

About the Influence of the Particle Size on the Thermal Behavior of Inorganic Powders

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Introduction

In order to investigate the effect of particle size on the physical properties of crystalline materials, different particle sizes of crystalline substances that were generated by grinding were analyzed by thermal analysis methods, such as thermogravimetry (TGA) [1], differential scanning calorimetry (DSC) [2] and dilatometry [3].

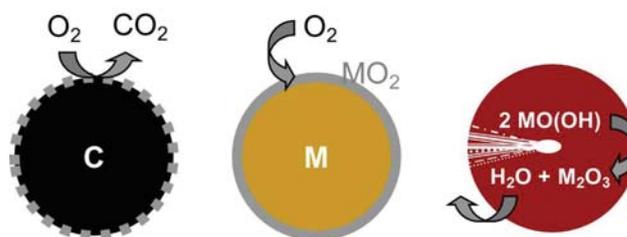
Relatively small variations in particle size produced significant changes in thermal processes that were investigated by these methods.

The thermal processes that were investigated can be divided into four categories:

- Melting of metals (solid-liquid)
- Reactions at the particle surface (combustion of carbon)
- Release of gaseous reaction products (dehydration and decomposition)
- Sintering

Melting

Particle size variation in the milli- and micrometer range, according to Schmid [4], does not significantly influence the melting behavior of particles. For spherical particles with diameters greater than 50 nm, particles at the surface account for less than 6% of the bulk and therefore have negligible effect. For smaller particle sizes ($r < 25$ nm), the percentage of coordinatively unsaturated particles near the surface increases, causing a significant decrease in the melting temperature [6] according to the Reifenberger model [5].



1 Schematic of different reaction mechanisms and transport processes

Reactions at the Particle Surface

The combustion of carbon particles can be used as a model for a surface reaction. The gaseous oxygen can be supplied evenly to the particle surface and reacts there to form CO₂, a gaseous and therefore easily removable product. A fresh, reactive surface is generated by the reaction itself. The carbon particle decreases in size until it is completely converted to CO₂. By contrast, the metal oxide surface layer produced during the oxidation of metal particles presents a passive barrier layer that hinders oxygen access to the metallic core beyond a certain thickness, thereby preventing quantitative conversion (figure 1).

Measurement Results

Despite their comparable particle sizes (~50 nm), different types of carbon black exhibited very different combustion behavior, as shown in figure 2. The differences are likely due to differences in the porosities of the materials, which affect their surface areas. Thus, the particle size alone is only a rough determination of oxidation behavior.

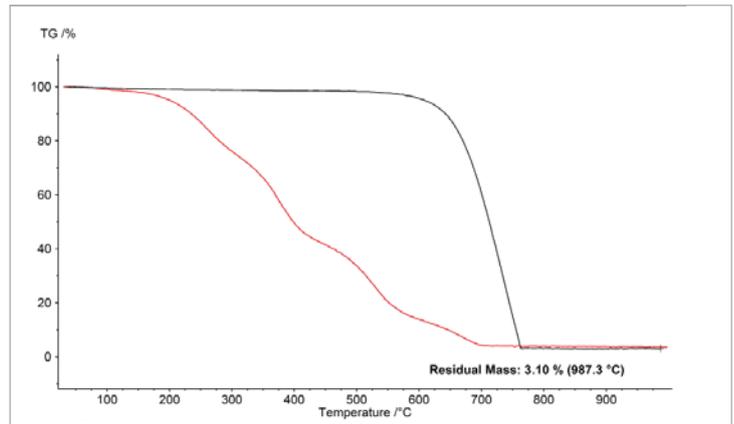
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Release of Gaseous Reaction Products

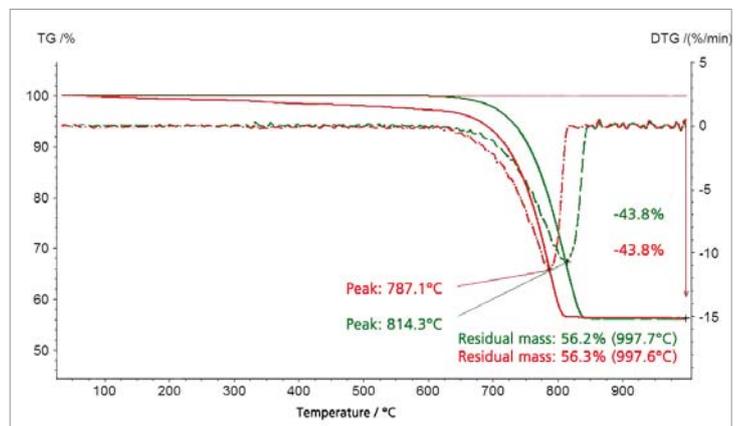
Although decomposition reactions require no additional gaseous reactant, they are, nevertheless, significantly influenced by transport processes. Although the surface area is not crucial in this case, the distance over which released gases must be transported from the interior to the surface of the particle via pores or channels depends on particle size. Hence, this process is considerably more efficient for very small particles.

