

## Formation Studies on the Nonaqueous Synthesis of Metal Oxide Nanoparticles in a 1.5 L Reactor System

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In the last years, the nonaqueous synthesis has been demonstrated as a highly versatile method for the simple synthesis of highly crystalline metal oxide nanoparticles and nanomaterials. Thereby, we have presented the synthesis of a multitude of different metal oxides (e.g.,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{Fe}_3\text{O}_4$ ). The mechanisms of particle formation as well as the influence of process parameters on the particle properties however remain largely unknown so far, as the molecular mechanisms are rather complex. In this paper, we show that the synthesis of metal oxide nanoparticles is feasible also on a multi-gram reactor scale on the example of anatase  $\text{TiO}_2$  nanoparticles. Using a reactor system equipped with a sampling system for withdrawal of samples at different stages of the reaction, the kinetics of particle formation could be determined and compared to the formation of organic side products and water. Additionally, insights into the influence of different process parameters on the particle properties are shown and can be utilized to tailor size and morphology of the product nanoparticles.

**Keywords:** Nanoparticle synthesis, metal oxide, titania, processing, formation mechanism.

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### 1. INTRODUCTION

Metal oxide nanoparticles are highly desired for a multitude of applications ranging from cosmetic products to optics and medicine, due to their great variety in properties and functions. Advanced applications however require a precise control of the particle properties, especially with regard to their size and morphology, as well as highly homogeneous products, i.e., narrow size distributions. While conventional aqueous sol-gel or hydrothermal methods often lack these requirements, leading to non-uniform products with broad size and shape distributions, in the last years nonaqueous synthesis approaches have been presented that result in highly homogeneous products [1]. Further advantages of this synthesis strategy are the good crystallinity of the resulting nanoparticles, the possibility of preparing a multitude of different binary and ternary metal oxides, and the simplicity of the reaction system, consisting of only the metal oxide precursor and the reaction medium [2]. Additionally, the precursor can be utilized in rather high concentrations, and the yields of the synthesis are generally high with up to 100 %, which renders the method highly promising for commercial applications [3].

Despite the experimentally simple systems, however, the underlying reaction mechanisms have turned out to be complex, as organic condensation mechanisms occur prior to or simultaneously with the inorganic condensation, and thereby the reaction medium has a great influence on the synthesis mechanism [4]. We have recently presented studies on the formation of iron oxide nanoparticles in two different solvents, benzyl alcohol and triethylene glycol, showing that not only the formation kinetics is highly different for those two media, but also the crystallization is a distinct step after particle formation and its kinetics are as well

influenced by the used reaction medium [5]. Although the strong influence of organics had been reported by us before [6], the high influence of the organics on both particle formation and crystallization still is remarkable and in stark contrast to studies on the thermal decomposition synthesis method, where no influence of the reaction medium is generally assumed [7].

### 2. RESULTS AND DISCUSSION

In order to study the mechanisms and kinetics of particle formation for a simple system in more detail, we have looked at the reaction of titanium(IV) alkoxides in benzyl alcohol to form crystalline  $\text{TiO}_2$  nanoparticles [8]. The reaction was thereby carried out in a reactor system with a double wall that was heated via an external thermostat for precise temperature control. The reactor system was completely sealed during the reaction, thereby resulting in the development of autogenous pressure as a result of heating and chemical reaction. Additionally, the reaction system was equipped with a sampling system to enable the straightforward withdrawal of samples at any point during the reaction (Fig. 1).

Based on previous studies on the reaction of metal alkoxides in benzyl alcohol [9], the reaction was expected to consist of two steps: an initial ligand exchange reaction, and the subsequent elimination of organic ethers to induce condensation and the formation of M–O–M bridges. As a rather similar reaction, the synthesis of titania nanoparticles from titanium(IV) tetrachloride had been investigated by us earlier [10], revealing an alkyl halide elimination mechanism as well as a concurrent ether elimination mechanism being responsible for the formation of the metal oxide, both proceeding with first-order kinetics. When observing the pressure for the reaction of titanium(IV) alkox-

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ides, however, not a continuous but a step-wise behavior was observed. During the initial heating the pressure rose to about 1–3 bar overpressure (dependent on the process temperature) where it remained for up to 24 h before it suddenly increased further to 2–5 bar overpressure. The reaction was stopped after 48 hours, and a milky dispersion removed from the reactor. After centrifugation, washing with ethanol and again centrifugation, a white powder was obtained. Fig. 2 shows a TEM image of TiO<sub>2</sub> nanoparticles obtained from the reaction of titanium(IV) isopropoxide in benzyl alcohol, having a size of about 10 to 20 nm. About 15 g of nanoparticles were obtained in one synthesis.



Fig. 1 – 1.5 L reactor equipped with sampling system and instruments

As the reaction system turned from completely transparent to milky within the short amount of time of the pressure increase, this timespan was studied more closely. First, in order to check the presence of nanoparticles in the reaction mixture immediately before the pressure rise, methanol was added to the mixture in order to induce precipitation. Despite the addition in a molar ratio of 5:1, however, no precipitate at all was obtained. Therefore, we expect that nanoparticles are completely absent in the reaction mixture before the pressure increase.

