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Thermal decomposition kinetics of MgAl layered double hydroxides

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ABSTRACT

Structural, thermal profiles and kinetic behavior of two different sol–gel samples of MgAl layered double hydroxides (LDHs) were studied. In situ FT-IR study was used to follow the chemical composition changes, and thermal evolution of specific chemical species in each stage was monitored with a dynamic sampling mass spectrometer (TPD-MS analysis). The identified gas products were mainly OH, H_2O, CO_2, and organic species, mainly C_2H_5, originated from the alkoxy groups. The thermal evolution of intercalated compounds occurred in at least four steps related to dehydration, dehydroxylation of layers, interlayer anion decomposition, shrinkage and collapse of the layered structure, and finally crystallization of spinel $MgAl_2O_4$. Kinetic analysis in terms of activation energy (*Ea*), suggest that decomposition mechanism is a complex process that involves decomposition of several species and phase transformations.

1. Introduction

In the past decades, layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, have received much attention due to their versatility and vast applicability [1–3]. The basic structure of an LDH may be derived from that of brucite, $Mg(OH)_2$, where Mg-OH octahedra share edges to form infinite layers (see Fig. 1a and b). An LDH is created by partial isomorphous substitution of a fraction of M^{2+} cations by M^{3+} cations, such that the layer acquires a positive charge. The resulted charge is electrically counter balanced by anions located in the interlayer region along with hydration water molecules. Given that, a variety of compounds with basic LDH structure may be prepared, which are represented by the general formula $[M_{(1-x)}{}^{2+}\ M_x{}^{3+}\ (OH)_2]\ A_{x/n}{}^{n-}\cdot mH_2O$, where the divalent and trivalent cations may be Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, etc., x is the trivalent cation substitution degree, and takes values in the range $0.2 \leq x \leq 0.33$, and A^{n-} may be almost any organic or inorganic anion [1–3].

LDHs have found a wide range of applications as flame retardants, antacids, PVC additives, hybrid composites, drug delivery carriers, etc. [1–3]. Furthermore, calcination of LDHs yields a mixed oxide, where MgO is the only phase detected by XRD. Lattice constant a is smaller than that of pure MgO, indicating the incorporation of smaller Al^{3+} cations; thus, this phase is commonly denoted as Mg(Al)O. This solid solution presents Lewis basicity, relatively large specific surface area and thermal stability; therefore, these materials have been widely studied as catalysts or catalyst precursors in numerous chemical reactions [4–7]. Also, for this reason, the structural changes that take place during thermal treatments and the decomposition mechanisms of LDHs are the object of several investigations [8–15].

Traditionally, LDHs are synthesized by the coprecipitation method [1], in some cases followed by hydrothermal, ultrasound or microwave treatments in order to modify the physicochemical properties of the material [16,17]. Several alternative methods have been reported, the suitability of which depends on the intended application. Among these are included the urea hydrolysis method [17,18], the decoupling of nucleation and aging methodology [19], an environmentally friendly method for large scale production [20], and the sol–gel method [15,21–24]. For certain applications, the sol–gel method presents several advantages, as it is a simple way to obtain colloidal particles, which may be easily cast as thin films. The conditions throughout the process are mild, enabling an eventual intercalation of delicate organic molecules. Furthermore, morphology, particle size and crystallinity are readily controlled by appropriate hydrothermal treatments, allowing fundamental studies that yield information about LDH properties that are not easily observed by other synthetic procedures [14,22].

Regardless of the extensive studies on the layered double hydroxides (LDHs), only a few studies have been focused on the kinetic processes taking place during the thermal decomposition of MgAl LDHs [25–28]. Accordingly, in the present study, the combination of Hi-Res/modulated TGA analysis, X-ray diffraction, electron microscopies (TEM and SEM), in situ FT-IR spectroscopy and TPD-mass spectrometry were used to investigate the thermal decomposition mechanisms and the kinetics of the transformation

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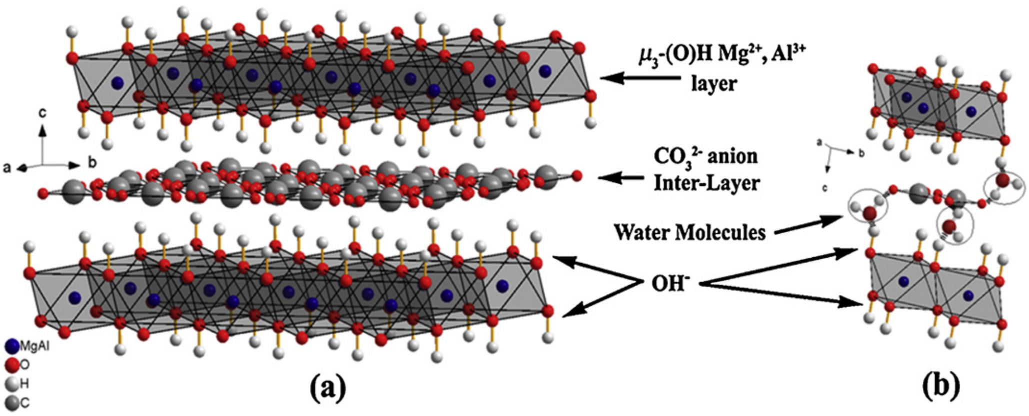

