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Thermal evolution of V(III)-containing layered double hydroxides

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Abstract

A study is reported on the thermal evolution of Mg, V layered double hydroxides with interlayer carbonate anions and different Mg/V molar ratios (from 1 to 4). Decomposition in O_2 occurs at lower temperature than that in N_2; the stability of the layered structure decreases as the V content increases. Oxidation of layer V^{3+} cations occurs in the same temperature range as dehydroxylation and decarbonation. The nature of the crystalline phases formed upon calcination at high temperatures strongly depends on the Mg/V molar ratio in the initial solid.

Keywords: Hydrotalcite; Layered double hydroxides; Thermal properties; Magnesium vanadium oxides

1. Introduction

Layered double hydroxides (LDHs), one of the few families of layered materials with positive layers and negative species in the interlayers, are deserving increasing interest in recent years, probably because the wide scope of applications which are continuously emerging for these and derived materials: catalysis, adsorption, anionic exchange, electroactive materials, water purification, etc. [1,2]. The origin probably lies on the rich chemistry which they show, related to their peculiar structure: isomorphous, partial substitution of M^{2+} cations in brucite-like layers by trivalent cations, and simultaneous intercalation of anions in the interlayer space to balance the electric charge. The wide possibilities with regards to the nature of the layer cations, as well as to the interlayer anions, should be in the origin of this interest [3]. The most outstanding properties can be summarized as follows: (i) metal ratio in the layers is similar to that in the starting solution; (ii) easily oxidizable cations are, however, stabilized in the layers; (iii) solids can be prepared with a given cation in different oxidation states and different environmental geometry; (iv) solids with many different metal cations, well dispersed in the anion matrix can be obtained.

Upon calcination, these solids lead to formation of mixed oxides whose chemical composition can be easily tuned when preparing the parent LDH, and depending on the decomposition process and even on the precise composition of the starting material, different crystalline species can be obtained. However, LDHs calcined at intermediate temperatures are usually amorphous. The specific surface area increases with the calcination temperature (if volatile anions exist in the interlayer space), then reaching a maximum and decreasing at higher temperatures, when crystallization also occurs [4,5]; the change in the strength of surface acid/base sites, and the modification in the hydrothermal stability with respect to similar compounds (e.g. MgO) have been also reported [6,7]. Although many studies have been reported on the thermal evolution of LDHs containing

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non-oxidizable cations in the layers, and many studies refer to the particular case of hydrotalcite (containing Mg^{2+} and Al^{3+}, with carbonate in the interlayer) [8–11], few studies have been reported on systems where thermal decomposition takes place simultaneously with oxidation processes, thus, deeply modifying the nature of the crystalline species finally formed [12]. In this study, we report on the thermal decomposition of a Mg/V LDH, as followed by differential thermal analysis (DTA) and thermogravimetric analysis (TG); differential thermogravimetric analysis (DTG) is also performed.

2. Experimental

2.1. Samples preparation

The samples were prepared following a method similar to that described by Reichle [13], i.e. coprecipitation at constant pH of Mg^{2+} and V^{3+}, by adding chloride solutions of these cations to a solution containing sodium hydroxide and carbonate. The molar Mg/V ratios were kept to values of 1–4. The solids obtained were washed until total elimination of sodium and chloride, and submitted to hydrothermal treatment at 120°C for 7 days in Teflon lined stainless steel bombs. Samples are named as *X*MgV1, where *X* stands for the nominal Mg/V molar ratio.

2.2. Characterization

Samples have been characterized by elemental chemical analysis, powder X-ray diffraction and Fourier-transform infrared spectroscopy, and the results have been given elsewhere [14]. Thermal analyses have been carried out using a differential thermal analyzer DTA7 and a thermogravimetric analyzer TGA7, both from Perkin-Elmer; the curves have been recorded in O_2 or N_2 (from L′Air Liquide, Spain) at a heating rate of 10°C/min.

