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

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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.

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

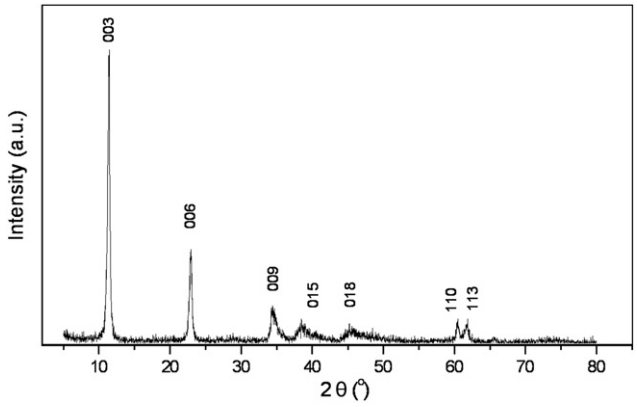

Fig. 2. XRD pattern of dried hydrotalcite (LDH-DR).

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

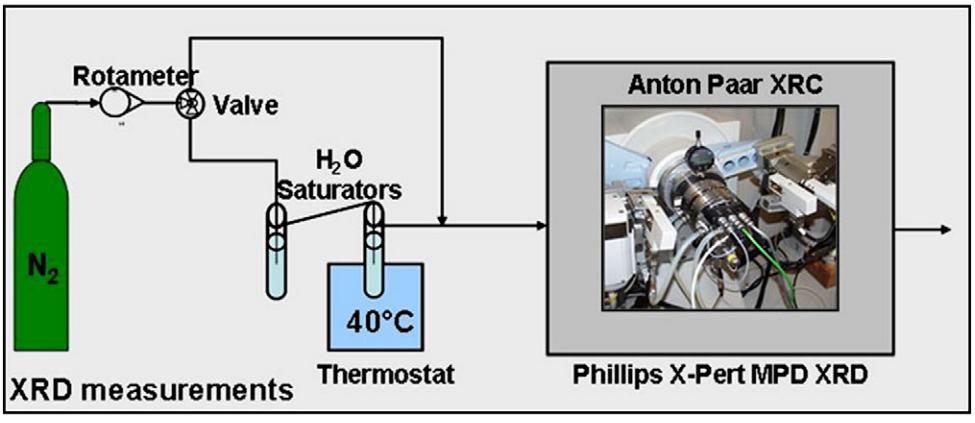

Fig. 1. Schematic drawing of the setup for hydration of LDH-CA using in situ XRD Anton Paar XRC 900 heating attachment (right).