

Synthesis and crystallization of titanium dioxide in supercritical carbon dioxide (scCO₂)

A Kaleva¹, S Heinonen, J-P Nikkanen, E Levänen

¹Department of Materials Science, Tampere University of Technology, FIN-33101 Tampere, Finland

E-mail: aaretti.kaleva@tut.fi

Abstract. In this work, a simple and low-temperature method to synthesize titanium dioxide (TiO₂) particles with supercritical carbon dioxide is presented. The particles were synthesized by measuring 5 ml of tetra-n-butyl orthotitanate precursor to the supercritical chamber. The pressure was maintained at 15.0 MPa for all experiments. Reaction temperatures used were 50 °C or 70 °C. After reaching treatment parameters 10 ml of deionized water was introduced to the chamber with a co-solvent pump. A mixer was used inside the chamber to ensure proper mixing of water and precursor. Reaction times of 10, 60 and 300 min were used. Characterization of the particle crystal phase was determined by X-ray diffraction, differential scanning calorimetry and transmission electron microscopy. The specific surface areas were measured with nitrogen adsorption tests (BET). The results showed that the particles synthesized with reaction times of 10 and 60 min contained brookite as the crystalline phase. With longer reaction time of 300 min the phase shifted to anatase. In most experiments there was also significant amount of amorphous phase present. The specific surface areas varied between 274.3–566.6 m²/g.

1. Introduction

Titanium dioxide is a material which exhibits high photocatalytic activity. It is used for example in antibacterial, self-cleaning, solar cell, water and air purification applications. The photocatalytic activity of titanium dioxide is affected by its particle properties such as crystalline phase, crystallinity, particle size and specific surface area. Titanium dioxide has three phases in nature: rutile, anatase and brookite. Among the three polymorphs of titanium dioxide anatase has proved to be more effective in photocatalytic applications than rutile or brookite. However, the photocatalytic activity of brookite varies between studies. The main reason for this is the challenges in the synthesis of brookite leading to fluctuation in its characteristic properties. Brookite is often synthesized in high pressures via hydrothermal route since it is reported to be a high pressure phase.[1, 2]The conventional synthesis methods for photocatalytic titanium dioxide require relatively high temperatures[3]. These methods also include the use of different solvents and catalysts which can be harmful for human and environment.

Supercritical carbon dioxide route is a processing method which is used in combination with sol–gel method to produce nanoparticles and also in other chemical processes [4]. When pure substances are pressurized and heated above their critical point they transform into supercritical fluids (SCF). SCFs have liquid-like solvation power and gas-like diffusion. Supercritical carbon dioxide is the most used supercritical fluid due to its low critical point of 31.2 °C and 7.38 MPa [5]. It is a green synthesis method because it is rather inert, non-toxic and a low-temperature process. Moreover, carbon dioxide



can be recycled to prevent its release to the atmosphere. The reaction parameters, e.g., temperature and pressure, can be easily changed and accurately controlled to change the properties of supercritical fluids.[6]

In this work, titanium dioxide was synthesized by sol-gel method at low temperature using supercritical carbon dioxide as a solvent. The effect of reaction temperature and reaction time to the properties of the synthesized particles was then studied.

2. Experimental

2.1. Synthesis procedure

All experiments were done with supercritical carbon dioxide apparatus (Thar RESS 250) which consists of high-pressure pump, co-solvent pump, high-pressure vessel, heating systems and a mixer. Synthesis precursors used were carbon dioxide ($\geq 97\%$, AGA) tetra-n-butyl orthotitanate ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$, $\geq 97\%$, Sigma-Aldrich) and de-ionized water. The reaction pressure was 15.0 MPa in all experiments. Reaction temperatures were 50 °C or 70 °C and the reaction times were 10, 60 or 300 min. The synthesis procedure was started measuring 5 ml of tetra-n-butyl orthotitanate to the reaction vessel and increasing the temperature and pressure to the preferred values. After reaching the reaction parameters 10 ml of water was pumped to the vessel by using the co-solvent pump with 3 ml/min speed. The precursors were mixed throughout the whole process using a stirrer inside the chamber. The reaction time was measured when water was first introduced to the chamber to the start of depressurization of the vessel since the depressurization time was between 2–5 min. The samples were then dried in 60°C for 1 h.