3. Results and discussion

The formulae of the LDHs prepared, as calculated from elemental chemical analysis for metal cations and from thermogravimetric analysis for interlayer water content, are given in Table 1. The molar Mg/V ratios measured were acceptably similar to those for these cations in the original water solutions. The powder X-ray diffraction diagrams [14] confirm their layered structure, lattice parameters (*a* and *c*) being also included in Table 1, the only crystalline species detected correspond to the so-called hydrotalcite structure, $[Mg_{1-x}V_x(OH)_2](CO_3)_{x/2}\cdot nH_2O$. According to the FT-IR data, the only interlayer anion was carbonate, which became distorted through interaction with the interlayer water molecules and layer hydroxyl groups, thus, decreasing its symmetry from D_{3h} for the free anion, thus, activating mode ν_1, while visible-ultraviolet spectra, recorded using the diffuse reflectance technique, confirmed the presence of V^{3+} ions (d^2) in an octahedral environment; the amount of possibly oxidized V^{n+} ($n > 3$) species was below the detection limit of the techniques used. No major differences were found when the samples were submitted to hydrothermal treatment, but only an improvement in their crystallinity degrees.

As expected, the thermal behavior of these LDHs containing oxidizable V^{3+} cations depends on the nature of the atmosphere surrounding the sample during the analysis. As an example, Fig. 1 includes the DTA traces recorded for sample 2MgV1 in oxygen and in nitrogen. The DTA curves are very different: while in nitrogen two endothermic effects are recorded, a single one, at a slightly lower temperature than the first effect recorded in nitrogen, is recorded in

Table 1
Formulae, lattice parameters (Å) and carbonate FT-IR bands for the samples studied

Sample	Formula	*c*	*a*	ν (CO_3^{2-})
1MgV1	$[Mg_{0.52}V_{0.48}(OH)_2](CO_3)_{0.24}\cdot 0.86H_2O$	22.66	3.06	1509-1421-1360, 855, 692
2MgV1	$[Mg_{0.72}V_{0.28}(OH)_2](CO_3)_{0.14}\cdot 0.83H_2O$	23.48	3.10	1483-1368, 1058, 851, 670
3MgV1	$[Mg_{0.76}V_{0.24}(OH)_2](CO_3)_{0.12}\cdot 0.78H_2O$	23.58	3.12	1510-1383, 1050, 867, 687
4MgV1	$[Mg_{0.80}V_{0.20}(OH)_2](CO_3)_{0.10}\cdot 0.68H_2O$	23.70	3.12	1453-1385, 878, 675

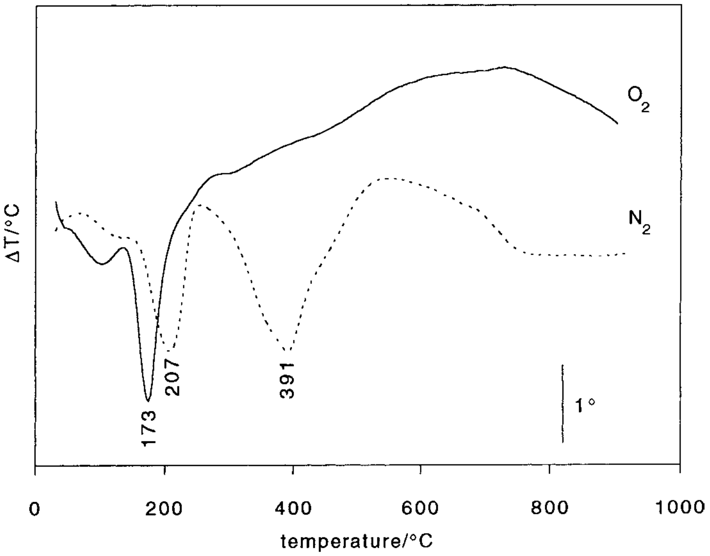

Fig. 1. DTA traces for sample 2MgV1 recorded in O_2 and in N_2. The positions of the minima are given in °C.

oxygen. This behavior has been already reported for LDHs containing Mg^{2+} and V^{3+} [15]; the two endothermic effects in the trace recorded in N_2 is in agreement with a dehydration (first endothermic effect, removal of interlayer water molecules) and dehydroxylation of the layers simultaneous to removal of interlayer carbonate as CO_2, respectively. This is the behavior commonly expected for decomposition of a hydrotalcite containing exclusively non-oxidizable cations in the layers [8,16–18] and the nature of the gases evolved at the different temperature ranges has been checked by gas chromatography, mass spectrometry and temperature-programmed desorption [17,19,20].

