

Thermal transformation of La(OH)₃ – Insight into a complex solid state reaction

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The interest in oxide lanthanum compounds has risen intensively during the last decades due to their wide range of applications. Numerous synthesis reactions for oxide lanthanum compounds have been published. For example, lanthanum oxide (La₂O₃) catalyzes numerous reactions like selective synthesis of phytosterol ester, heterogeneous synthesis of biodiesel, oxidative coupling of methane etc. [1, 2, 4].

The thermal transformation of hexagonal lanthanum hydroxide (La(OH)₃) runs via monoclinic lanthanum hydroxide oxide (LaOOH) to hexagonal lanthanum oxide (La₂O₃) [2]:



The reverse reaction of La₂O₃ already takes place at room temperature in a humid atmosphere to La(OH)₃ within 24 h [1,2].

La(OH)₃ has to be handled carefully because of the high CO₂ affinity forming partial basic carbonates. The carbonation of La₂O₃ in air is much weaker than its hydration. Due to the amount of possible applications of oxide lanthanum compounds, it is very important to investigate the hydration and especially the carbonation when exposed to a humid CO₂ containing atmosphere, like air. Investigation of the purity of laboratory- and commercial-quality La(OH)₃ and La₂O₃ by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (EDS) cannot be relied upon to detect carbonate-containing impurities, due to the small particle size and the associated detection threshold. However, in combination with thermal analytical investigations (TG-IR, DSC) it is possible to gain insight into the problematics surrounding the carbonate formation of La(OH)₃ and their resulting influence on the thermal transformation [4]. Transmission electron microscopy (TEM) detect the morphological changes of the crystalline structure caused by the loss of water and CO₂ [5].

In a humid CO₂ containing atmosphere, like air, the amount of carbonate impurities in La(OH)₃ remains constant over a long time. However, in a humid CO₂ atmosphere

with higher content of water and CO₂ La(OH)₃ and La₂O₃ transform to La₂(CO₃)₃·x H₂O via La(OH)CO₃, whereas La₂O₃ firstly forms La(OH)₃. In a dry CO₂ atmosphere, La(OH)₃ forms only a small amount of carbonate impurities. La₂O₃ does not react at all with CO₂ in absence of water. Therefore, water is essential for the conversion of La(OH)₃ to La₂(CO₃)₃·x H₂O. TEM investigations allowed observing the morphology changes during the thermal decomposition. Independent of the compound and the storage time, all samples showed a rough morphology with pores like hexagonal pores at 525 °C. At 800 °C the amount of pores decreased and the surface became smooth.

References

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