2.2 Characterization methods

Morphological characterization and particle size calculations were performed using emission scanning electron microscope (FE-SEM, Zeiss ULTRAplus). The BET specific surface areas were measured with nitrogen gas adsorption apparatus (Coulter Omnisorp 100CX). The crystal structures of titanium dioxide samples were determined with a Panalytical Empyrean Multipurpose Diffractometer. The crystallite sizes were estimated from XRD patterns using a Scherrer formula. Relative crystallinity between the samples were analysed from differential scanning calorimetry measurements (Netzsch Phoenix DSC 204 F1) by heating the samples to 500 °C with a 5 °C/min heating rate. Crystallite size was determined also from transmission electron microscope (JEM-2010 JEOL) pictures.

3. Results and discussion

3.1. Morphology, particle size and specific surface area

The SEM figures of the synthesized samples are presented in figure 1. The particles were agglomerated and the particle morphology was spherical. The spherical shape is expected to form when the pumped water enters the chamber and forms emulsion with supercritical carbon dioxide since they are only slightly soluble with each other. The dissolved tetra-n-butyl orthotitanate starts to react on the surface of the water droplets by hydrolysis and condensation reactions[4]. These reactions finally result in solid titanium dioxide particles. Some of the particles appeared to join together into irregular shapes which can be seen clearly from figure 1F resulting when the emulsion droplets fuse together while the precursors are reacting.

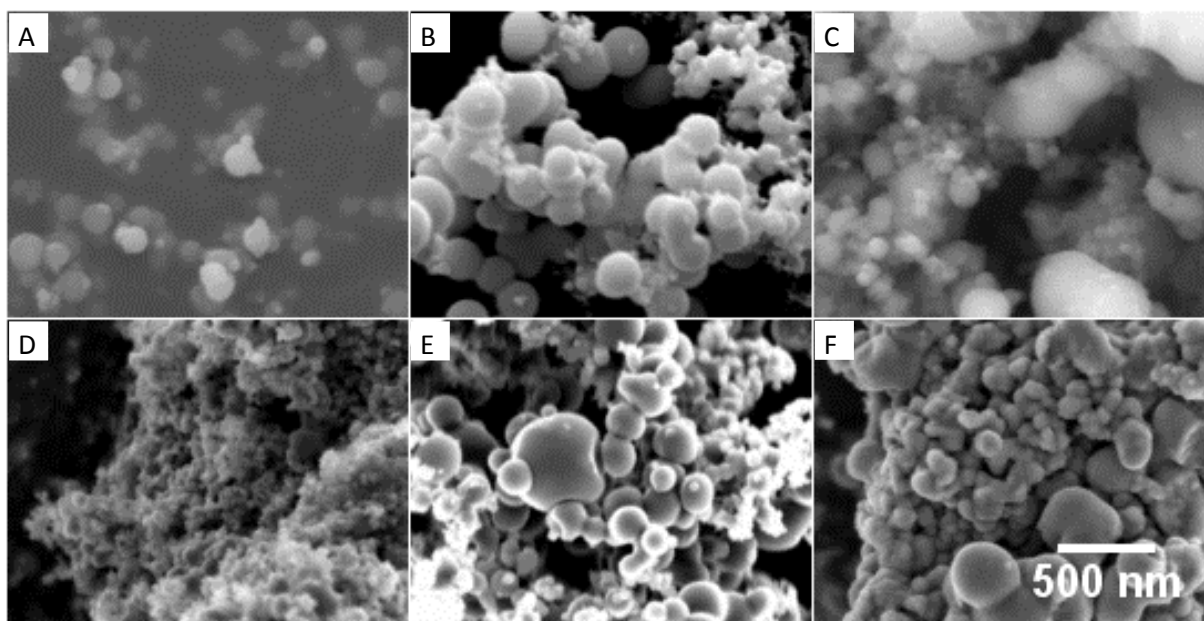


Figure 1. SEM micrographs of synthesized samples prepared at 50 °C with reaction time of 10 min (A), 60 min (B), 300 min (C) and at 70 °C with reaction time of 10 min (D), 60 min (E), 300 min (F)