The CaCO_3 (figure 3) and goethite (figure 4) examples illustrate the effect of smaller particle size in lowering the temperatures at which the materials decomposed with the release of CO_2 or H_2O [6]. The thermogravimetric results confirm that the stoichiometries of the gases released are unaffected by variation of the particle size.

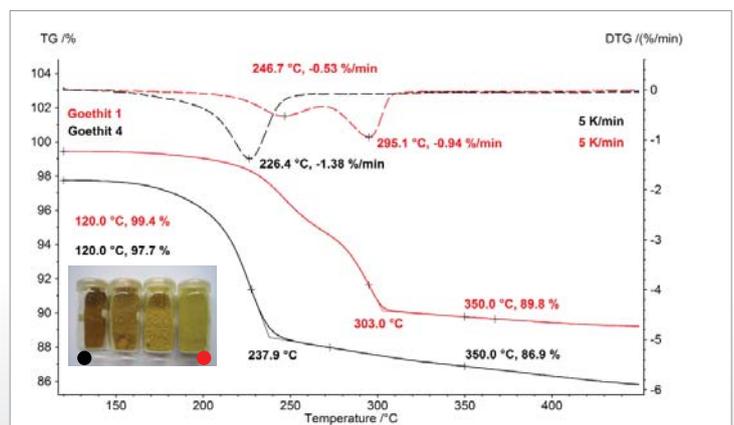
Thermokinetic analysis of the dehydration of $\alpha\text{-FeOOH}$ (goethite) to $\alpha\text{-Fe}_2\text{O}_3$ (hematite) showed that the formal kinetic model for the reaction was simpler for the small particles than for large particles. Measurements at different heating rates were modeled by a reaction process consisting of two consecutive n^{th} order steps and an activation energy of 150 kJ/mol [7]. Quantification of the mass-loss steps between 120°C and 350°C confirms the expected values for the stoichiometric conversion of goethite to hematite. The rate of mass loss (DTG) – indicated with dashed lines – shows that the reaction peak is shifted to lower temperatures with smaller particle sizes. The photo in figure 4 shows the change in the appearance of the goethite samples with varying particle size.



2 Comparison of the thermogravimetric results of the combustion of carbon black with different specific surfaces (red: higher specific surface; black: smaller specific surface)



3 Comparison of the thermogravimetric results of two calcium carbonate samples with a median value of the particle size distribution of 10.8 µm (green) and 1.75 µm (red)

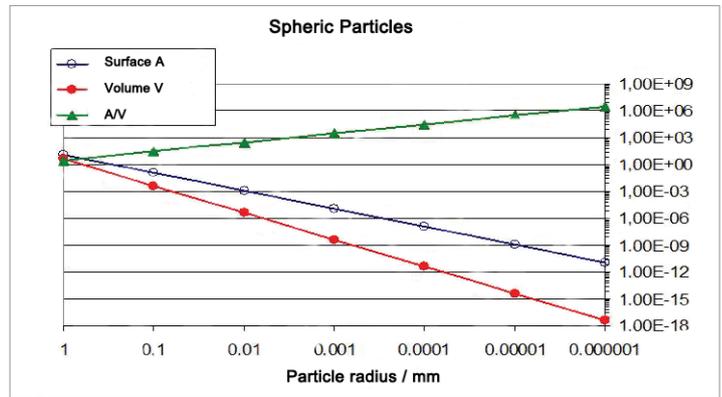


4 Comparison of the thermogravimetric results of two goethite samples, red (1.2 x 0.25 x 0.25 µm), black (0.1 x 0.01 x 0.01 µm)

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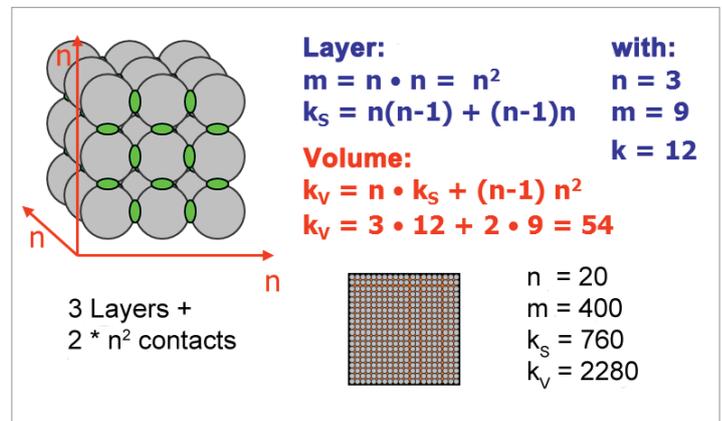
Sintering

The particle size-dependent effects observed during the sintering of pressed powder pellets can not be explained by increased surface area alone (figure 5). In contrast to melting behavior, particle size effects on sintering occur at dimensions as large as the micrometer range. Significant reductions in the sintering temperature occur with relatively small variation of the particle size.

