Thermal decomposition, gas phase hydration and liquid phase reconstruction in the system Mg/Al hydrotalcite/mixed oxide: A comparative study

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ARTICLE INFO

ABSTRACT

The thermal decomposition of a synthetic Mg/Al hydrotalcite and the subsequent hydration of the calcined products in the presence of water vapor at 30 °C were studied by in situ XRD. A comparative study between the gas phase hydration and reconstruction of calcined hydrotalcite in Na_2CO_3 solution at 25 and 70 °C was investigated. TG coupled to a mass spectrometer was used to study the thermal behaviour of synthetic hydrotalcite. SEM images were taken to show the layering and size of crystals. Thermal decomposition of hydrotalcite led to the formation of a dehydrated intermediate phase at 200 °C, followed by crystalline MgO formation at 450 °C. Hydration of calcined hydrotalcite in H_2O/N_2 resulted in the formation of broad patterns of the meixnerite phase after 2 h. This phase retained its structure even after 52 h exposure to water vapor. Reconstruction of the calcined products in carbonated water at 25 and 70 °C resulted in intensified patterns of the hydrotalcite phase. Due to the different structural and compositional properties of the layered products obtained by different chemical reactions of the mixed oxide phase a clarification of nomenclature for all phase transforming steps is proposed.

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1. Introduction

Layered materials are an interesting group to develop new materials with tailored nano-design, controlled accessibility to the active sites and a wide range of applications (Vaccari, 1999; Gil et al., 2000; Ding et al., 2001; Sels et al., 2001; Tichit and Coq, 2003; Albertazzi et al., 2004; Serwicka and Bahranowski, 2004; Ferreira et al., 2005; Li and Duan, 2006; Williams and O'Hare, 2006; Herrero et al., 2007). Today many structural, textural and compositional modifications are known for layered materials, allowing a fine-tuning and thus a control of the catalytic reactivity (De Stefanis and Tomlinson, 2006; Lucrédio and Assaf, 2006). Among layered materials the so-called layered double hydroxides (LDH's) or hydrotalcite-like materials (HTlcs) form the basis for new environment-friendly technologies, involving cheaper and more efficient ways to catalyze chemical reactions (Corma et al., 1994; Di Cosimo et al., 2000; Ono, 2003). LDHs are typically synthesized by coprecipitation. They have the general formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+}[A^{m-}_{x/m}nH_2O]^{x-}$, where the most typical M^{2+} ion is Mg^{2+} and Al^{3+} for M^{3+} ion. A is the interlayer anion

with valence m^- where the positively charged layers are encountered by negatively charged anions such as CO_3^{2-}, NO_3^- and SO_4^{2-}. The value of x is equal to the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$ (Cavani et al., 1991; Braterman et al., 2004; Evans and Duan, 2006; Vágvölgyi et al., 2008). The thermal decomposition of hydrotalcites carried out at a certain temperature results in a collapse of the layered structure. The resulting metal oxides are mixtures at the atomic scale, which are directly related to the arrangement of the metals in the hydrotalcite layers. Thanks to the memory effect, the calcined material can be reformed to a hydrotalcite-like structure upon treatment with water and anions (Rao et al., 1998; Roelofs et al., 2001; Erickson et al., 2004; Abelló et al., 2005). Recently, it was shown that microwave irradiation or sonication during aging in hydrotalcite synthesis provides materials with larger surface area and smaller particles compared to conventionally prepared materials (Bergadá et al., 2007).

For the analysis of phase transformations during thermal or chemical reactions, methods for in-situ analysis are more preferred than ex-situ methods to exclude effects of separation steps or sample preparation. For this reason TG-MS, in-situ XRD, XAFS, FTIR and Raman spectroscopy were used by several research groups to investigate the structural changes during thermal decomposition of hydrotalcites (Kanezaki, 1998a,b; Kloprogge and Frost, 1999; Millange et al., 2000; Van Bokhoven et al., 2001; Perez-Ramirez et al., 2001; Yang et al., 2002; Pérez-Ramirez et al., 2007a,b). However, detailed studies during the reformation process of calcined hydrotalcites back to layered structures are scarce (Millange et al., 2000; Rajamathi et al., 2000; Pérez-Ramirez et al., 2007a,b). In this study, in-situ XRD

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measurements were conducted to investigate phase transformations during calcination of hydrotalcites and gas phase hydration of the obtained metal oxides. Here, the main motivation is to point out how important it is to properly distinguish between terms like hydration and reconstruction. For this purpose a second way of transforming the mixed oxide back into a layered structure — namely reconstruction in a carbonate containing liquid phase — was applied, and the properties of the obtained layered material are compared with those of the gas phase hydration product.

