense and nearly spherical particles are formed at sufficiently long residence time and irregularly shaped particles at shorter residence time. The crystallinity of particles has been reported to increase from amorphous to FCC ZrO_2 when temperature is increased [3]. In our study the strongest crystal structure marks are also observed at higher temperature 500 °C. Likewise, the decreasing particle size with increasing reactor temperature in the case of pyrolysis was reported by Adachi *et al.* [3].

In summary, the zirconia particles were prepared by pyrolysis and hydrolysis of ZTBO vapor in a tube flow reactor. The ZTBO concentration affects the primary and agglomerate particle size and also the number concentration of large particles. The particle morphology for pyrolysis is strongly different from that of hydrolysis. The limiting step for the particle synthesis is the thermal decomposition rate. The produced particles were mainly FCC ZrO_2,but at temperature 400 °C the presence of FCC ZrO was also confirmed. The reactor temperature has an influence both on particle size and crystal structure.

Acknowledgments

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