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Thermal decomposition products of hydrotalcite-like compounds: low-temperature metaphases

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Synthetic hydrotalcite-like samples with composition $[M^{2+}_{1-x}Al^{3+}_x(OH)_2](CO_3)_{x/2}\cdot nH_2O$, where M = Mg, Ni, $x = 0.25$ and 0.33, $n = 2x$ and $1.5x$, are studied by XRD, DTA, TG and IR spectroscopy after heating in the temperature interval 120–260 °C and rehydration in air and water. Structural models of the two metaphases obtained are proposed. Metahydrotalcite-D (HT-D) is formed at 140–180 °C by the reversible dehydration of the interlayer. Metahydrotacite-B (HT-B) is formed at temperatures 240–260 °C as a result of the dehydroxilation of a part of OH groups of the brucite-like layer and inclusion of two oxygenes from the CO_3-group in the same layer. The HT-B has a specific crystal structure. Rehydration does not restore the initial structural state but leads to the formation of a phase (HT-B-r) characterized with increased thickness of the interlayer, high content of water and a low temperature of dehydration. The properties of HT-B depend on the ratio M^{2+}: Al of the initial sample. The substitution Mg ↔ Ni does not influence the properties of the metaphases in the low temperature region. *© 1999 Kluwer Academic Publishers*

1. Introduction

The mineral hydrotalcite (HT) is a layered Mg-Al containing hydroxycarbonate hydrate with Mg-to-Al ratio between 3 : 1 and 2 : 1 [1–4]. There is a great number of papers in the literature concerned with synthetic analogous with general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, where cations M^{2+} = Mg, Ni, Fe, Zn, etc. and M^{3+} = Al, Cr, Fe, Mn occupy octahedron positions in brucite-like layers, while $A^{m-} = CO_3^{2-}, SO_4^{2-}, OH^-, Cl^-, NO_3^-$ etc. is the only interlayered anion [5–10]. The value of x for the Mg-Al system varies between 0.20 and 0.33. The structure of HT-like compounds consists of consequent positively charged brucite-like layers and compensating negative anion-water interlayers [11, 12]. These materials are interesting due to their various applications. HT-like compounds have been used as antiacide, antipeptin, catalyst support, flame retardant, absorbing agent, anion exchangers, acid residue scavengers, stabilizers for polymers etc. [13]. Many of their properties are closely related with the thermal activation and the high temperature products formed. Some dehydrated and pillared forms of these compounds have properties of molecular sieves.

Due to practical interest to partly or totally calcined products there are lots of papers concerned mainly with processes of thermal decomposition [6, 14–20]. The majority of authors consider that the main processes of thermal decomposition (dehydration, dehydroxylation, and decarbonization) proceed in the temperature intervals: 20–300, 300–700, and above 700 °C. In the first temperature interval one suggests that there is a reversible loss of interlayer molecular water [6, 14, 15], but some data on TG-analysis [21] and MAS NMR [17, 18] has also indicated partial dehydroxylation of the brucite-like layer. In the second temperature interval, 300–700 °C, dehydroxylation of the remaining OH groups and interlayer decarbonization proceeds. There have been different opinions about the duration and mechanism of evolving of H_2O and CO_2 [6, 19, 20]. During the heating in the third temperature interval, above 700 °C, the final decomposition products, $M^{2+}O$ and $M^{2+}M^{3+}_2O_4$, are formed.

In spite of the numerous investigations on the processes of thermal decomposition of hydrotalcite-like compounds by various modern methods, many inexplicable and contradictory problems remain. In this work, we aim at clarifying the composition, structure and properties of thermally decomposed metaphases in the temperature interval 20–300 °C, which would make possible to understand the processes of decomposition and regeneration of hydrotalcite-like compounds.

2. Experimental

Two Mg-Al-CO_3 samples with $x = 0.25$ (1HT) and 0.33 (2HT) were prepared by dropwise-mixing of acid of

$Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with alkali solution of NaOH and Na_2CO_3. The temperature and the pH of the reaction mixtures were 50 °C and 10–10.5, respectively. The resulting gels were aged in polypropylene bottles for 48 h at 90 °C. The precipitates obtained were filtered, washed until washing water reaches a pH of 8–8.5 and then dried at room temperature. Using the same procedure samples were obtained in which Mg was replaced for Ni either in half (MN-1HT; MN-2HT) or entirely (N-1HT; N-2HT). The samples obtained in that manner were annealed at various temperatures in the range 120–260 °C. After heating, the samples were kept either in air, at room temperature and humidity, or in water at 20 °C and 90 °C for different time periods, thus providing the opportunity to investigate the processes of rehydration and rehydroxylation.

Identification of the starting compounds and characterization of the annealed samples was performed by DTA and TG analysis, X-ray powder diffraction and IR spectroscopy. In a desiccator above a saturated solution of NaBr we have studied the sorption of water vapors in some samples under controlled relative air humidity.

The differential thermal analyses and the thermogravimetric investigations were carried out on Stanton Redcroft STA 780 apparatus at the following conditions: temperature heating rate 10°/min, static air; 16.0–16.5 mg, samples weight and Al_2O_3 as a reference material.

The powder X-ray diffraction (XRD) patterns were recorded on a TUR M62 diffractometer using CoK_α radiation.

The IR spectroscopy was performed on a UR-20, Karl Zeis using KBr pellet technique.

3. Results and discussion

3.1. Mg-Al-CO_3 hydrotalcite with $x = 0.25$ (1HT)

Figs 1–3 show DTA curves, powder XRD patterns and IR absorption spectra of the initial samples and the products obtained by annealing and rehydration in air and in water. Our results for the initial samples are in accordance with published data for materials of similar composition [19, 22]. DTA curve of the initial sample (Fig. 1a) reveals four endothermic effects: the first, a flat one, passes at 160–180 °C into a second, sharp effect centered at 237 °C. The third energy absorption process at about 370 °C reveals as a shoulder of the fourth sharp peak at 416 °C. A marked plateau separates the DTA curve into high- and low-temperature parts between the second and the third peaks.