2. Experimental

2.1. Hydrotalcite preparation

Synthetic hydrotalcite with the chemical formula $Mg_6Al_2CO_3(OH)_{16} \times H_2O$ (Ref. Pattern from Joint Committee on Powder Diffraction Standards 22-0700, JCPDS) was prepared by coprecipitation using two solutions (A) and (B). Solution (A) contained the desired amount of Mg and Al nitrates and solution (B) consisted of the precipitating agents NaOH and Na_2CO_3. Within 5 min the two solutions were added simultaneously into the reaction vessel while the pH was maintained at ca. 10 under vigorous stirring at 30 °C for 17 h by ultrasound. Finally, the sample was washed by dispersion in distilled water under gentle stirring followed by filtration. This washing/filtration step was repeated 5 times till the precipitate was free from sodium ions as confirmed from ICP analyses. The precipitate was dried under N_2 gas at 80 °C for 12 h. (LDH-DR).

For calcination the as-synthesized hydrotalcite sample was heated for 3 h at 450 °C in a muffle furnace (CA-450).

For reconstruction experiments in liquid phase the calcined hydrotalcite (CA-450) was stirred for 1 h in an aqueous solution of 1 M Na_2CO_3 at 25 and 70 °C, then filtered and dried at 80 °C over night (RC25 and RC70).

2.2. Characterization techniques

Elemental chemical analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES Plasma 400, Perkin Elmer, USA).

TG was carried out on Thermal Analyst type STD 2960 (TA instruments, USA). Samples weighing 10 ± 0.1 mg were heated up to 900 °C at 10 °C min^{-1} in a flow of 100 ml min^{-1} N_2 gas. A gas evolution mass spectrometer type Thermostar 2000 (BALZERS) was coupled to the exhaust pipe of the thermal analyses instrument.

X-ray powder diffraction (XRD) patterns were collected on a Philips X'pert Pro diffractometer operated at 40 kV and 40 mA using
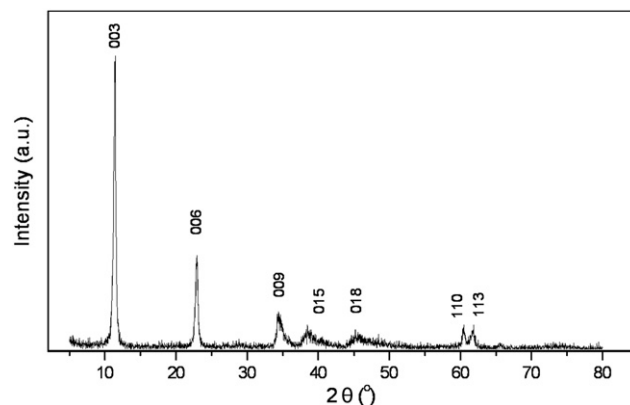

Fig. 2. XRD pattern of dried hydrotalcite (LDH-DR).

CuK_α radiation in the 2 theta range from 2 to 80° in steps of 0.02° with a sampling time of 1 s per step. An Anton Paar "XRC 900 Reactor Chamber" (Fig. 1) was used for in-situ XRD measurements. First, LDH-DR was heated in the XRC chamber at 1 K/min to 450 °C under a flow of dry nitrogen. Before each measurement, the respective temperature was kept constant for 10 min. Then, the calcined sample was cooled in dry N_2 to 30 °C and contacted with H_2O saturated nitrogen gas at 30 °C (100 ml min^{-1}) for the analysis of the hydration process.

Scanning electron microscopy (SEM) was used to study the morphology of some selected samples using ultra high resolution FESEM, model ULTRA55, Carl Zeiss MST AG, Germany.

3. Results and discussion

3.1. Elemental chemical analysis (ICP)

ICP analysis of LDH-DR was performed to determine its chemical composition. The analysis revealed that the Mg/Al molar ratio in the solid was 2.7, which is very close to the nominal molar composition of the pre-calculated Mg/Al molar ratio of 3 in the precipitate. This result confirmed the effectiveness of the precipitation process.