The particle sizes and specific surface areas of the particles are presented in Table 1. With the lowest reaction times the particle sizes are smallest compared to longer reaction times from 0.148 to 0.303 μm with both reaction temperatures. This is due to the higher amount of amorphous titanium dioxide which is confirmed by the DSC results in the subsequent chapter. [7] Amorphous phase is present since the reaction time was too short to crystallize the particles. Particle size increases significantly when reaction time is increased to 60 min and it levelled out at 300 min reaction time. The particle size increases slightly also with the increase of reaction temperature. The particle size distribution is high as can be seen from the standard deviations of the particle size measurements. Specific surface areas for all treatments were very high. The highest surface areas of over 500 m^2/g were obtained with the shortest reaction times due to the higher amount of amorphous phase. With 60 min and 300 min reaction times the surface areas were between 274.3–319.8 m^2/g . With over 60 min reaction times the surface area decreased compared to the 10 min samples. Reaction temperature had a minor effect to the surface areas.

Table 1. Particle size averages deviations from all samples measured from SEM figures. BET specific surface areas from all samples

Treatment	Particle size average \pm standard deviation (μm)	Specific surface-area (m^2/g)
150 bar 50 °C 10 min	0.303 \pm 0.208	566.6
150 bar 50 °C 60 min	0.483 \pm 0.437	319.8
150 bar 50 °C 300 min	0.488 \pm 0.323	274.3
150 bar 70 °C 10 min	0.148 \pm 0.076	527.2
150 bar 70 °C 60 min	0.629 \pm 0.525	294.7
150 bar 70 °C 300 min	0.635 \pm 0.404	305.9

3.2. Relative crystallinity

The relative crystallinities of the powders were analysed by differential scanning calorimetry. The results are presented in Figures 2 and 3 for samples treated at 50°C and 70°C, respectively. Three different peaks can be seen from the results. The endothermic peak at 100°C is due to the evaporation of water. One sample treated at 50°C with 10min reaction time has endothermic peak at 275°C which is due to the decomposition of organic residuals from precursor tetra-n-butyl orthotitanate. The only exothermic peak occurs at 390°C at which the crystallization of amorphous titania starts and forms anatase [7, 8]. The largest peaks indicate highest amount of amorphous phase while the smallest peaks higher crystallinity. The results show that the peak is biggest in 10 min samples in each treatment temperature which correlates well with particle size and specific surface area results. The samples treated at 50°C with 300 min treatment time and at 70°C with 60 and 300 min reaction times do not exhibit a peak at 390°C temperature which indicates high crystallinity. The results show that the increase in reaction temperature and reaction time increases the crystallinity as well.