With respect to the trace recorded in oxygen, the behavior observed is generally attributed to the oxidation of V^{3+} to V^{5+} species (as oxovanadates are usually identified in the crystalline phases formed above this temperature), an exothermic process taking place simultaneously to collapsing of the layered structure due to dehydroxylation and decarbonation [15]. The extremely weak, rather broad effect recorded at ca. 100°C is probably due to removal of water physisorbed on the external surface of the crystallites.

The weight loss corresponding to the first endothermic effect is generally used to quantify the amount of interlayer water, and the value is close to 15% of the initial sample weight [1,2,21,22], changes being usually attributed to the drying of the sample; also, although in a minor extent, the M^{2+}/M^{3+} ratio could have a small effect on the water content: as this ratio decreases, more and more anions are needed in the interlayer space, thus, decreasing the space available to accommodate water molecules [1,2].

The DTA and TG-DTG traces, recorded in oxygen, for all four samples studied, are included in Figs. 2 and 3. As expected from its chemical composition (extremely large vanadium content), sample 1MgV1 shows a behavior rather different to those of the other samples. First of all, the endothermic effect recorded below 200°C and commonly ascribed [8,11] to removal of physisorbed and interlayer water, is very broad, and seems to be composed of, at least, two overlapped effects, with minima at 122 and 153°C. Between 400 and 600°C, two exothermic effects are recorded at 505 and 575°C and, finally, a weak, but detectable, endothermic effect is recorded at 750°C. The corresponding TG curve shows a large, continuous, weight loss, amounting 29% of the initial sample weight, with two steps at 472 and 572°C, according to the DTG traces, which should correspond to the exothermic effects. However, the endothermic effect recorded in the DTA curve at 750°C has no counterpart in the TG curve, suggesting it corresponds to a melting or phase change process.

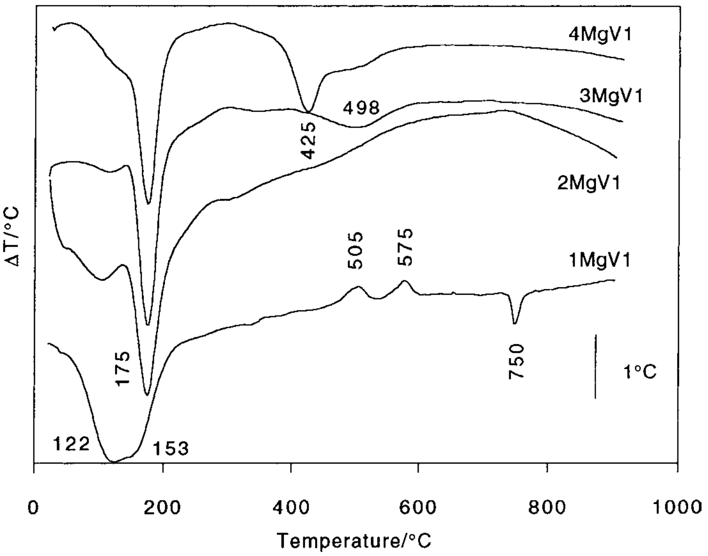

Fig. 2. DTA traces of the samples studied, recorded in O_2.