3.2. X-ray diffraction

X-ray powder diffraction patterns of dried hydrotalcite (LDH-DR) are shown in Fig. 2. The investigated solid was the typical crystalline
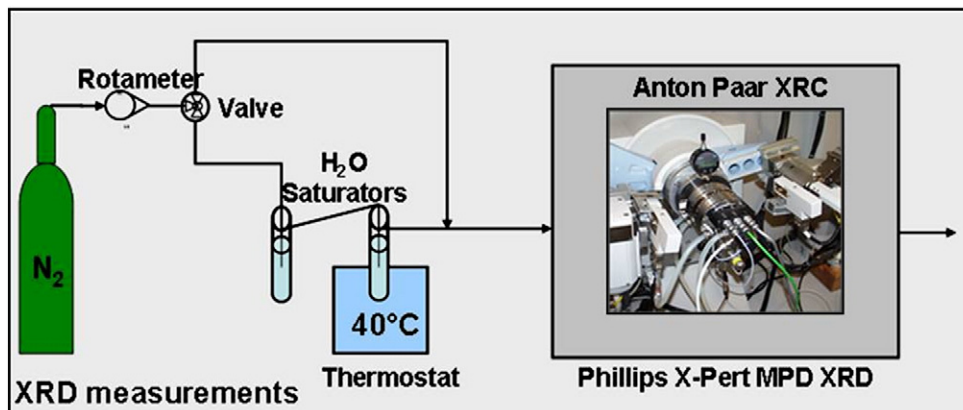

Fig. 1. Schematic drawing of the setup for hydration of LDH-CA using in situ XRD Anton Paar XRC 900 heating attachment (right).
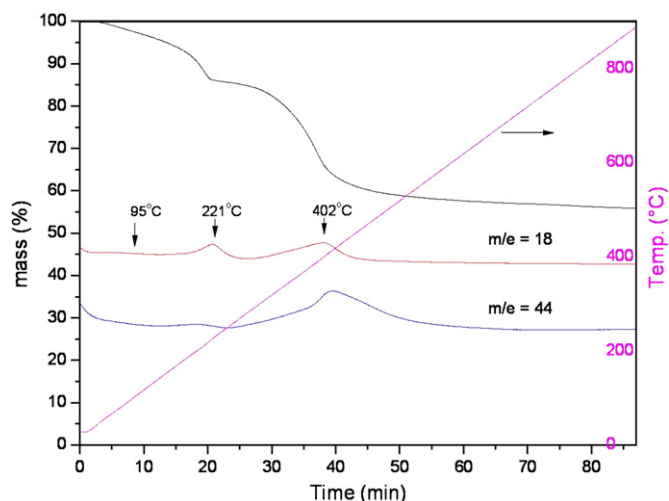
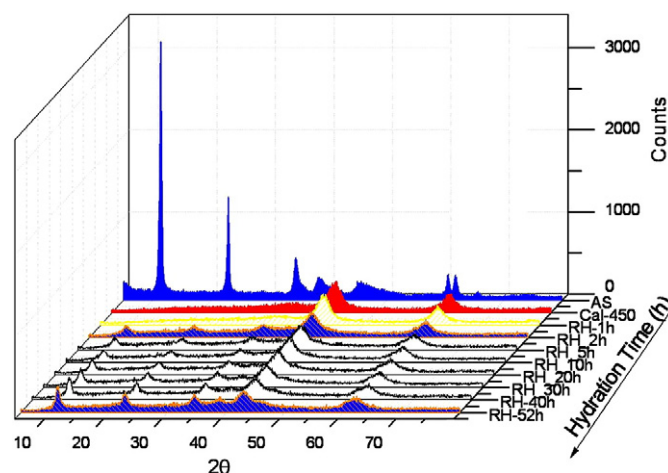Fig. 3. TGA thermogram of LDH-DR and corresponding MS signal profiles.

Fig. 5. In situ XRD patterns during the hydration of calcined LDH-DR at 30 °C in a flow of H_2O/N_2 (100 ml min^{-1}).

phase of a carbonate containing hydrotalcite (Ref. Pattern 22-0700, JCPDS) with sharp and intense (003), (006), (009), (110) and (113) reflections and broadened (015) and (018) reflections.

