

Kinetic analysis of the thermal transformation from goethite to hematite



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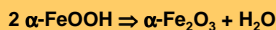
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Introduction

The thermal transformation from goethite to hematite can be described by the simple equation:



On the other hand, the dehydration mechanism is much more complex and depends on the particle size of the goethite needles (figure 1) [1]. Synthetic goethite pigments (Bayerferrox[®]) of different particle size (table 1) were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC).

The following model for the mechanism of the dehydration process was described: at an early stage of the dehydration, water leaves the crystal lattice in the [010] direction of the crystal by forming dehydration channels parallel to the crystallographic c-axis [001]. The matrix between the channels is formed by hematite (figure 2).

In cases where the crystal dimensions are relatively large (length of needles $\geq 0.3 \mu\text{m}$), the dehydration channels within the outer crystal regions begin to grow together, forming a compact hematite layer at the crystal surface before the dehydration front within the needle reaches the crystal center, i. e. the dehydration process is not finished yet.

The compact surface hematite layer acts as a barrier which hampers further dehydration, because an additional amount of enthalpy must be provided to overcome the dehydration barrier and thus allow the dehydration front to proceed into the needle center until the dehydration is complete. Experimental evidence for this model consists of a second peak in the DTG and DSC plots of goethite samples.

In cases where the crystal dimensions are relatively small, the dehydration is finished before a dehydration barrier can be formed.

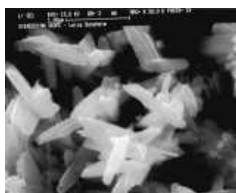


Figure 1: REM image of goethite 1; magnification: 30 000x

Table 1: Specific surface area of goethite samples (from BET-measurements in nitrogen) and characteristic particle geometry (from SEM images)

Sample	Specific surface / $\text{m}^2\cdot\text{g}^{-1}$	Particle geometry / $10^{-18}\cdot\text{m}^3$
goethite 1	10	1.2 · 0.25 · 0.25
goethite 2	14.5	1.0 · 0.15 · 0.15
goethite 3	67	0.3 · 0.03 · 0.03
goethite 4	149	0.1 · 0.01 · 0.01

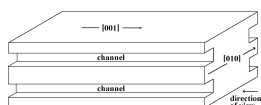
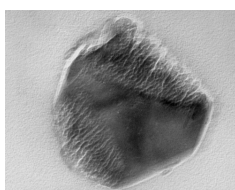


Figure 2: TEM image of a partly dehydrated goethite 1 needle cut perpendicular to the needle axis; magnification 225 000x

Experiments

Goethite samples of different particle size were investigated by simultaneous TG-FTIR (Netzsch 209C *Iris*[®]; Bruker Optics TENSOR[™]) and by DSC (Netzsch 204 *Phoenix*[®]). Kinetic analysis helps to calculate the activation energy and the reaction rate for the dehydration of goethite.

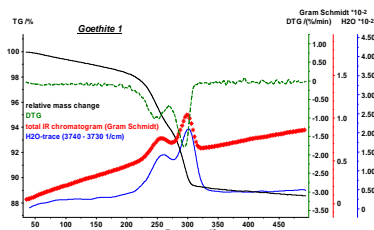


Figure 3: Simultaneous TG-FTIR plot of goethite 1

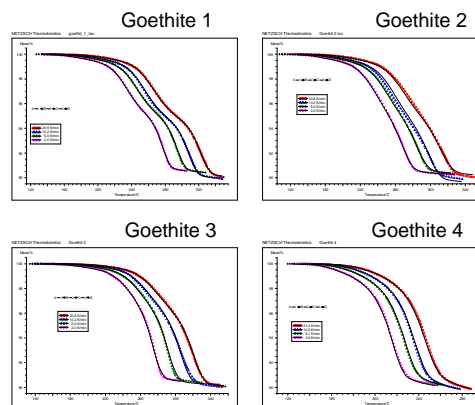


Figure 4: Results of the kinetic analysis (different heating rates) of the goethite to hematite transformation; observed (points) and calculated (lines)

Results

Simultaneous TG-FTIR investigations (figure 3) of the goethite samples confirmed, that there is no impurity effected by an unknown compound during the dehydration reaction. Only the loss of water was detected.

Kinetic analysis using multivariate non-linear regression gives some further insights into the mechanism of the dehydration reaction [2]. A multi-step model provides an excellent description of the experimental TG results (figure 4).

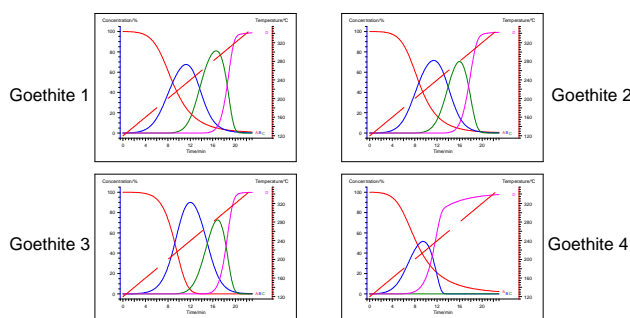


Figure 5: Formal reactants versus time of goethite samples calculated by kinetic analysis; heating rate: 10 K/ min

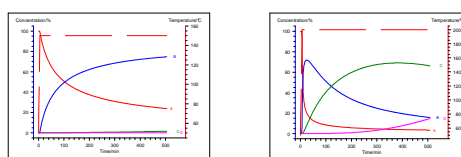


Figure 6: Predictions of the formal reactants (goethite 1) at different isothermal conditions (left: 150°C; 500 min and right: 200°C; 500 min)

As presented in figure 4 the activation energy of the second step (B to C: ~160 kJ/mol) is significantly higher than the activation energy of the first step (A to B: ~125 kJ/mol). Taking this into account, experimental conditions as depicted in figure 6 could be successful in order to synthesize and identify product B and C.

Literature

- Walter, D.; Buxbaum, G.; Laqua, W., J. Therm. Anal. Cal. 2001, 63, 733-748
- Opfermann, J. R., J. Therm. Anal. Cal. 2000, 60, 641-658