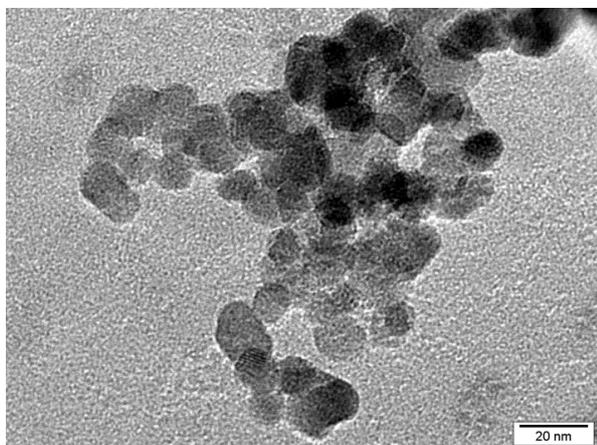


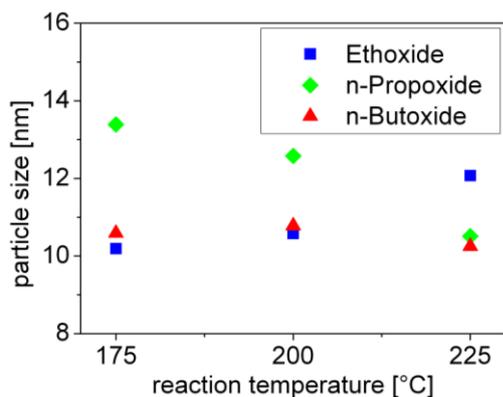
Fig. 2 – TEM image of TiO<sub>2</sub> nanoparticles

Additionally, the cause of the pressure increase was investigated by means of NMR spectroscopy and Karl Fischer titration analysis. As the content of water increases rapidly especially in the gaseous phase within the reaction mixture during the pressure increase, the formation of water via an ether elimination reaction is determined to be the underlying cause. Table 1 shows the quantities of water and benzyl ether determined in the reaction mixture before, during and at the end of the pressure increase. It is clearly visible that both the water content and the ether content increase similarly and this increase is concurrent to the pressure increase. As benzyl ether has a rather high boiling point (298°C) and therefore low volatility, water must be the main cause for the pressure increase.

Table 1 – Development of the molar ratio of ether and water in the reaction mixture with time

Time after pressure increase [min]	Ether [mol/mol aromatics]	H <sub>2</sub> O [mol/mol aromatics]
0	0.017	0.001
10	0.070	0.029
40	0.098	0.043
80	0.100	0.052
1200	0.100	0.055

The variation of process parameters is generally expected to be a powerful means to adapt and tune the size and morphology of the resulting nanoparticles, in order to realize different applications. When varying the process parameters, it was found that not only the reaction kinetics was influenced but also the particle size. While the reaction rate was enhanced exponentially with increasing temperature, the sizes of the obtained TiO<sub>2</sub> nanoparticles depended strongly on the nature of the used titanium precursor as shown in Fig. 3. Using titanium(IV) ethoxide, particles about 10 nm in size were obtained at 175°C, with an increase in size to 12 nm being observed for higher reaction temperatures up to 225°C. As opposed to this, for titanium(IV) n-propoxide there is a decrease in particle size from 13.4 to 10.5 nm when increasing the temperature within the given range. Furthermore, using titanium(IV) n-butoxide, the size of the particles was nearly constant with 10.3 to 10.6 nm. When comparing the different precursors, it can be said that no clear trend is observable, with the precursor of shortest chain length leading to largest particles at higher reaction temperatures but not at lower temperature, whereas the results are fully reproducible within a range of ±0.5 nm for a given precursor and temperature. Therefore, the particle size can be tuned to some extent; however there is no clear dependence on reaction temperature but a strong influence of the used precursor.



**Fig. 3** – Development of the particle size according to the reaction temperature and to the used titanium precursors

### 3. CONCLUSION

The nonaqueous synthesis of metal oxide nanoparticles can be carried out also on a larger scale in a 1.5 L reactor system, enabling the synthesis of highly crystalline and homogeneous metal oxide nanoparticles in the 10-30 g scale. As the reactor was equipped with a sampling system as well as precise temperature control and pressure measurement, the reaction could be further studied by withdrawal of samples at critical points in the course of the synthesis. In contrast to earlier

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studies, it was found for the reaction of titanium(IV) alkoxides in benzyl alcohol that no continuous organic reaction mechanism takes place but a step-type increase in pressure after a long lag time, concurrent to the release of water by an ether condensation reaction. The reaction temperature has a very strong effect on the reaction kinetics, with strong enhancement for higher temperatures, but only a rather limited influence on the size of the resultant nanoparticles. Additionally, the observed trends depend on the chemical nature of the utilized precursor. For different n-alkoxides investigated, however, no clear trend for the influence of the chain length on the particle size could be detected. This is subject to our ongoing investigations, as a tailoring of particle size and shape also for a synthesis on a larger scale is crucial for the realization of applications of nanomaterials.

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