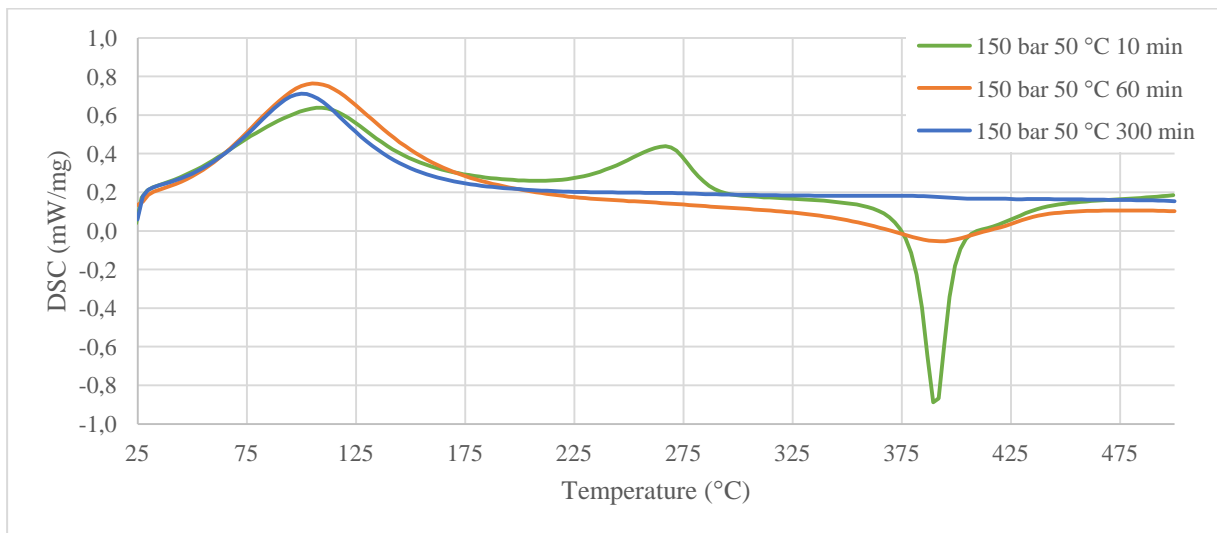


Figure 2.The DSC curves for samples treated in 50 °C with reaction times of 10, 60 and 300 min.

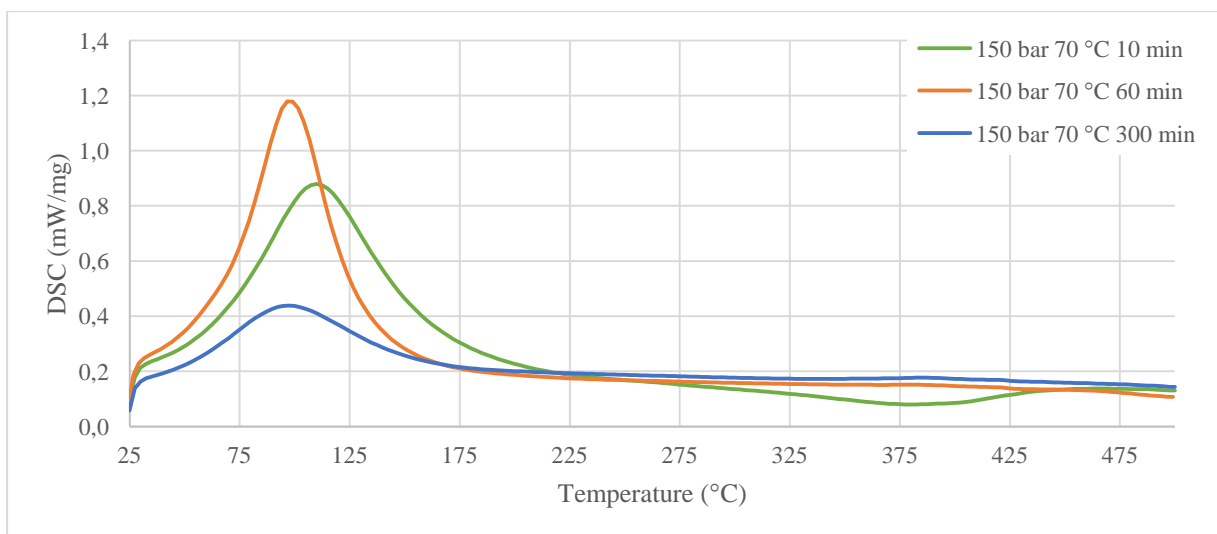


Figure 3.The DSC curves for samples treated in 70 °C with reaction times of 10, 60 and 300 min.

