Memory Effect in Co/Mg/Al Nanosized Hydrotalcites

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Synthesis Methods Influence on Crystallite Size

EXPERIMENTAL

Three methods of hydrotalcite (HT) synthesis have been used to evaluate the influence of synthesis parameters on crystallite size.

Nitrate solutions of Co, Mg and Al with atomic ratio of 0.45/2.55/1.00 correspondently and drop-wise addition of NaOH and $NaHCO_3$ were used for hydrotalcite synthesis. **HTCo3-M3-LS** hydrotalcite was produced by coprecipitation under low supersaturation (LS) – the rate of instillation was 4 ml/min and then received gel was aged for 24 hours at 80 °C [1]. **HTCo3-M3-HS** hydrotalcite was produced by coprecipitation under high supersaturation (HS) – the rate of instillation was 83 ml/min and received gel was aged for 30 min at 80 °C [2]. The third series was prepared by adding the solution as done in coprecipitation under low supersaturation and gel was aged in a microwave oven (650 W; 2.45 GHz) with 10% and 30% power output, for 20 and 10 min (samples named **HTCo3-M3-MW-10-20** and **HTCo3-M3-MW-30-10** respectively). All samples have been filtrated, washed and dried.

RESULTS

Methods of synthesis have a considerable influence on crystal size of hydrotalcite (Fig.1 and 2). More intensive methods of synthesis, such as high supersaturation and microwave method, cause remarkable lowering of crystal size (from 41 nm in LS method up to 14-15 nm in microwave irradiated samples) Hydrotalcite, produced under high supersaturation condition, forms smallest crystallites (about 10 nm) possibly owing to the high number of crystallization nuclei.

Thermal Treatment Influence Investigation

The thermal decomposition of the Co/Mg/Al hydrotalcite includes structural sequence of dehydration, dehydroxylation and decarbonization (Fig.3). During these processes a series of metaphases are formed. The losses of water from interlayer decrease the size of crystallite and at 300 ºC pseudocrystalline material is left. According usual practice hydrotalcite structure decompose at 400-600 ºC temperature with periclase type oxide formation.

RESULTS

As the whole synthesized hydrotalcite follows described layout. Hydrotalcite derived oxides (Fig.4a and Fig.2), formed during decomposition, independently of production method and size of hydrotalcite crystallites, appear the practically the same crystallite size and similar intensity of grow.

Memory Effect Influence on Hydrotalcite Crystallite Size

The term "memory effect" is used in the literature to describe the regeneration of the initial structure as a result of wetting with water (or water solutions) of hydrotalcites, which have been thermally decomposed into a periclase-like metaphase.

EXPERIMENTAL

Thermally decomposed in the range of 400-600ºC Co/Mg/Al hydrotalcite have been subjected to regeneration in air at room temperature and humidity.

RESULTS

Reconstituted hydrotalcite not only returns to its structure, but also mostly returns its crystallite size (Fig.2 and Fig.4b).In contrast to literature data [3, 4], in this investigation is shown that the level of cristallinity of hydrotalcite after reconstitution doesn't increase and is very similar to level of crystallinity of initial material.

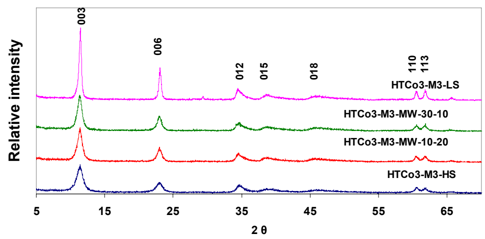

Fig. 1 XRD patterns of HTC synthesized using different methods.

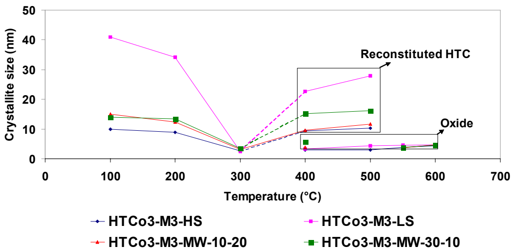

Fig. 2 Crystallite size of HTC and oxides.

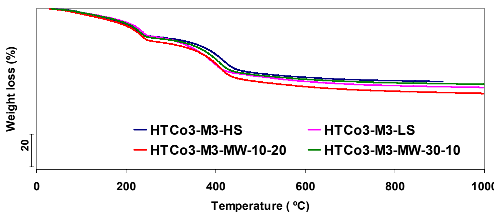

Fig. 3 TG profiles of hydrotalcites.

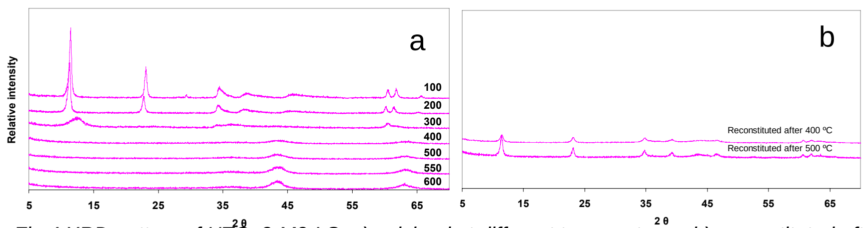

Fig.4 XRD patters of HTCo3-M3-LS: a) calcined at different temperatures; b) reconstituted after calcination at different temp.

Dicussion and Conclusions

Investigations of synthesis, thermal decomposition and reconstitution (Memory Effect) of Co/Mg/Al hydrotalcites showed, that as whole these processes follow usual scheme. More intensive technologies of synthesis (i.e. high supersaturation and irradiation effect) create smaller crystallites (Fig.1). After thermal decomposition independently of previous hydrotalcite crystal size HT derived oxides have the same phase composition (periclase as in Fig.4a) and crystallites size (about 3nm). However after reconstitution (Memory Effect) received hydrotalcite is formed with reconstitutions not only phase composition, but also crystallite size (Fig. 4b and Fig. 2). This feature permit to presume that previous structure of hydrotalcite don't decompose totally during thermal treatment in the range of 400-600 °C, retaining some topological components, which are used during the structure rebuilding in Memory Effect.

References

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