3.3. TG coupled with mass spectrometry

Mass spectrometry was used to identify the gases accompanying each mass loss stage of the thermogravimetric experiment. The mass signal (m/e) of 18 refers to water, m/e 44 shows carbon dioxide. Three main mass loss steps can be recognized for the hydrotalcite (LDH-DR) (Fig. 3): (a) a weak mass loss at 50–100 °C, which can be attributed to the loss of physisorbed water; (b) a sharp mass loss signal at 100–250 °C with maximum at 207 °C, which is mainly due to the loss of structural interlayer water (Di Cosimo et al., 1998; Tichit et al., 1998; Rocha et al., 1999; Pérez-Ramirez and Abelló, 2006); (c) a large mass loss between 250 and 600 °C (maximum at 385 °C) due to the evolution of H_2O vapor and CO_2, which confirms the dehydroxylation process of the brucite structure as well as the decomposition of carbonates in the interlayer space leading to the formation of metal oxides.

3.4. In situ XRD investigations

The in situ XRD patterns for the thermal decomposition of LDH-DR were collected in the temperature range 30–450 °C (Fig. 4).

At 200 °C the (006) and (009) reflections disappeared completely and the (003) reflection shifted to a higher 2θ value. The decrease in intensity of some reflections and the shift in the basal (003) reflection are evidence for the removal of interlayer water which results in the formation of a so-called intermediate dehydrated phase (Pérez-Ramirez et al., 2007a). The structure of this intermediate phase was retained up to 300 °C. The existence of reflections at 2θ values of 13.5 (003), 36 (009) and 60.4°, even after heating the solid up to 300 °C, proved the thermal stability of this phase. Heating above 300 °C resulted in disappearance of the basal reflection (003) and formation of an amorphous structure. Between 350 and 450 °C, crystallization of MgO (periclase: Ref. Pattern 45-0946, JCPDS) was observed. This behavior could be attributed to the dehydroxylation of the brucite like layers and the removal of the interlayer anions (CO_3^{2-}) as observed during the thermogravimetric measurement.

The gas phase hydration of the calcined hydrotalcite back into a layered structure was also investigated by in situ XRD. The XRD patterns for the hydration process at 30 °C after different time intervals are given in Fig. 5.
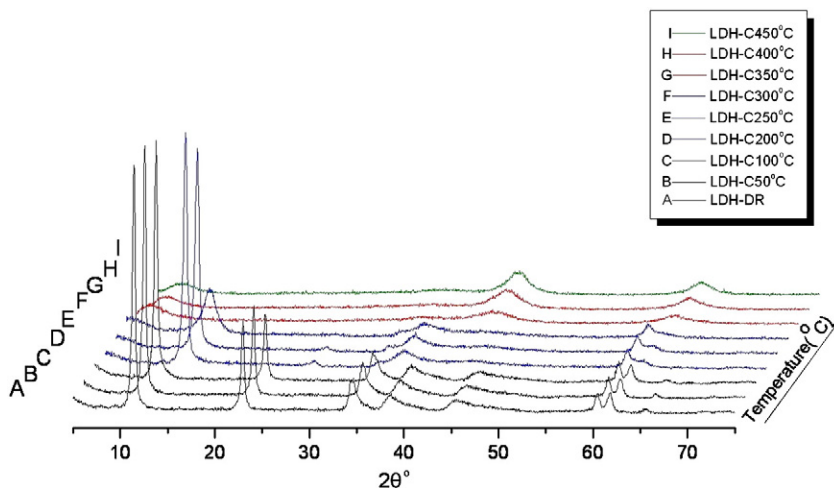