All contemporary studies have indicated that in the low temperature region subsequently detached are adsorbed water, interlayer water and water molecules formed in the recombination of hydroxyl groups from the brucite-like layer. The last ones, according to data of TG analysis [21, 23], are formed during the second sharp endothermic effect in which a quarter of the hydroxyl groups in the layer are destroyed forming two water molecules per one formula unit.

In the detachment of adsorbed and interlayer water a state is formed referred to later on as metahydrotalcite-D.

3.1.1. Metahydrotalcite-D (1HT-D)

X-ray diffraction pattern and IR spectrum of this phase do not change considerably except for the molecular water absorption band at 1630 cm^{-1}, which disappears.

Lattice parameters remain the same, i.e., the interlayer thickness does not change. The resulting product strongly adsorbs water molecules from the air and thus rapidly regenerates its content of water (Fig. 4). The DTA curves and IR spectra of the rehydrated products are the same as those of the starting material (Figs 1b and 3b).

The results presented indicate that 1HT-D has a pillared structure in which carbonate groups, without changing position and symmetry, play a role of pillars (Fig. 5b). The metaphase has an adsorption volume of 0.27 cm^3 per 1 cm^3 hydrotalcite accessible for water molecules and, possibly, for other small-size molecules.

The phase 1HT-D is formed by heating above 100 °C and preserves up to 160–180 °C, when changes in its diffraction pattern and IR spectrum occur, indicating the appearance of a new structure, named metahydrotalcite-B (1HT-B), which is the only phase in the temperature range 240–260 °C.

3.1.2. Metahydrotalcite-B (1HT-B)

The powder X-ray diffraction pattern of this phase differs substantially from that of the initial sample in that only the lines 003 and 110 remain both with decreased intensity (Fig. 3c). The interlayer spacing d_{003} decreases from 7.84 to 6.60 Å and a week shallow line appears at about 2.4 Å.

Similarly to the metaphase D, the phase 1HT-B adsorbs water vapors from the air even at low air humidity (Fig. 4), when d_{003} increases up to 8.06 Å. In air with relative humidity of 70–80%, d_{003} changes from 6.60 to 8.06 Å in 10–15 min (Fig. 6). At the same time, all other lines in the diffraction pattern are recovered, but with lower intensities and some weak changes in the intensity ratios.

The close similarity between the X-ray diffraction patterns of the starting phase and the rehydrated metaphase B (1HT-B-r) was used in a number of papers to suppose regeneration of hydrotalcite. The comparison of DTA curves and IR spectra of the 1HT-B-r and the initial samples (Figs 1a–d and 3a–d) indicate that, in contrast to the high temperature phase (300–700 °C) [5, 13], the phase-B has not regenerated into hydrotalcite and differs in its specific crystal-chemical behavior and composition. This phase preserves these peculiarities during a long stay at room temperature both in air and even in water as well as after repeated heating and rehydration.

The sharp peak at 237 °C, which corresponds to dehydroxylation of part of the OH groups in the brucite-like layer, disappears in the rehydrated 1HT-B-r DTA curve (Fig. 1c–e). Instead of it, a relatively deep, symmetric endothermic peak, centered at about 109 °C, and a corresponding step in the TG curve appear (Fig. 7), which corresponds to a weight loss of 14.4%, approximately equal to that in the initial sample at 280 °C (which is 15.6%).