Fig. 1. (a) Schematic representation of LDHs structure; (b) detailed schematic view of some physisorbed water molecules within layers. Bonds represented as discontinuous tries to depict the hydrogen bond interactions.

from LDH to Mg(Al)O mixed oxide. With the purpose of correlating the crystal morphology to kinetic behavior, two dissimilar samples were selected: one having very small crystallites with nanocapsular morphology, which has mainly organic species as charge-compensating anions, and a second sample, which is prepared following the same methodology, but submitted to a hydrothermal treatment, and thus has carbonate as main charge-balancing anion, large crystallites and the traditional platelet morphology of LDHs.

2. Experimental part

2.1. Synthesis procedure

The synthesis procedure has been reported previously [15,22,23]. Briefly, LDHs were prepared by dissolving aluminum tri-*sec*-butoxide (ATB) in ethanol at 70 °C under constant stirring for 1 h. Nitric acid (3 N) was then added dropwise. After 1 h, the system was taken to room temperature and acetic acid (AA) was added to complex the aluminum alkoxide. One hour later, the temperature was lowered to 0 °C, and magnesium methoxide was added dropwise. The system was stirred for 24 h at room temperature, and finally deionized water was added. The sample obtained after drying this sol at 70 °C overnight is named MgAl-E. For the preparation of sample MgAl-TH1-W, after the aforementioned synthesis procedure was completed, the sol was placed in a sealed digestion bomb. A 50 vol.% excess of bidistilled water was added, and the gel was hydrothermally treated at 120 °C under autogenous vapor pressure for 24 h. The molar ratios of reactants were ATB:EtOH = 1:60, ATB:HNO_3 = 1:0.03, ATB:AA = 1:1, M^{2+}:M^{3+} = 3:1, ATB:H_2O = 1:1. The Mg/Al molar ratio, as determined by inductively coupled plasma atomic emission spectrometry, was 2.8 and 2.6 for MgAl-E, and MgAl-TH1-W, respectively.

2.2. X-ray diffraction (XRD)

The XRD patterns of the samples were measured in a θ–θ Bruker D-8 Advance diffractometer with Cu Kα radiation, a graphite secondary-beam monochromator, and a scintillation detector. Diffraction intensity was measured between 4 and 80°, with a 2θ step of 0.02° and a counting time of 9 s per point.

2.3. Electron microscopies (TEM and SEM)

Samples were analyzed through transmission electron microscopy (TEM) in a JEOL JEM-2200FS with a Schottky-type field emission gun, operating at 200 kV. Samples were dispersed in ethanol before placing them on Lacey Formvar carbon coated copper grids. Digital images were obtained using a CCD camera and Digital Micrograph Software from GATAN, Inc.

Scanning electron microscopy (SEM) analysis was carried out in a Philips XL30 ESEM with an acceleration voltage of 25 kV. Prior to analysis, the samples were covered with gold and were subsequently mounted on aluminum stub over double coated carbon film.

2.4. Thermal analysis (TGA–DTA)

Thermal decomposition study of MgAl LDHs was carried out in a simultaneous TGA–DTA (SETARAM, SETSYS 12) apparatus. In order to mitigate the difference of heat and mass transfer, the sample mass was kept at ~22 mg. The samples were heated from room temperature up to 700 °C, using a high-purity nitrogen atmosphere and a flow rate of 30 mL $\min^{-1}$, at atmospheric pressure. Simultaneous TGA–DTA measurements were performed at different heating rates of 2.5, 5 and 10 °C $\min^{-1}$ and the DTG data collected at different heating rates were used to estimate the activation energy involved in each stage and its dependence on the degree of reaction extent α.

2.5. Modulated heating rates (Hi-Res/modulated-TGA analysis)

The experiment was implemented using a thermogravimetric Analyzer Q5000 IR by TA Instruments, Inc. (USA). The sample (about 10 mg) was placed in an open ceramic pan of Al_2O_3 and heated from room temperature to 600 °C at a heating-rate of 2 °C $\min^{-1}$, under a high-purity nitrogen flow of 25 mL $\min^{-1}$ with temperature perturbation amplitude of ±3 °C and a period of 200 s. Precision on temperature measurements is not worse than ±0.1 °C. The resulting TGA curve was analyzed using TA Instruments, "Universal Analysis" program to obtain the activation energy of each process across the entire weight loss for the samples.

2.6. Infrared spectroscopy (FT-IR)

The in situ IR (FT-IR) spectra for both samples (MgAl-E and MgAl-TH1-W), were recorded on a Nicolet, Magna-IR 560 Fourier transform spectrometer using a Harrick, Praying Mantis diffuse reflectance (DRIFT) accessory, equipped with a high temperature cell. The changes as a function of temperature in the solid of hydrotalcite were studied in situ in nitrogen atmosphere (20 mL $\min^{-1}$). For each sample, 50 scans were recorded in the range 4000–500 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were