3.3. Characterization of crystalline phase and crystallite size

X-Ray diffraction was used to determine the crystalline phase of the particles and the results are shown in Figure 4. With 10 and 60 min samples in both temperatures the peaks were wide and slightly indistinct. There appeared to be a peak at 30° which would indicate the presence of brookite which has a characteristic peak at 30.8° [1]. However, since the peaks are not so distinct and the amorphous phase is present in these samples, the dominant phase still remains uncertain. The formation of brookite could be due to the high pressure of the synthesis. With 300 min samples it was clear that the dominant crystallite phase was anatase in both temperatures. The crystallite size of anatase was determined with XRD by using the Scherrer equation to be approximately 3-4 nm with no clear change between different reaction parameters. In Figure 5, there are TEM micrographs from two samples with 60 min reaction time in different temperatures. TEM micrographs were used as complementary data for the determination of the crystallite size of the particles. The measured crystallite size was 2.7–4.5 nm which supports the XRD data.

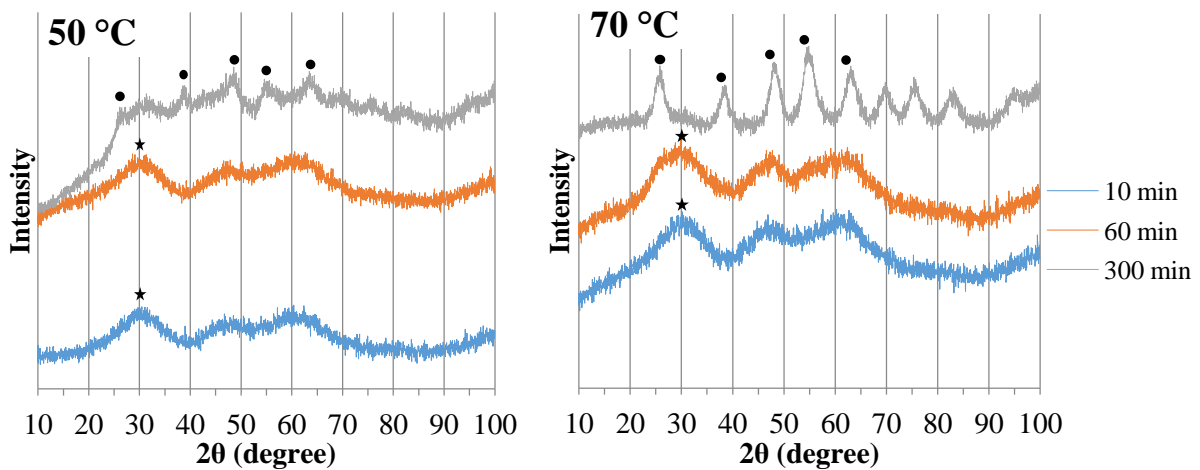


Figure 4. XRD patterns of prepared samples. The characteristic peaks for anatase and brookite are marked as sphere and star, respectively

