

PRESSURE DEPENDENCY OF THE THERMAL TRANSFORMATION FROM MOOH TO M₂O₃ (M = Fe, La)



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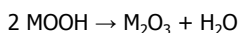
Summary:

Thermal behaviour of lanthanum hydroxide and iron hydroxide oxide was studied by means of Evolved Gas Analysis (EGA) consisting of Thermogravimetry and Fourier Transform Infrared Spectroscopy (TG-FTIR) as well as High Pressure Differential Scanning Calorimetry (HP-DSC) within a broad pressure range of nitrogen atmosphere (10⁻² to 150000 mbar).

With increasing pressure the dehydration is shifted to higher temperatures. It seems as if pressure has no influence on the reaction mechanism, but grain size of the goethite needles obviously has.

Introduction:

Thermal transformation from metal hydroxide oxides to metal oxides of lanthanum and iron can be described by the following equation:



In case of lanthanum MOOH was formed in situ by thermal treatment of M(OH)₃ according to:



In case of iron goethite pigments were produced by the well-established industrial process called Penniman and Laux [1].

Results:

Lanthanum hydroxide tends to adsorb humidity at the surface of the powder grains and to react with carbon dioxide from the atmosphere in order to form lanthanum carbonate.

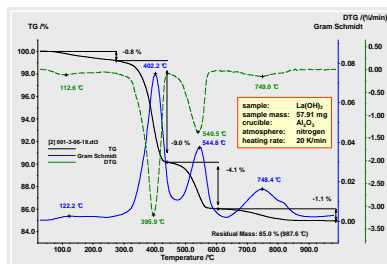


Figure 1: TG-FTIR results of La(OH)₃

Temperature dependent mass changes as well as the Gram-Schmidt trace are depicted in figure 1 for the decomposition of La(OH)₃. As described at the equations above two dehydration reactions are observed. Additionally the release of humidity (0.9%) and a further mass loss step between 600 and 800°C is detected. Figure 2 proves that only the mass loss steps between 300 and 600°C are related to the dehydration of La(OH)₃.

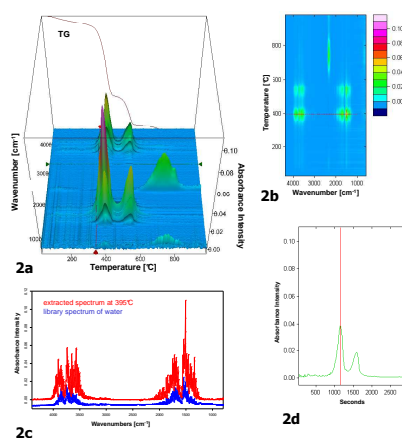


Figure 2: (a) 3D-view of all detected IR spectra, temperature-scaled with TG signal, (b) contour plot, (c) extracted single spectrum at 395°C compared with library spectrum of water, (d) time-dependent change of the water absorbance intensity, trace at 1700 cm⁻¹

The following mass loss step between 600 and 800°C is due to carbon dioxide. This clearly disproves the interpretation of Yamamoto et al. [2].

By means of TG-FTIR the dehydration reaction of goethite does not show any mass loss steps but those that are related to water.

The pressure-dependency was measured with the NETZSCH DSC 204 HP Phoenix®. By means of REM the particle size of La(OH)₃ was determined to be 0.25 to 0.5 µm. Increasing pressure obviously has different influence on each dehydration reaction of La(OH)₃ (Fig. 3).

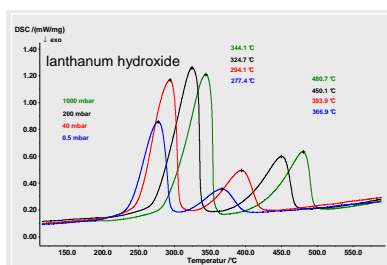


Figure 3: HP-DSC results of La(OH)₃ at reduced pressure

The peak temperature for the second reaction (2 LaOOH → La₂O₃) is more shifted to higher temperatures than the first reaction (La(OH)₃ → 2 LaOOH). This indicates a broader stability range with increasing pressure for LaOOH (Fig. 4).

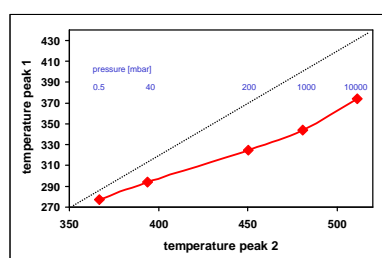


Figure 4: Pressure-dependent peak temperatures for La(OH)₃

In contrast to the lanthanum hydroxide iron hydroxide oxide shows a basically parallel shift of peak temperatures with increasing pressure (Fig. 5). For both systems investigated it seems as if the mechanism would not change when different pressures are applied. But significant changes of the dehydration mechanism are observed if the particle size is reduced to nano-scale. Figure 6 presents the dehydration of goethite needles with a length of 0.1 µm. These results confirm both, the kinetic investigations carried out by means of TG [3] and the HP-DSC measurements at higher pressure [4].

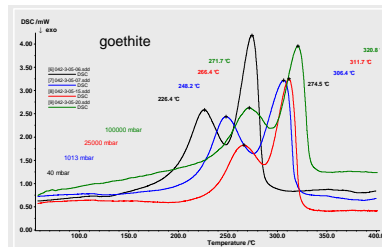


Figure 5: HP-DSC results for goethite needles (length: 1 µm)

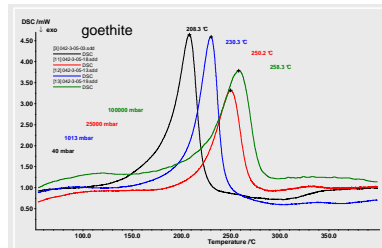


Figure 6: HP-DSC results for goethite needles (length: 0.1 µm)

References:

- [1] G. Buxbaum, H. Printzen, *Ullmann's Encyclopedia of Industrial Chemistry* **A20** (1992) 297.
- [2] O. Yamamoto, Y. Takeda, R. Kanno, M. Fushimi, *Solid State Ionics* **17** (1985) 107.
- [3] D. Walter, E. Füglein, J.R. Oefermann, *Proceedings Book: 9. European Conference on Solid State Chemistry* **248** (2003).
- [4] D. Walter, E. Füglein, *Proceedings Book: 27. Jahrestagung der Gesellschaft für Thermische Analyse, Braunschweig*, **43** (2004).