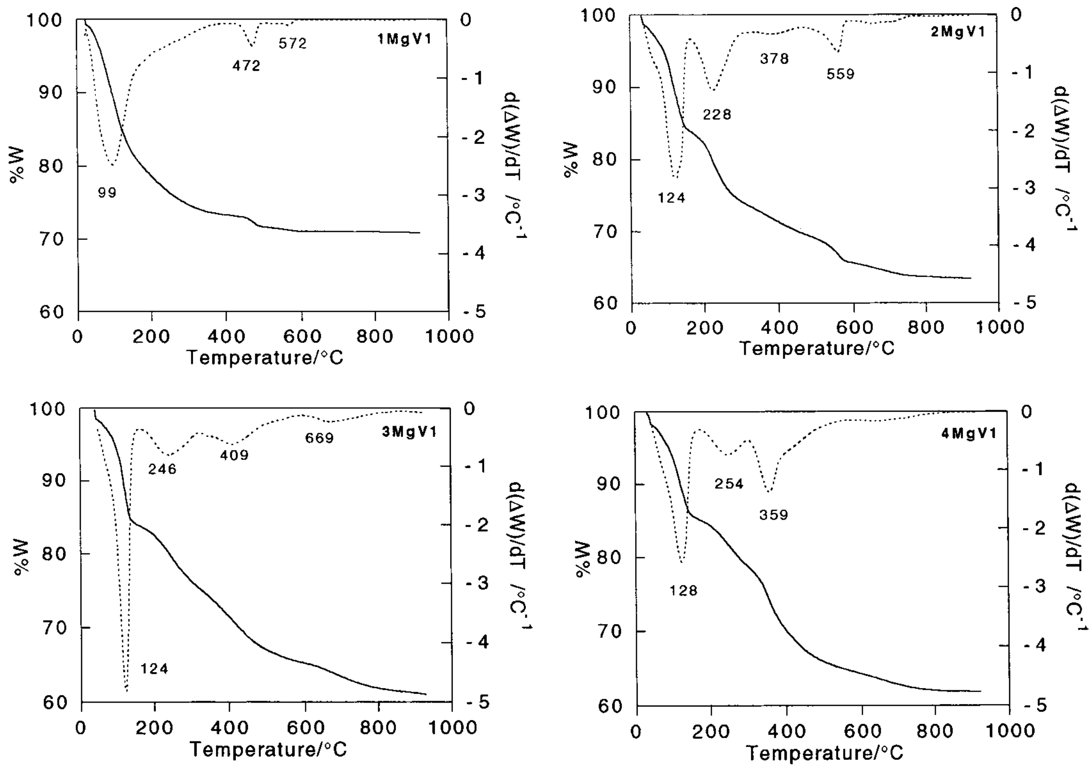

Fig. 3. TG (solid lines) and DTG (dotted lines) traces of the samples studied, recorded in O_2.

The traces are, however, rather similar for the remaining samples. The main endothermic effect is recorded at 175°C for all three samples and it is markedly sharp, although a broad, weaker, effect is still recorded, and probably corresponds to physisorbed water. The exothermic effects between 500 and 600°C have vanished, as well as the endothermic effect at 750°C. Although the curve for sample 2MgV1 does not show any additional effect to the endothermic one due to water release, a broad, weak effect at 498°C is recorded for sample 3MgV1, which remains for sample 4MgV1, but in this case with a medium intensity endothermic effect at 425°C. The behavior shown by this last sample is rather similar to what one would expect for a "normal" LDH with interlayer carbonate anions, the first peak being due to removal of interlayer water, and the second, complex, effect, due to decarbonation and dehydroxylation of the layers.

The TG traces are also rather similar (Fig. 3). That for sample 2MgV1 (total weight loss 36%) still shows, but weaker, a step at ca. 550°C, and consecutive steps at lower temperatures can be envisaged from the DTG curve. The TG traces for samples 3MgV1 and 4MgV1 (total weight loss 39 and 38%, respectively) show also such features, but the step close to 550°C has disappeared.

The behavior observed is in agreement with the presence of several consecutive endothermic processes, i.e. dehydration, dehydroxylation and decarbonation. Simultaneously, V^{3+} cations become oxidized (an exothermic process) when the layered structure is destroyed, thus, coinciding in the same temperature range where dehydroxylation and decarbonation occur. Consequently, in samples where the amount of vanadium is appreciable, the exothermic effect cancels the endothermic one corresponding to dehydroxylation/decarbonation. When the vanadium content is decreased, the oxidation process becomes relatively weaker, and the endothermic effects are clearly detected.