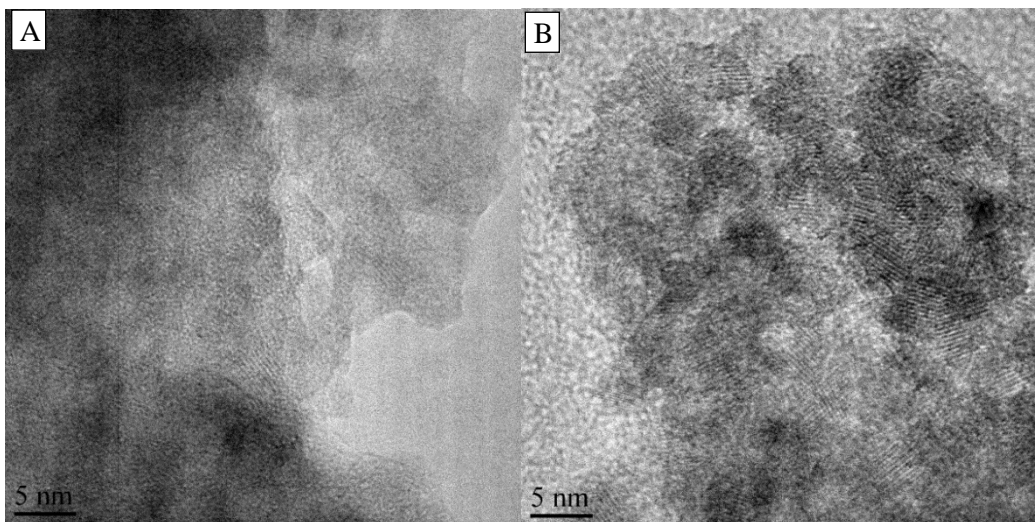


Figure 5. TEM micrographs of samples prepared in 15.0 MPa pressure for 60 min at 50 °C (A) and 70 °C (B)

4. Conclusions

Titanium dioxide with high surface area and small crystallite size (approximately 4 nm) was successfully synthesized by using only supercritical carbon dioxide, water and tetra-n-butyl orthotitanate. The particle morphology was mostly spherical and particle sizes were between 0.15–0.63 μm . The smallest particle sizes formed with the shortest reaction times of 10 min and the particle size increased with increase in temperature and reaction time up to 60 min. The specific surface areas of all samples were very high ranging from 274–567 m^2/g . The highest surface areas formed with the shortest reaction times due to higher amounts of amorphous titanium dioxide. With the more crystallized samples the surface area was still high with no significant change by increasing temperature or reaction time above 60 min. The crystallinity of the particles increased by increasing temperature, reaction time or both. XRD results showed the formation of two titania phases: anatase and brookite. However, the amount of brookite phase in the synthesized powders remained uncertain and will need further studies. Moreover, the crystallization behaviour of titanium dioxide in supercritical carbon dioxide demands additional research, e.g., the effect of other reaction parameters like pressure to formation of titanium dioxide should be studied.

References

- [1] Kandiel T, Robben L, Alkaim A, and Bahnemann D 2013 Brookite versus anatase TiO_2 photocatalysts: phase transformations and photocatalytic activities *Photochem. & Photobiol. Sci.* **124** pp 602–609
- [2] Nikkanen J-P, Heinonen S, Saarivirta E.H, Honkanen M and Levänen E 2013 Photocatalytically active titanium dioxide nanopowders: Synthesis, photoactivity and magnetic separation *IOP Conf. Ser. Mater. Sci. Eng.* **47** 012066
- [3] Fröschl T, Hörmann U, Kubiak P, Kučerová G, Pfanzelt M, Weiss C.K, Behm R.J, Hüsing N, Kaiser U, Landfester K and Wohlfahrt-Mehrens M 2012 High surface area crystalline titanium dioxide: potential and limits in electrochemical energy storage and catalysis *Chem. Soc. Rev.* **41** p 5313
- [4] Zhang X, Heinonen S and Levänen E 2014 Applications of supercritical carbon dioxide in materials processing and synthesis *RSC Adv.* **4**105 pp 61137–52
- [5] Sanli D, Bozbag S.E and Erkey C 2012 Synthesis of nanostructured materials using supercritical CO_2 : part i. Physical transformations *J. Mater. Sci.* **47** pp 2995–3025
- [6] Beckman E.J 2004 Supercritical and near-critical CO_2 in green chemical synthesis and processing *J. Supercrit. Fluids* **28** 2–3 pp 121–191
- [7] Xie H. Q, Xi T. G, Zhang Q. H and Wu Q. R 2003 Study on the phase transformation behavior of nanosized amorphous TiO_2 *J. Mater. Sci. Technol.* **195** pp 463–466
- [8] Prefectural A and Nishishinwari G 2001 “Effects of heat treatment on photocatalytic property of sol-gel derived polycrystalline TiO_2 ,” *J. Sol-Gel Sci. Technol.* **22** pp 83–89