Fig. 4. In situ XRD patterns of as-synthesized hydrotalcite at different calcination temperatures.
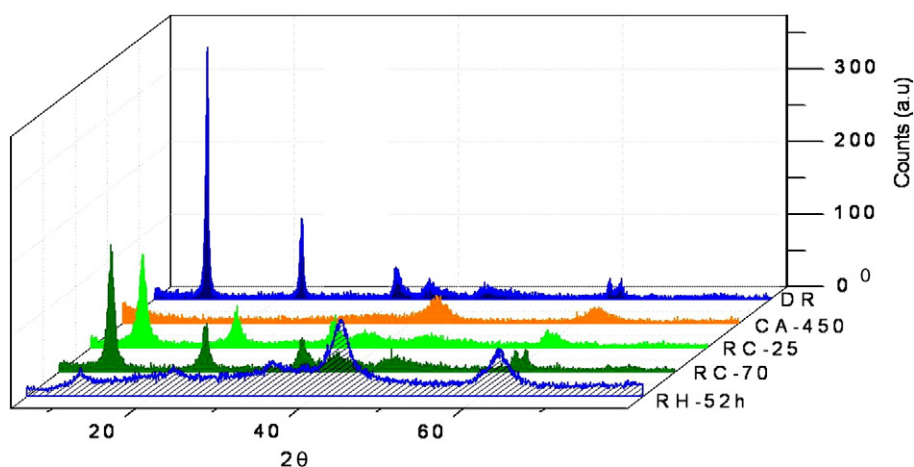
Fig. 6. XRD patterns of original (DR), calcined (CA-450), reconstructed (RC-25 and RC-70) and hydrated (RH-52h) hydrotalcite phase.

The reference pattern of dried hydrotalcite LDH-DR is recorded first (AS), followed by the pattern of the calcined product (CAL-450). XRD patterns of the calcined product represent periclase. At 30 °C the metal oxide transformed gradually into meixnerite. The characteristic XRD pattern (Mineralienatlas, 2009) appeared already after 2 h exposure to the H_2O saturated N_2 atmosphere. The intensity of the meixnerite phase (see pattern 'RH-52h') increased with the time of exposure to water vapor. However, the XRD pattern of the reformed structure ('RH-52h') did not fully match that of the initial hydrotalcite ('AS'). Due to the decreased structural order, the pattern of the meixnerite phase showed broader reflections of less intensity, and the (110) and (113) reflections of the original hydrotalcite disappeared. In contrast to the original hydrotalcite, containing mainly carbonate ions as charge balancing anions, the layer charge in meixnerite was only compensated by hydroxyl ions (Mineralienatlas, 2009).

Since a new structure (meixnerite) was obtained and no recovery of the original chemical composition was achieved, the formation of meixnerite by contacting the mixed oxide with water is a hydration process. Thus, contrary to the literature (Pérez-Ramirez et al., 2007a) the word *rehydration* should only be used to describe the reverse reaction of dehydration processes like the transformation of the intermediate dehydrated phase back into the originally composed material. The formation of meixnerite by contacting the mixed oxide with water is a *hydration* process since a new material is obtained and no recovery of the original composition is achieved. In contrast to this, the word *reconstruction* can be used to describe the reaction of the mixed oxide obtained by calcination of a carbonate containing hydrotalcite-like material with carbonate containing water to regenerate the material in its original composition and structure. In order to confirm our suggestion for the right definition of these processes, we also studied
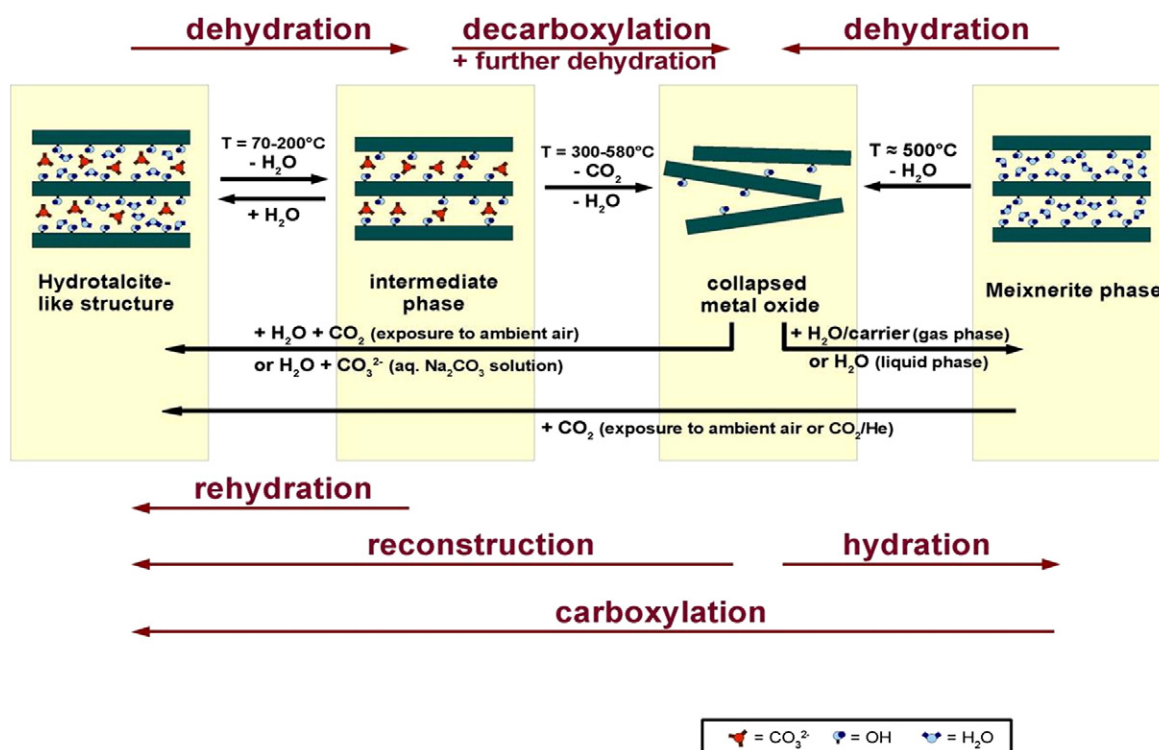

