THERMAL BEHAVIOUR OF LANTHANUM HYDROXIDE IN DEPENDENCY OF PRESSURE

Ekkehard Füglein and Dirk Walter

E. Füglein, NETZSCH-Gerätebau GmbH, Wittelsbacherstraße 42, D-95100 Selb, Germany

D. Walter, Institut für Chemie der Technischen Universität, Straße des 17. Juni 135, D-10623 Berlin

Summary:

Thermal behaviour of lanthanum hydroxide 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.

Introduction:

Thermal transformation from lanthanum hydroxide to oxide is a two step mechanism. The intermediate product is lanthanum hydroxide oxide:

$$2\ La(OH)_3 \rightarrow 2\ LaOOH + 2\ H_2O$$

Lanthanum hydroxide oxide decomposes in a second step in order to form the oxide according to:

$$2\ LaOOH \rightarrow La_2O_3 + H_2O$$

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.

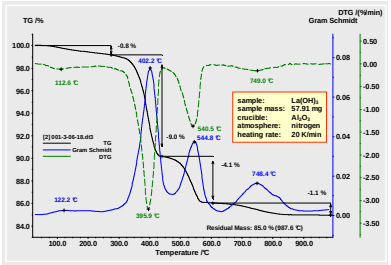

Figure 1: TG-FTIR results of $La(OH)_3$

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 $La(OH)_3$.

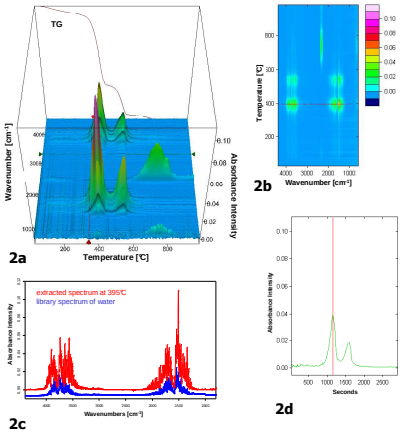

Figure 2: (a) 3D-view of all detected IR spectra, temperature-scaled with TG signal, (b) contour plot, (c) extracted single spectrum at 395°C compared with library spectrum of water, (d) time-dependent change of the water absorbance intensity, trace at 1700 cm^{-1}

The following mass loss step between 600 and 800°C is due to carbon dioxide. This clearly disproves the interpretation of Yamamoto et al. [1]. Purified lanthanum hydroxide can be obtained by treatment of lanthanum oxide with water at ambient temperature under protective gas.

By means of REM the particle size of $La(OH)_3$ was determined to be 0.25 to 0.5 µm.

The pressure-dependency was measured with the NETZSCH DSC 204 HP *Phoenix®*. Increasing pressure obviously has different influence on each dehydration step of $La(OH)_3$ (Fig. 3). The peak temperature for the second reaction (2 LaOOH → La_2O_3) is stronger shifted to higher values than the first part of the dehydration reaction ($La(OH)_3$ → 2 LaOOH). Similar behaviour is observed in the pressure range between 0.1 and 10 MPa (Fig. 4). Different pressure-dependencies of both dehydration steps indicate a broader stability range of the intermediate lanthanum oxide hydroxide (LaOOH) with increasing pressure.

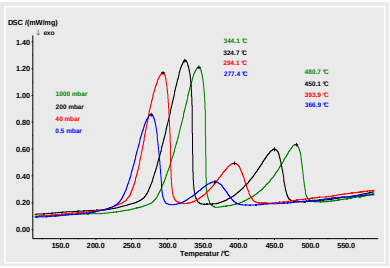

Figure 3: HP-DSC results of $La(OH)_3$ at reduced pressure [2]

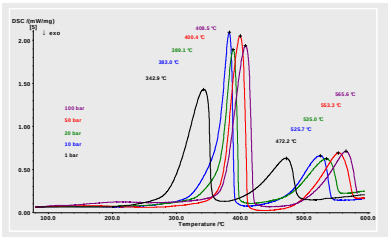

Figure 4: HP-DSC results of $La(OH)_3$ between ambient pressure and 10 MPa

Figure 5 depicts a comparison of both peak temperatures for the reduced pressure range (red) and for the high pressure range (blue). The structure of lanthanum hydroxide oxide was determined by X-ray powder diffraction methods, and subsequent Rietveld refinement (Fig. 6). LaOOH crystallizes in the monoclinic space group $P2_1/m$ (no. 11) with the lattice parameters a = 444.76(9) pm, b = 397.10(7) pm, c = 661.9(1) pm, and ß = 111.93(1)° [3][4].

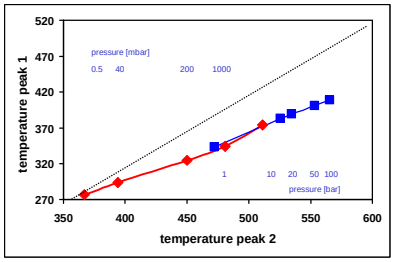

Figure 5: Pressure-dependent peak temperatures for $La(OH)_3$

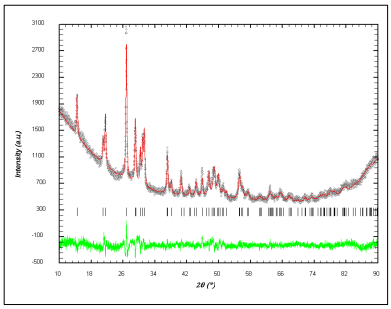

Figure 6: Rietveld refinement for lanthanum oxide hydroxide (LaOOH)

References:

[1] O. Yamamoto, Y. Takeda, R. Kanno, M. Fushimi, *Solid State Ionics* **1985,** *17,* 107.
[2] E. Füglein, D. Walter, *Z. Kristallogr. Suppl.* **2006**, *24,* 82.
[3] D. Walter, A. Neumann, *Z. Kristallogr. Suppl.* **2006**, *24,* 31.
[4] A. Neumann, D. Walter, *Thermochim. Acta* **2006**, *445,* 200.