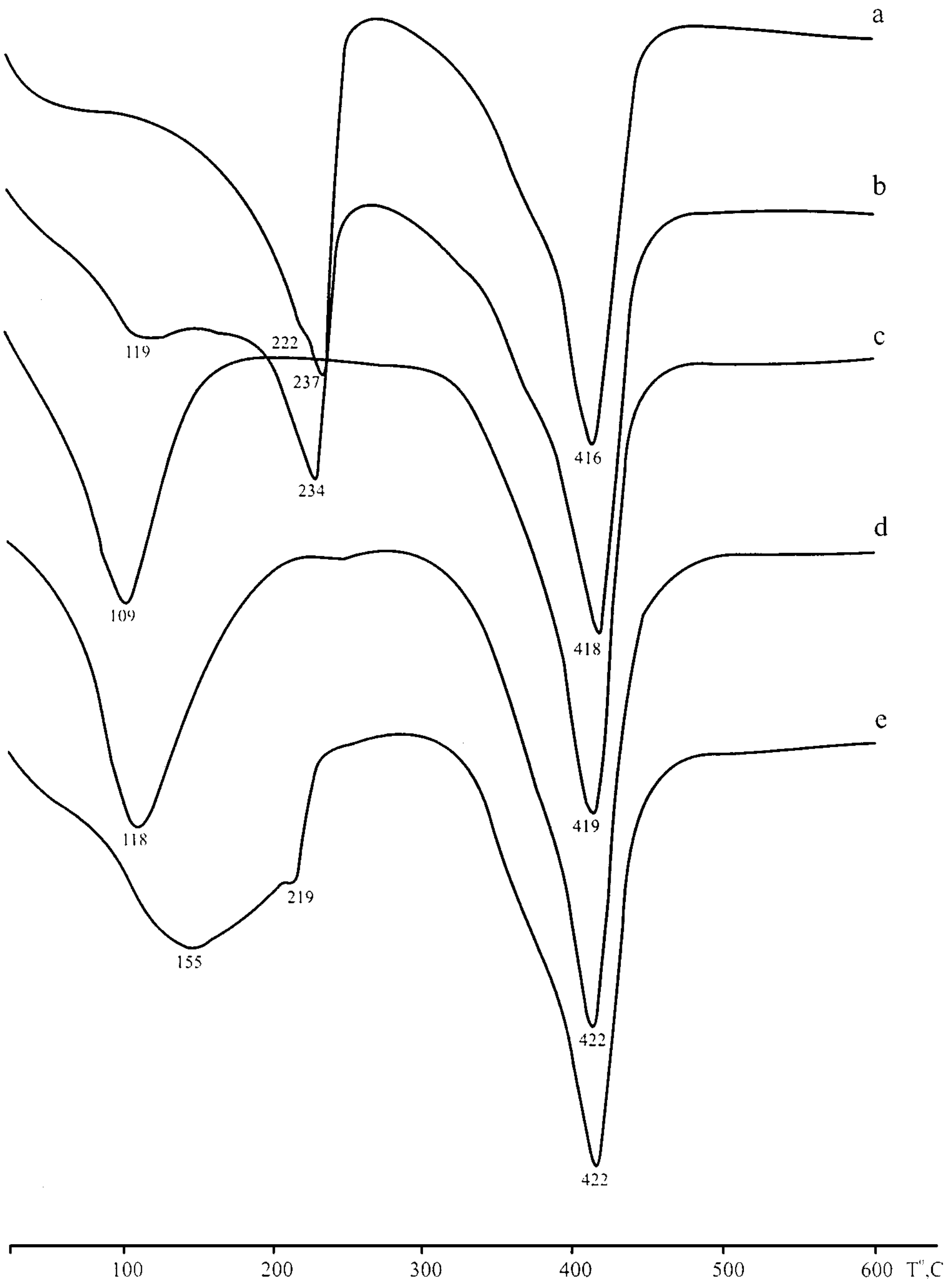


Figure 1 DTA curves of: (a) 1HT—initial sample; (b) heated for 2 h at 180 °C, then kept in air; (c) 4 h at 260 °C, 48 h in air; (d) 4 h at 260 °C, 48 h in water at 20 °C; (e) 4 h at 260 °C, 7 h in water at 90 °C.

The IR spectrum of 1 HT-B differs markedly from that of the initial samples mainly in the absorption bands of the carbonate anion. The band v_3 at 1383 cm^{-1} splits into two well-formed and separated bands. This splitting has been discussed by some authors [19, 20] and has been explained by the appearance of bidentate bonds and a corresponding change in the carbonate group symmetry from D_{3h} to C_{2v} [18]. This bidentate CO_3^{2-} anion is the most characteristic feature of the metaphase and this is the reason to use the symbol B for its labeling. In addition, an absorption band at 1045 cm^{-1} appears, which corresponds to the vibration v_1 (IR inactive in D_{3h} symmetry group).

To construct an adequate structural model of the considered metaphase 1HT-B one should take into account the following arguments:

1. The formation of HT-B is connected with the collapse of d_{003} from 7.84 to 6.60 Å, which is evidently due to reduction of the interlayer thickness from 3.1 to 1.9 Å. This distance is smaller than the diameter of an oxygen anion and, consequently, it is impossible to place the carbonate group therein.

2. TG analysis data indicates that the sharp endothermic peak at 273 °C corresponds to dehydroxylation of two hydroxyl groups per Al atom in the reaction $2OH^- \rightarrow H_2O + O^{2-}$. In this process, at room temperature, OH groups are not recovered in the brucite-like layer neither in air nor in water. Even after many-hour boiling one can find only initial indications for layer rehydroxylation (Figs le, 2f, and 3e).

3. NMR data for ^{27}Al and ^{25}Mg [16, 18] as well as IR spectra show that independently of the loss of hydroxyl

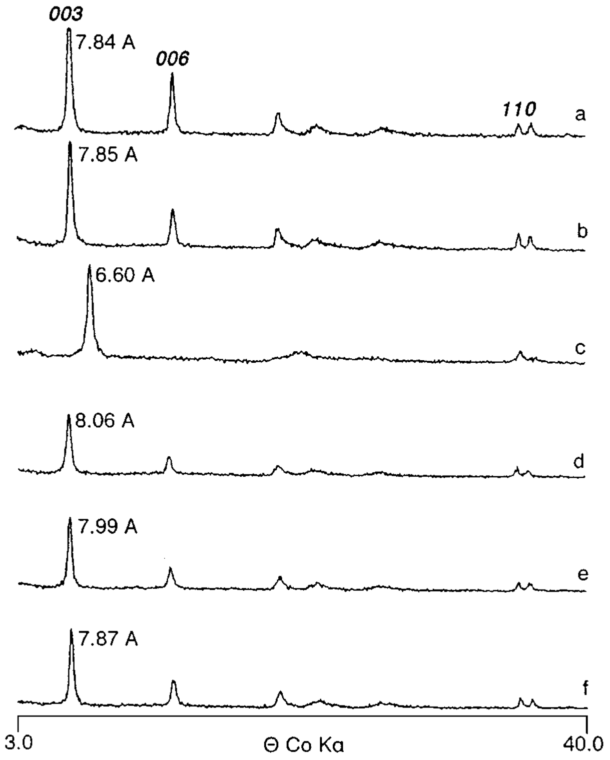


Figure 2 X-ray diffraction patterns of: (a) 1HT—initial sample; (b) heated for 2 h at 180 °C, then kept in air; (c) 4 h at 260 °C, recorded immediately hereafter; (d) 4 h at 260 °C, 48 h in air; (e) 4 h at 260 °C, 48 h in water at 20 °C; (f) 4 h at 260 °C, 7 h in water at 90 °C.

groups both aluminum and magnesium preserves its octahedral surrounding.

4. The structure preserves its layered character and rehydrates in air and in water adsorbing in its interlayer 50% more water molecules than 1HT-D.

5. The changes in IR spectra demonstrate a sharp change in the surrounding of the CO_3^{2-} groups, which results from a possible changing of its crystal-chemical role in the structure.

Such a change is confirmed by the close correspondence observed between that parts of the IR spectra of 1HT-B and the mineral dawsonite, $NaAl(OH)_2CO_3$, which are generated by carbonate group vibrations [24]:

	v_3 (cm^{-1})		v_1 (cm^{-1})
HT-B	1553,1534	1382, 1360	1045
Dawsonite	1550	1390	1090

This correspondence can result from an analogous interaction of the carbonate group with octahedral cations.