In addition, the presence of a large amount of vanadium favors crystallization of phases at temperatures lower than for other samples where the Mg/V ratio is larger [14], thus, accounting for the exothermic effects at 505 and 575°C in the DTA curve for sample 1MgV1. For a Mg:V molar ratio close to 1 (as in sample 1MgV1) it is impossible to locate isolated $V(OH)_6$ octahedra, which should be consequently sharing edges with neighbor $V(OH)_6$ octahedra, thus, introducing an additional instability in this structure, which collapses at lower temperature than the other samples studied.

Total weight losses were 29–38%, depending on the precise sample studied. These values are in agreement with formation of MgO and V_2O_5, ($[(1-x)\mathrm{MgO} + (x/2)\mathrm{V_2O_5}]$, from the general formula for these compounds) at the maximum temperature reached (where the TG curve approaches to an horizontal line), or any combination of both yielding a magnesium vanadate.

The nature of the crystalline species formed after calcination at some temperatures has been followed by PXRD. The results are summarized in Table 2. Again, the Mg/V molar ratio has an important effect on the nature of the phases formed. So, for the V-richest sample crystallization of monoclinic $Mg_2V_2O_7$ is observed at 550°C, changing to the triclinic phase at 800°C. Again, the V-rich sample behaves different to the other samples studied, for which only amorphous species can be detected upon calcination at 200 or even at 550°C. Crystallization of new phases is observed only after calcination at 800°C, developing $Mg_3(VO_4)_2$ in all three cases, together with MgO in samples 3MgV1 and 4MgV1. These results indicate that, on one hand, the Mg/V ratio somewhat controls the stoichiometry of the phases formed, from $Mg:V = 1$ in $Mg_2V_2O_7$ for sample 1MgV1, to $Mg:V = 1.5$ in the other samples; seggregation of MgO, above the stoichiometric amount of Mg to react with vanadium ions, is observed in 3MgV1 and

Table 2
Crystalline phases detected by powder X-ray diffraction in the calcined samples

Calcination temperature (°C)	1MgV1	2MgV1	3MgV1	4MgV1
200	HT[a]	Amorphous	Amorphous	Amorphous
550	$Mg_2V_2O_7$ monoclinic	Amorphous	Amorphous	Amorphous
800	$Mg_2V_2O_7$ triclinic	$Mg_3(VO_4)_2$	$Mg_3(VO_4)_2$+MgO	$Mg_3(VO_4)_2$+MgO

[a] HT: hydrotalcite.

4MgV1. But, in addition, the presence of large amounts of vanadium favors crystallization processes at temperatures lower than for the other samples.

The nature of the phase formed upon calcination at 200°C of sample 1MgV1 is not, however, definitive. The diffractogram seems to correspond to a layered species, but the spacing for the first basal plane is too low to permit location of carbonate ions between the brucite-like layers, even if the sample is assumed to be completely dehydrated. Similar results have been reported previously for hydrotalcites with intercalated oxometalates [23–26], and even for carbonate-containing hydrotalcites [11]. Carbonate should not have been removed at this rather low temperature, as it can be concluded from the FT-IR spectrum of this sample, which shows the absorption close to 1400 cm^{-1} due to mode ν_3 [27].

4. Conclusions

Thermal decomposition of layered double hydroxides with the hydrotalcite-like structure possessing V^{3+} cations in the layer is extremely sensitive to the Mg:V ratio, as well as to the atmosphere during decomposition. A large V content enhances thermal decomposition, due to the high stability of the mixed oxides and, probably, to the rather metastable situation originated by the presence of edge-sharing $[V(OH)_6]$ octahedra in the brucite-like layers. Overall, decomposition follows the same trend previously reported for other LDHs, with a first, endothermic effect corresponding to removal of physisorbed and interlayer water. A second endothermic effect, due to dehydroxylation and decarbonation, is clearly observed when the analysis is performed in an inert atmosphere (e.g. nitrogen), but in oxygen the simultaneous exothermic oxidation of V^{3+} to V^{5+} cancels the endothermic effect for large V^{3+} contents, which is exclusively recorded for low V contents. Weight losses are in agreement with these interpretations.

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