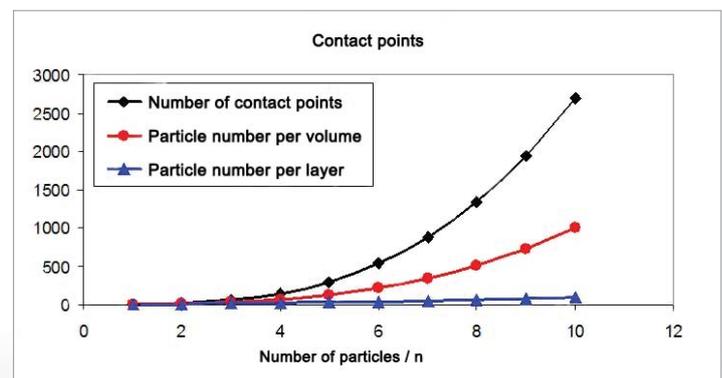


5 Variation of the surface and volume with the particle size

The amount of contact points between spherical particles increases much faster than the surface-to-volume-ratio (figures 6 and 7). For the increase in sintering activity, the contact points between the particles are important. Particles ranging from 10 μm to 130 nm in diameter were generated by grinding the materials with the NETZSCH ZETA® RS4 beat mill system.



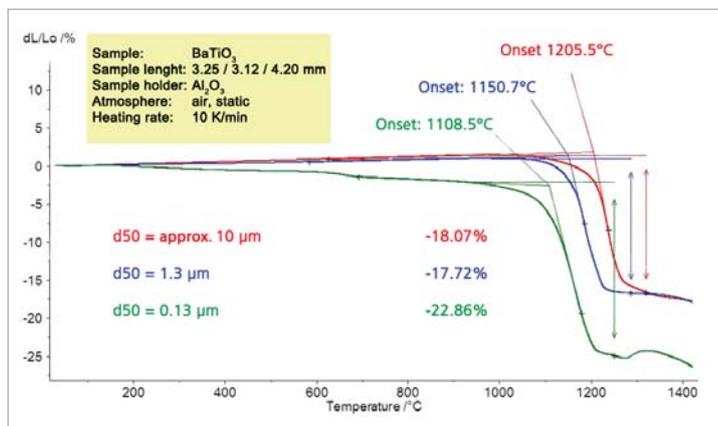
6 Calculation of contact points between spherical particles



7 Calculation of the amount of the contact points of spherical particles

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Figure 8 shows the sintering activity dependence on particle size for BaTiO₃. The 1108°C sintering temperature for the smallest particles (extrapolated onset temperature) is almost 100 K lower than the sintering temperature of the larger particles (1205°C).



8 Results of the sintering behavior of three BaTiO₃ samples with particle sizes of 1.3 μm, 10 μm and 130 nm (d₅₀)

Summary

With the help of thermoanalytical measurements, it could be demonstrated that the particle size has a significant effect on the kinetics and, hence, temperature dependence of processes such as dehydration, decomposition, combustion and sintering. Sample preparation, particularly the particle size, is thus an important parameter to consider when interpreting measurement results.

Thermal analysis methods offer a relatively easy and quick means of measuring the effects of particle size on sample properties.

Literature

- [1] Deutsches Institut für Normung, DIN 51006 2005, „Thermische Analyse (TA) - Thermogravimetrie (TG) – Grundlagen“
- [2] Deutsches Institut für Normung, DIN EN ISO 11357-1, „Dynamische Differenz-Thermoanalyse (DSC) – Teil 1: Allgemeine Grundlagen“
- [3] Deutsches Institut für Normung, DIN 51045-1, „Bestimmung der technischen Längenänderung fester Körper – Teil 1: Grundlagen“.
- [4] G. Schmid, *Nanoscale Materials in Chemistry*, K.J. Klabunde (ed.) John Wiley & Sons, Inc. 2001, 15.
- [5] T. Castro, R. Reifemberger, E. Choi, R.P. Anders, *Phys. Rev. B*. 1990, 13, 8548.
- [6] E. Füglein, S. Mende, S. Jung, T. Schneider, *Produktgestaltung in der Partikeltechnologie* 2008, 4, 97.
- [7] E. Füglein, D. Walter, *14th International Conference on Thermal Analysis and Calorimetry (ICTAC)*, Sao Pedro, Brasilien, 2008.