In the structure of dawsonite Al^{3+} and Na^{+} are in octahedral positions surrounded by OH groups and oxygen atoms from CO_3 groups. Each Al atom has as neighbors 4OH groups and 2O atoms, two of the oxygen atoms in the CO_3 group are coordinated by one Al and

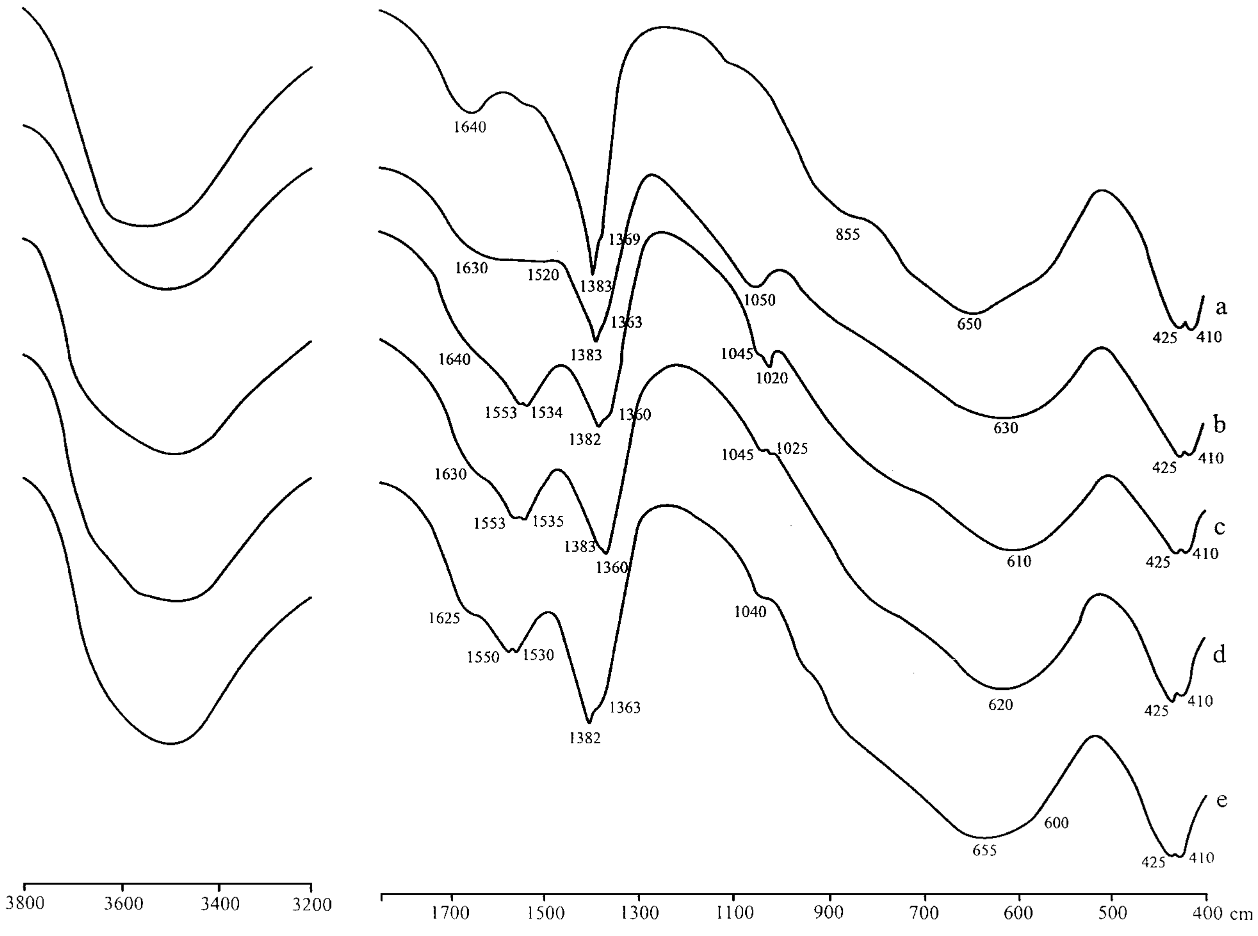


Figure 3 IR-spectra of 1HT—initial, heated and rehydrated forms (labels as in Fig. 1).

two Na atoms, while the third oxygen forms only hydrogen bonds with OH groups.

1HT-B forms a configuration similar to dawsonite if during the endothermic effect at 237 °C two hydroxyl groups in each Al octahedron recombine forming one removed water molecule and one O^{2-} anion, which remains in one of the octahedron apexes and compensates the excess charge of aluminum. The place of the removed OH group is occupied by one oxygen of the interlayer CO_3 group. The second oxygen of the CO_3 group is incorporated in the same way into the nearest Al-octahedron, while the third one remains in the interlayer, forming possible hydrogen bonds with the other brucite-like layer. The flat CO_3

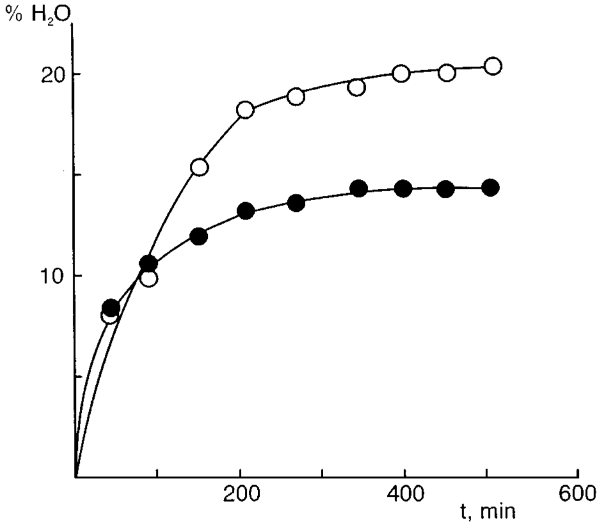


Figure 4 Water vapor adsorption in 1HT from air with relative humidity 23%: (●) heated for 2 h at 180 °C; (○) heated for 4 h at 260 °C.

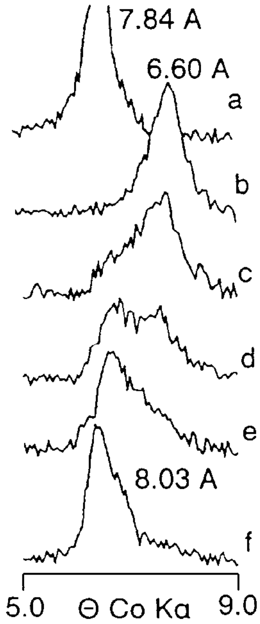


Figure 6 003 X-ray peak of: (a) 1HT—initial sample; (b) 4 h at 260 °C, recorded immediately hereafter; (c) kept for 6 min in air (RH 70–80%); (d) 10 min; (e) 16 min; (f) 20 min.