Fig. 7. Schematic overview of structural and compositional transformation processes during thermal or chemical reaction of Mg–Al hydrotalcite-like materials and Mg–Al mixed oxides.
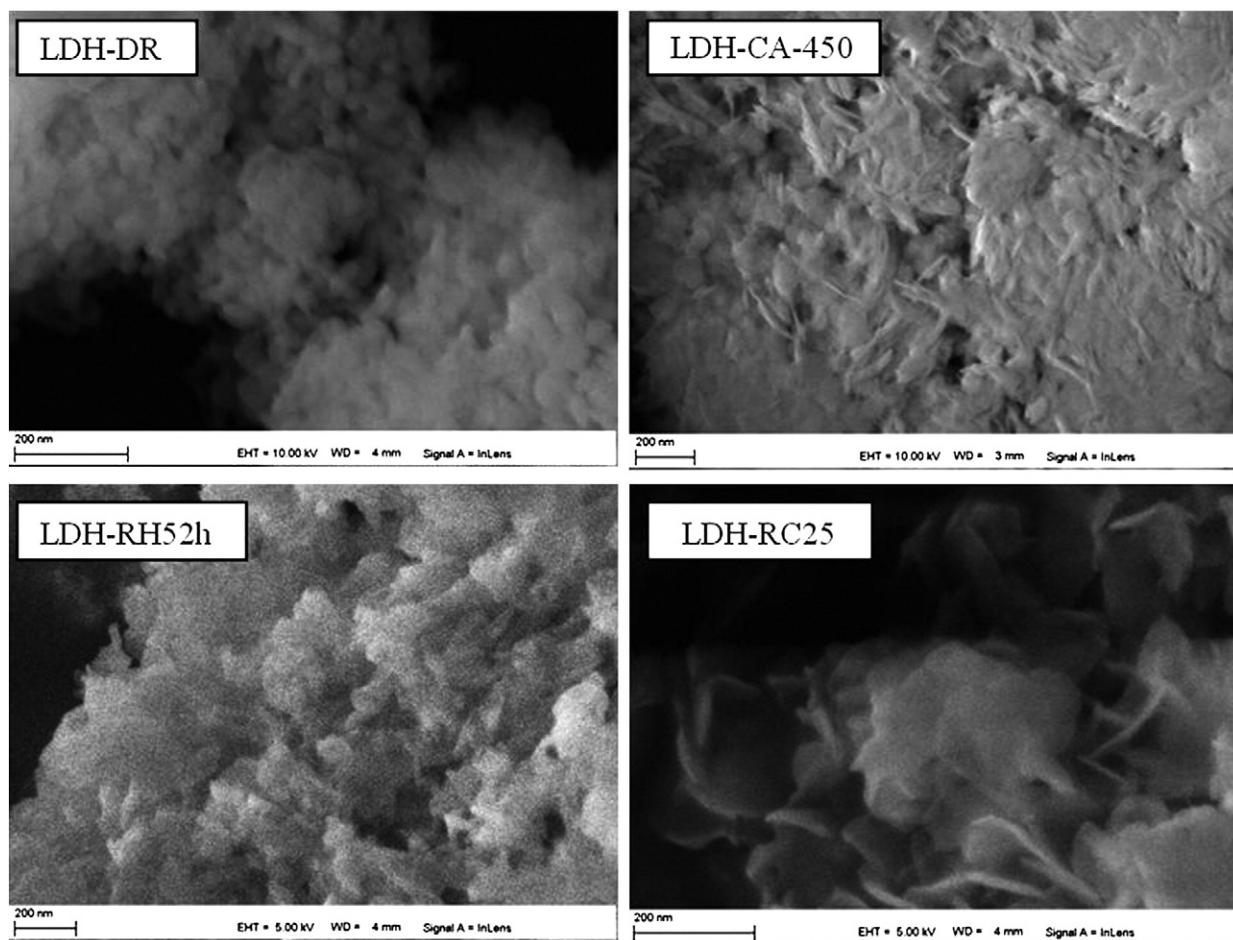
Fig. 8. SEM images of investigated materials.