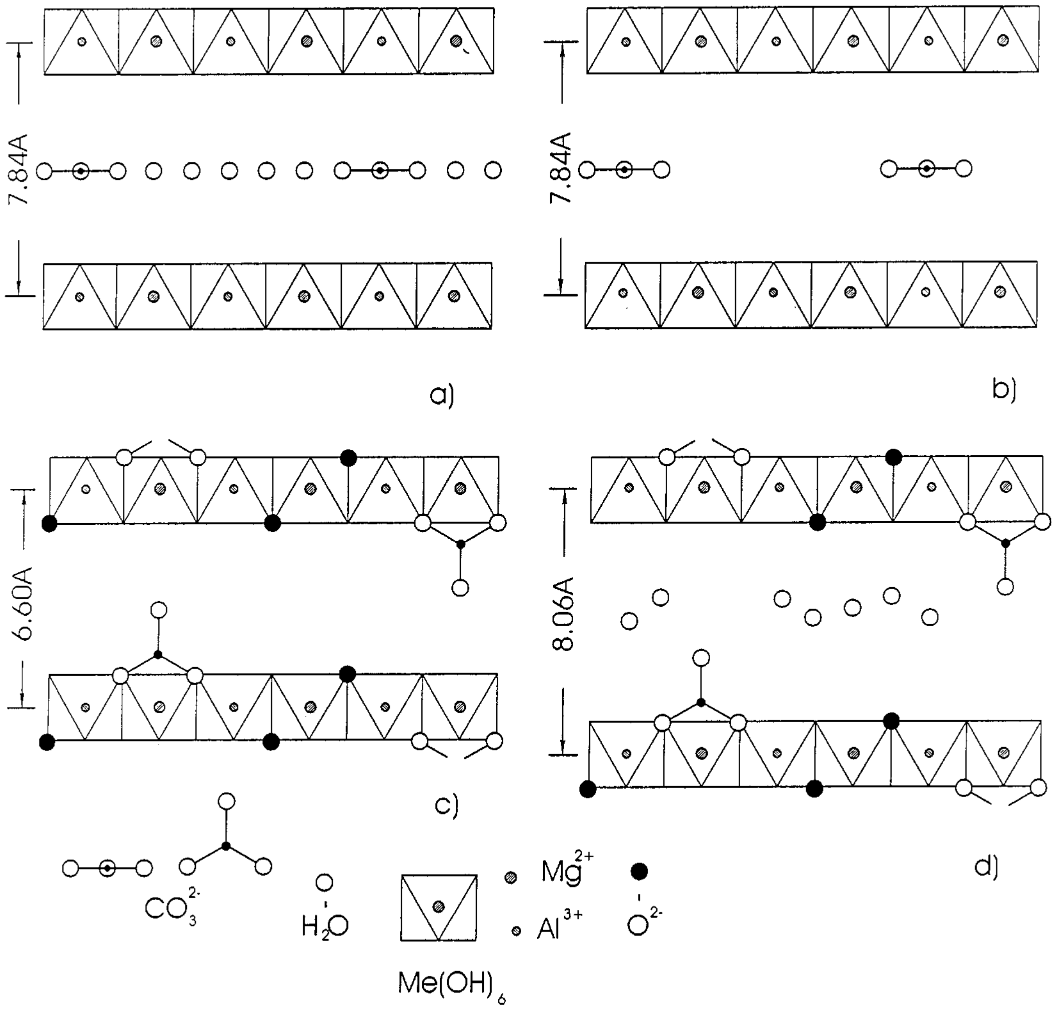


Figure 5 Structural schemes of: (a) HT; (b) HT-D; (c) HT-B; (d) HT-B-r.

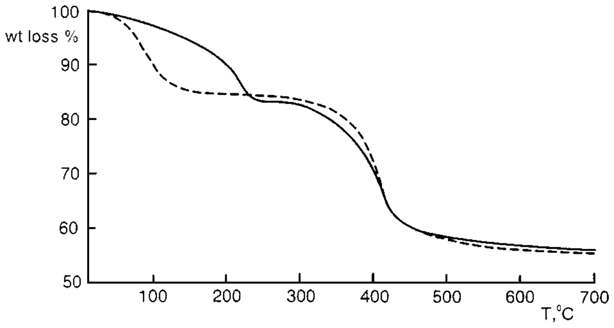


Figure 7 TG curves of 1HT (solid line) and 1HT-B-r (dashed line).

group is oriented across to the brucite-like layers (Fig. 5). The $Al(OH)_6$ octahedrons are transformed into $Al(OH)_4O^-O^{2-}$ octahedrons. Mg octahedrons placed between two Al octahedrons are with composition $Mg(OH)_4O_2^{2-}$, $Mg(OH)_4O_2^-$ or $Mg(OH)_4O^{2-}O^-$ and some of the other Mg octahedrons remain unchanged $Mg(OH)_6$.

The structure has the behavior of a layered structure, but the role of CO_3 groups changes, namely from interlayer's, only they become parts of both the interlayer and the brucite-like layer.

During rehydration, the brucite-like layers widen up to the thickness of a monomolecular layer of water molecules. As in the interlayer each CO_3 group contributes only with one oxygen, there should be two more water molecules per formula unit involved and, thus, the adsorption capacity should increase by 50%.

In fact, the observed adsorption volume of the phase 1HT-B is 0.38 cm^3 per 1 cm^3 hydrotalcite, i.e. 41% greater than that of 1HT-D.

The proposed model explains also the other peculiarities of the metaphase-B:

- preservation of the octahedral coordination of cations in spite of removal of 1/4 of the hydroxyl groups;
- change of the carbonate group symmetry and resulting spectroscopic effects;
- reduction of the interlayer to a value less than the oxygen atom diameter (Fig. 5c).
- preliminary data of unidimensional synthesis of I_{001} explain the disappearance of 006 and the lack of 009 in X-ray powder patterns of the metahydrotalcite-B:

Sample	I_{calc}/I_{obs}		
001	003	006	009
1HT	100/100	34/44	3/3.5
1HT-B	100/100	0.6/0	0.1/0

3.2. Mg-Al-CO_3 hydrotalcite with $x = 0.33$ (2HT)

Figs 8 and 9 show X-ray diffraction patterns and IR spectra of the sample with high Al content and the products obtained from it by the procedure described for 1HT. Comparison of the corresponding figures reveals differences known from the literature for the initial samples, namely reduced lattice parameters and a richer in peaks IR spectrum for 2HT including the sharp and non-split band at 1367 cm^{-1}. Obviously, these peculiarities are due to that, like in all hydrotalcite compounds, Al-OH-Al bonds cannot lay in the brucite-like layer [25]. For $x = 0.33$ (Mg : Al = 2 : 1) this is realized only for fully ordered cations in octahedral positions. The difference in the cation radii and in the layer charge are responsible respectively for the differing values of the parameters ***a*** and ***c***.

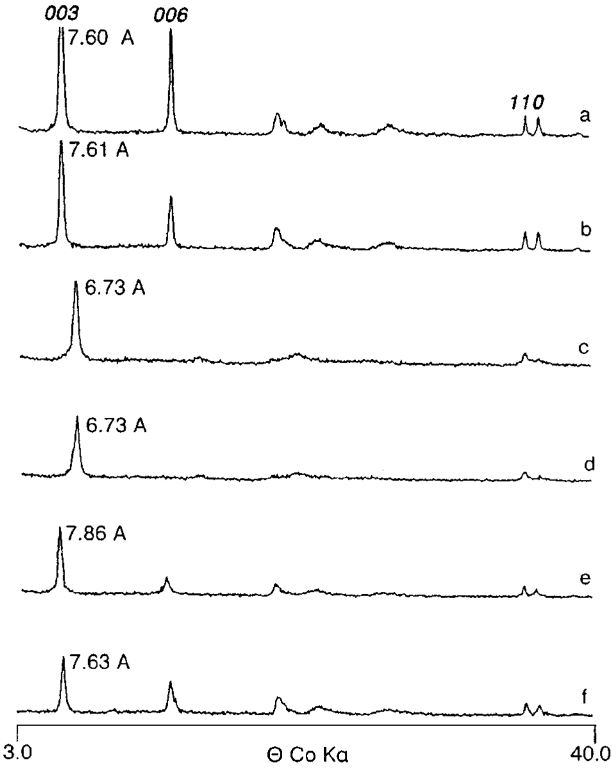


Figure 8 X-ray diffraction patterns of 2HT—initial, heated and rehydrated forms (labels as in Fig. 2).

The behavior of 2HT-D is very similar to that of 1HT-D. Quite similar are also the B-metaphases; however, some characteristic features exist, namely:

1. In 2HT-B d_{003} reduces from 7.60 to 6.73 Å (Fig. 8a and c), while in 1HT this reduction is from 7.84 to 6.60 Å. In the former compound the reflection 006, corresponding to $d = 3.36$ Å, remains visible.
2. The phase 2HT-B cannot be rehydrated in air (Figs 8d and 10c) for several mounts due, most probably, to the greater number of hydrogen bonds between the layers. However, for samples rehydrated in water, the diffraction patterns restore and the interlayer, as for 1HT-B, broadens with 0.22–0.26 Å (Figs 8e and 10d). Under condition of boiling, the interlayer restores its initial size (Figs 8f and 10e). The broadening is due probably by unordered filling of the interlayer by water molecules. However, it seems that under conditions of boiling the interlayer orders, which is confirmed by the reconstruction of the IR spectrum.
3. The long-wavelength spectral band corresponding to the υ_3 vibration of the bidentate CO_3 of 2HT-B does not split (Fig. 9c and d), whereas the short-wavelength one splits into two bands. The vibration υ_1 in this case appears at 1015–1020 cm^{-1}, while in the sample with low Al-content at 1045 cm^{-1}.

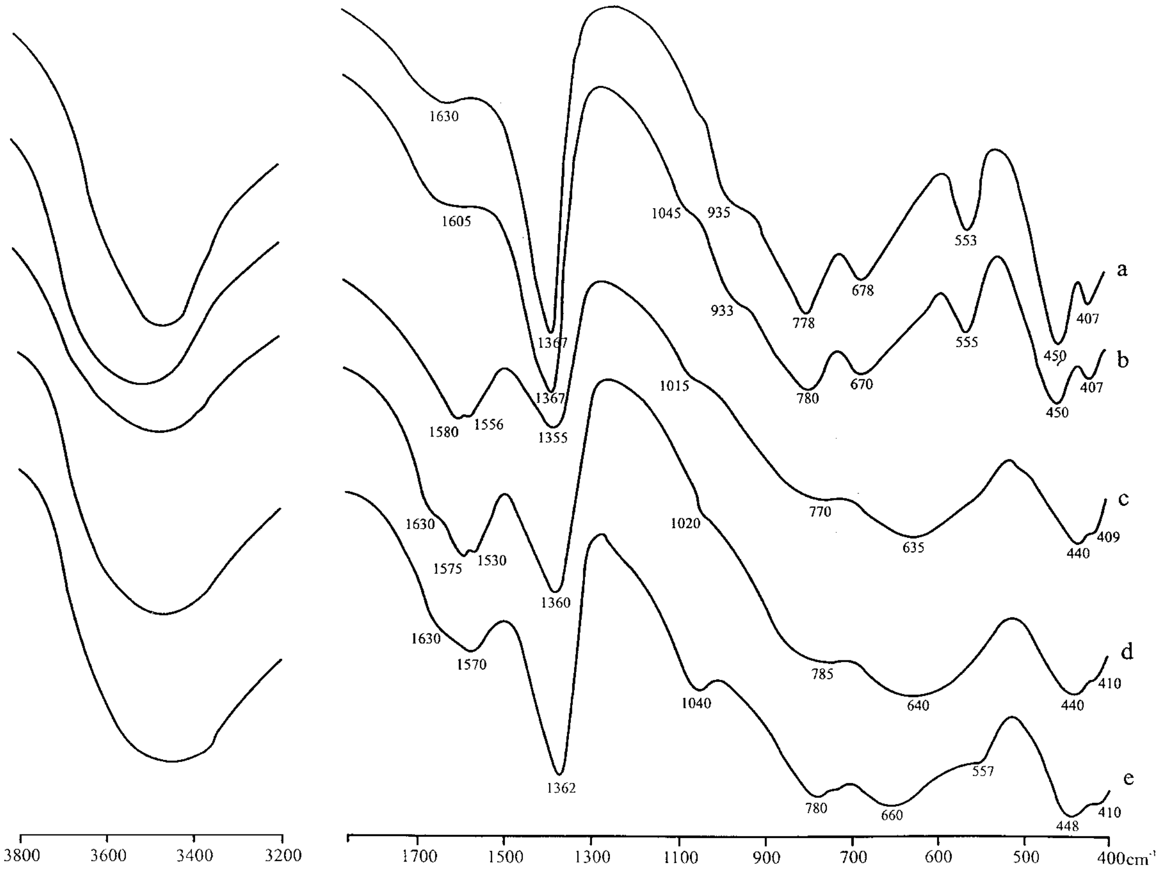


Figure 9 IR-spectra of 2HT—initial, heated and rehydrated forms (labels as in Fig. 1).