the reconstruction of calcined hydrotalcite in carbonated water (liquid phase) at two different temperatures of 25 and 70 °C.

Fig. 6 represents the XRD patterns of the reconstructed hydrotalcites. The original hydrotalcite structure (Fig. 6, 'DR') was completely regenerated in both cases ('RC-25' and 'RC-70'), and the intensity of the hydrotalcite pattern increased with the temperature of the carbonated water. These results for liquid phase reconstruction are in good agreement with the findings of Kloprogge and Frost (1999). The fast and complete reconstruction can be explained by the efficient wetting of metal oxide surfaces by sodium carbonate solution. A comparison of the reconstructed phase with the hydrated phase was important to clarify our idea of nomenclature. As seen in Fig. 6, there were significant differences between the XRD patterns of the layered material obtained from the mixed oxide phase either by contacting it with water vapor (hydration, 'RH-52h') or Na$_2$CO$_3$ solution (reconstruction, 'RC-25', 'RC-70'). This proves that the proposed terminology is useful and important to distinguish between these reactions (Fig. 7).

In Fig. 7 are also given the experimental conditions for the transformation steps found in the literature (Rajamathi et al., 2000; Prinetto et al., 2000; Abelló et al., 2005; Kustrowski et al., 2006; Chimentao et al., 2007; Angelescu et al., 2008) and the temperatures of Mg–Al LDH decomposition obtained by in-situ XRD investigations of our and other research groups (Yang et al., 2002; Pérez-Ramirez et al., 2007a,b).

3.5. SEM

SEM images (Fig. 8) of the dried hydrotalcite (LDH-DR) showed particles aggregation with lateral size 20–40 nm. The SEM micrograph

of the calcined hydrotalcite phase (LDH-CA) revealed the collapsed layer structure. The 52 h hydrated hydrotalcite and reconstructed hydrotalcite at 25 °C showed layered platelets. The appearance of such layers indicated the rebuilding of the layered structure by hydration and reconstruction of the 'collapsed' calcined phase and supported the information from the XRD measurements.

4. Conclusions

In-situ XRD measurements provided direct evidence for phase transformation processes during calcination at different temperatures and hydration of the calcined materials (Mg–Al mixed oxides). Hydrotalcites formed an intermediate dehydrated phase at 200 °C. This phase was stable up to ca. 300 °C before its decomposition led to the formation of periclase at 450 °C. The gas phase hydration of the calcined hydrotalcite yielded a less ordered hydrotalcite-like phase (meixnerite). In contrast, reconstruction of Mg–Al mixed oxides in 1 M Na$_2$CO$_3$ solution at 25 and 70 °C led to a properly reformed carbonate containing hydrotalcite. Because of these structural and compositional differences resulting from different reformation procedures for the layered structures, it should be well distinguished between the terms *hydration, rehydration* and *reconstruction*. The term *hydration* should be related to the reaction of the calcined hydrotalcite with water in gas or liquid phase, whereas the term *reconstruction* should only be applied in cases where the reaction of the calcined hydrotalcite recovered not only the layered structure but also the original chemical composition of the hydrotalcite-like material. The word *rehydration* should only be used for processes where a structure is reconstructed into the original material by hydration. This is not the

case when a meixnerite phase is created by hydration after calcining a carbonate containing LDH material.

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