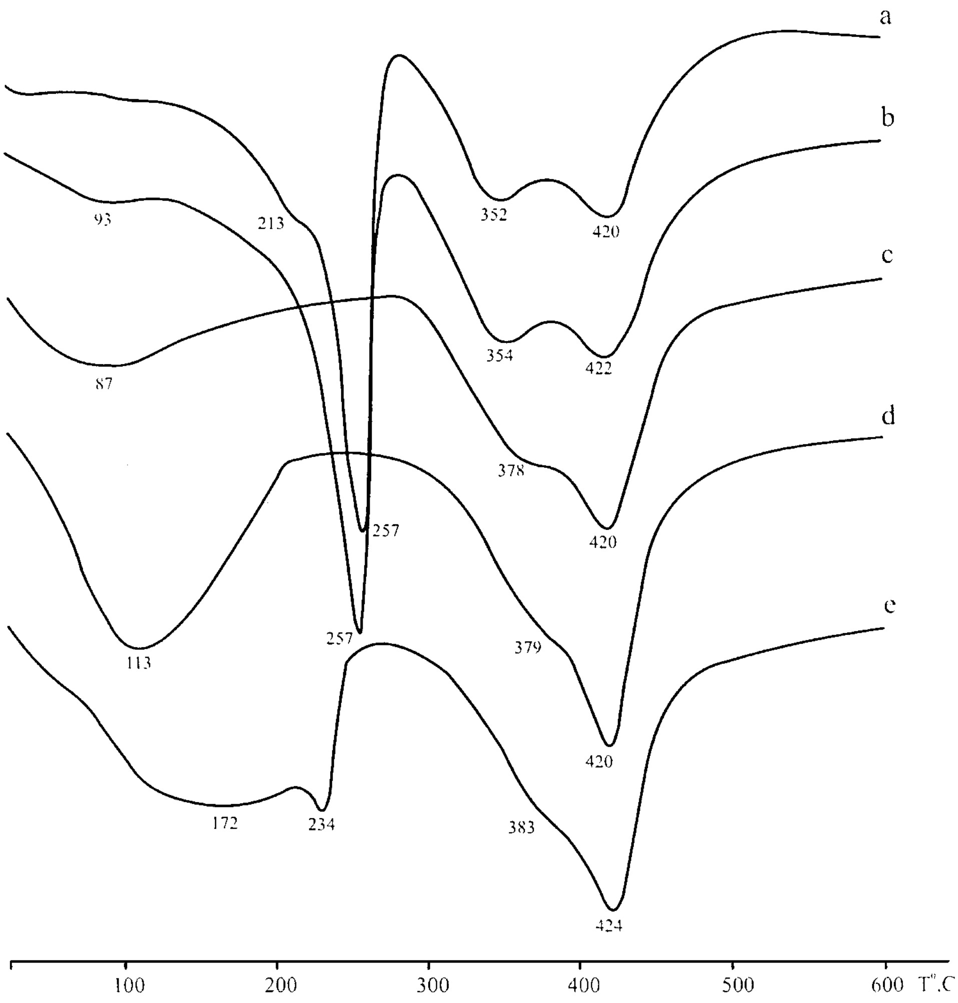


Figure 10 DTA curves of 2HT—initial, heated and rehydrated forms (labels as in Fig. 1).

3.3. Ni-containing hydrotalcite-like compounds

In the investigated temperature interval Ni- and Mg-Ni-containing samples reveal the same peculiarities as those characteristic of the Mg-containing samples. This demonstrates once again that the structural changes in this temperature interval result mainly from the common components: aluminum and carbonate groups.

Ni-containing samples are blue-green coloreds with different density, which depend on the content of Ni. Heated up to 260 °C they change the color to gray-green. It is known that Ni oxides and hydroxides are colored from blue-green to green, only Ni oxide-hydroxide is black in color [26]. One can suppose that the color change is due to O—OH coordination of Ni in the phase-B. Probably the darker gray color of the phase N-2HT-B is due to all Ni-octahedrons therein which are of hydroxide-oxide anions, in contrast to the case of N-1HT-B, where a part of them are built simply of hydroxide groups.

3.4. Comparison with carbonate-free hydrotalcite-like compounds

There are very sporadic data on the decomposition of such materials, which are concerned mainly with DTA studies of samples containing organic anions. These data can serve as basis for some preliminary conclusions:

1. The samples containing Al^{3+}, Fe^{3+} and bivalent, oxygen containing compensating anions (CO_3^{2-}, SO_4^{2-}, CrO_4^{2-}), are characterized by a sharp endothermic effect in the temperature range 220–260 °C [27].

2. The samples containing monovalent compensating anions (HCO_3^-, Br^-, OH^-) are characterized by a sharp endothermic effect at temperatures much higher than 400 °C [28].

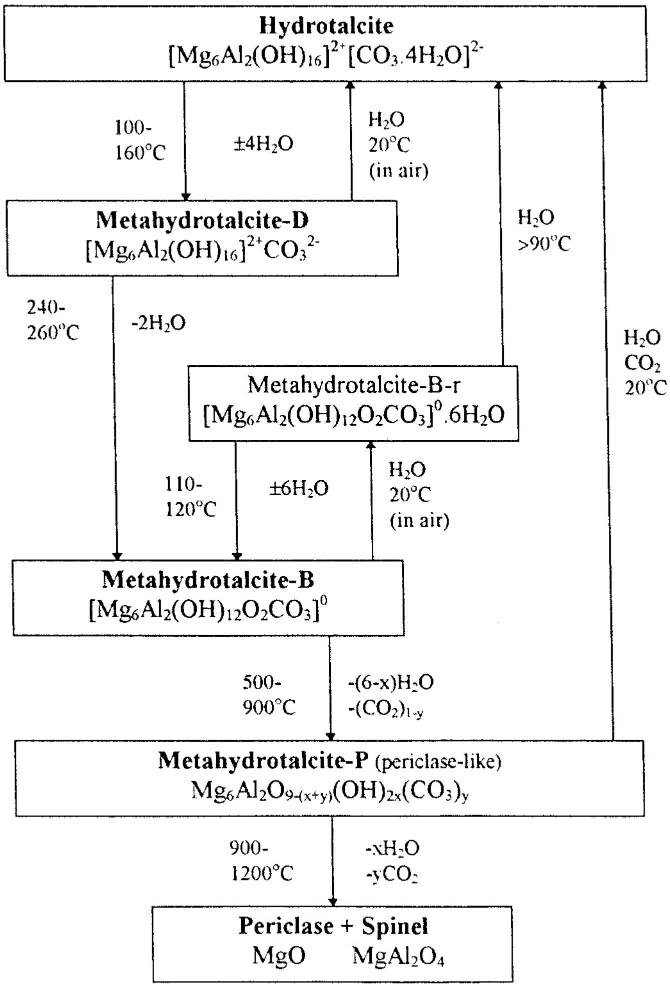
4. Conclusions

1. In the temperature interval 20–240 °C, the thermal decomposition of the compounds studied proceeds in two stages with consecutive formation of two metaphases:

(a) Metahydrotalcite-D resulting from interlayer dehydration, which in contact with atmosphere, reversibly transforms into the starting phase.

(b) Metahydrotalcite-B resulting from simultaneous dehydroxylation of two OH groups per Al^{3+} and inclusion of two oxygen atoms from the CO_3^{2-} group in the brucite-like layer. In this structural transformation, the positive charge of the octahedral layer vanishes, while the CO_3 group changes its symmetry from D_{3h} into C_{2v}. In the new layered structure 5–6 water molecules can be reversibly rehydrated (in air for 1HT-B and only by moistening in water for 2HT-B), and be removed at 110 °C.

The correspondence of the two metaphases with one another, with the starting phase and with the high temperature phases can be presented by the following scheme:



2. The change of the aluminum content in hydrotalcite influences the temperature of structural transformations in the investigated temperature range and the sorption properties of the obtained metaphases.

3. The replacement of Mg^{2+} for Ni^{2+} does not change the temperature of thermal effects in the low temperature region and does not affect the metaphases' properties.

4. Metahydrotalcite-B (1HT-B) is interesting with its sorption capacity for water vapor and its low temperature of activation.

References

1. FRONDEL, *Amer. Mineral.* **26** (1941) 295.
2. TAYLOR, *Mineral. Mag.* **39** (1973) 377.
3. MANDARINO, *Mineral Records* **25** (1994) 315.
4. ARAKCHEEVA, D. PUSHTAROVSKII, R. RASTSVETAEVA, D. ATENSIO and G. LUBMAN, *Krystallographia* **41** (1996) 1024 (Russian).
5. MIYATA, *Clays and Clay Minerals* **23** (1975) 369.
6. *Idem.*, *ibid.* **28** (1980) 50.
7. REICHLE, S. Y. KANG and D. S. EVERHARD, *J. Catal.* **101** (1985) 352.
8. REICHLE, *Solid State Ionics* **22** (1986) 135.
9. I. PAUCH, H.-H. LOHSE, K. SCHURMANN and R. ALLMANN, *Clays and Clay Minerals* **34** (1986) 507.
10. P. PORTA and S. MORPURGO, *Appl. Clay Sci.* **10** (1995) 31.
11. R. ALLMANN and H. P. JESPEN, *N. Jhb. Miner. Mh.* **12** (1969) 544.
12. R. ALLMANN, *Acta Crystallogr.* **24** (1968) 972.
13. F. CAVANI, F. TRIFIRO and A. VACCARI, *Catal. Today* **11** (1991) 173.
14. G. J. ROSS and H. KODAMA, *Amer. Mineral.* **52** (1967) 1036.
15. L. PESIC, S. SALIPUROVIC, V. MARCOVIC, D. VUCELIC, W. KAGUNYA and W. JONES, *J. Mater. Chem.* **2** (1992) 1069.
16. K. MACKENZIE, R. MEINHOLD, B. SHERRIFF and Z. XU, *ibid.* **3** (1993) 1263.
17. M. HUDSON, S. CARLINO and C. APPERLEY, *ibid.* **5** (1995) 323.
18. F. REY and V. FORNES, *JCS Faraday* **88** (1992) 2233.
19. T. HIBINO, Y. YAMASHITA, K. KOSUGE and A. TSUNASHIMA, *Clays and Clay Minerals* **43** (1995) 427.
20. F. M. LABAJOS, V. RIVES and M. A. ULIBARRI, *J. Mater. Sci.* **27** (1992) 1546.
21. T. STANIMIROVA and N. PETROVA, *Compt. Rend. Acad. Bulg. Sci.* **51** (1998), in press.
22. M. J. HERNANDES-MORENO, M. A. ULIBARRI, J. L. RENDON and J. SERNA, *Phys. Chem. Minerals* **12** (1985) 34.
23. T. STANIMIROVA and N. PETROVA, *Compt. Rend. Acad. Bulg. Sci.* **51** (1998), in press.
24. A. J. FRUEH, JR. and J. P. GOLIGHTLY, *Can. Mineral.* **10** (1967) 51.
25. G. W. BRINDLEY, *Mineral. Mag.* **43** (1980) 1047.
26. Handbook of Chemistry, Vol. 2, Chimia, Moscow (1963) 152 (Russian).
27. S. MIYATA and A. OKADA, *Clays and Clay Minerals* **25** (1977) 14.
28. L. L. MUSSELMAN and H. L. GREEN, US Patent no. 5,480,587 (1996).

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