THERMALLY INDUCED TRANSFORMATIONS IN POLYOXOMETALATE-PILLARED HYDROTALCITES

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Abstract

Thermal decomposition of magnesium-aluminum hydrotalcites intercalated with four different polyoxometalate anions ($V_{10}O_{28}^{6-}$, $Cr_2O_7^{2-}$, $W_7O_{24}^{6-}$ or $Mo_7O_{24}^{6-}$) was examined. The studied samples were prepared by the ion-exchange procedure starting from the parent carbonate-containing hydrotalcite. The successful synthesis was confirmed by powder X-ray diffraction and chemical analysis. The samples decomposed in two or three essential steps forming finally mixed metal oxides. The dichromate-containing hydrotalcite showed a thermal reduction of Cr^{6+} to Cr^{3+} ions.

Keywords: layered double hydroxides, polyoxometalate pillared hydrotalcites, thermal decomposition

Introduction

Hydrotalcite-like layered double hydroxides with general formula $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$ (where M^{II} and M^{III} are divalent and trivalent cations, x is equal to the ratio of $M^{3+}/(M^{2+}+M^{3+})$ with a value varying in the range of 0.17–0.50, and A stands for an anion) consist of positively charged octahedral brucite-like sheets compensated with negatively charged interlayers containing anions and water molecules [1]. Many materials with different cations (e.g. $M^{II}=Mg^{2+}$, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, and $M^{III}=Al^{3+}$, Cr^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, V^{3+}, Ga^{3+}) in the brucite-like layers were prepared, taking into account that the stability of hydrotalcite structure demands that M^{II} and M^{III} cations should have the ionic radii close to 0.65 Å (characteristic of Mg^{2+}). Another possibility of modification of hydrotalcite composition is an intercalation of various anions into the interlayers. Simple anions (inorganic or organic) and large complex species or polyoxometalate anions [2] may be introduced between the brucite-like sheets. Thermal decomposition of hydrotalcites results in a formation of homogeneously dispersed mixed metal oxides, exhibiting high specific areas, which are materials of increasing interest because of their potential use for catalytic application [3]. It is therefore very important to understand thermal behaviour of variously

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modified hydrotalcites. The thermal decomposition of the natural hydrotalcite containing magnesium and aluminium cations in the brucite-like sheets and carbonates in the interlayer space [4–7], as well as the studies of thermal behaviour of hydrotalcites, in which brucite-like layers were modified with transition metal cations [8–11] have been described in detail in the literature. Recently, decomposition of polyoxometalate-pillared materials has been also studied [12–14].

The aim of the present study is to investigate the thermal behaviour of Mg,Al-hydrotalcites intercalated with $V_{10}O_{28}^{6-}$, $Cr_2O_7^{2-}$, $W_7O_{24}^{6-}$ or $Mo_7O_{24}^{6-}$ anions. The samples characterized with respect to structure (XRD) and chemical composition (XRF, elemental analysis) were examined by TG/DTA/EGA methods.

Experimental

Samples preparation

The parent magnesium-aluminum hydrotalcite containing CO_3^{2-} as interlayer anions (hereinafter called HTC) was prepared according to the coprecipitation method at constant pH (10.0±0.2) and temperature (60±2°C). An aqueous solution containing $Mg(NO_3)_2$·$6H_2O$ (0.170 mol) and $Al(NO_3)_3$·$9H_2O$ (0.085 mol) was added dropwise to a vigorously stirring solution of Na_2CO_3 (0.050 mol). The amount of Na_2CO_3 was calculated to the relation of $[CO_3^{2-}]=0.5[Al^{3+}]$ and used with about 20% excess. The pH was maintained at constant level by a dropwise addition of 2 M NaOH solution. The precipitate was aged at 60°C for 1 h, then filtered and washed with distilled water until the filtrate was free of nitrates. The solid obtained in such a way was dried at 60°C overnight.

The anion exchange procedure was performed on the HTC precursor for the polyoxometalates intercalated hydrotalcites. The dried HTC was suspended in distilled water. pH of suspension was decreased by adding HNO_3 (1:1). The synthesis of $V_{10}O_{28}^{6-}$-pillared hydrotalcite (hereinafter called CV_{10}) was carried out at pH=4.5, $Cr_2O_7^{2-}$- and $W_7O_{24}^{6-}$-intercalated layered double hydroxides (hereinafter called CCr_2 and CW_7, respectively) at pH=5.5, whereas $Mo_7O_{24}^{6-}$ one (hereinafter called CMo_7) at pH=5.0. Separately, suitable metalates (NH_4VO_3, $(NH_4)_2CrO_4$, Na_2WO_4 or $(NH_4)_6Mo_7O_{24}$·$4H_2O$) were dissolved in water and pH was adjusted to the mentioned above value. The solution containing $V_{10}O_{28}^{6-}$, $Cr_2O_7^{2-}$, $W_7O_{24}^{6-}$ or $Mo_7O_{24}^{6-}$ anions was added dropwise to the vigorously stirring suspension of HTC kept at 60°C. The amount of polyoxometalates added corresponded to 20% excess of that needed for stoichiometric exchange of carbonates with the intercalating anions. The special attention was paid to keep the pH at constant level. The final product was isolated by filtration, washed with distilled water and dried under vacuum at 60°C for 24 h.

Experimental techniques

All the as-synthesized as well as calcined (at 700°C for 13 h) materials were examined by powder X-ray diffraction (XRD) with a PW3710 Philips X'pert diffractometer using CuK$_\alpha$ radiation (λ=1.54178 Å) in the 2θ-range from 5 to 80°.

The content of Mg, Al, V, Mo, Cr and W in the samples was determined by X-ray fluorescence (XRF) using an Oxford 2000 spectrometer, while C, N and H contents were measured in an elemental analyzer EuroVector EuroEA 3000.

TG/DTA/EGA measurements were carried out using Mettler Toledo 851^e apparatus equipped with a quadrupole mass spectrometer ThermoStar (Balzers) for analysis of gases evolved during a thermal treatment of sample. All the runs were performed in argon flow at a heating rate of $10°C\ min^{-1}$ from room temperature to 700°C (for CMo_7) or 1000°C (for the other hydrotalcites). The upper temperature of TG experiment for CMo_7 was limited owing to a possibility of molybdenum sublimation, which could cause a damage to the equipment. Gaseous products were continuously monitored for chosen mass-to-charge ratios (m/z=18 for H_2O, 30 for NO, 32 for O_2, 44 for CO_2).

Results and discussion

The powder X-ray diffraction patterns for the studied samples are shown in Fig. 1. The diagram of HTC is typical of layered double hydroxides structure [1] with sharp and symmetric basal reflections at low values of 2θ angles. The c parameter for the carbonate-containing hydrotalcite can be calculated for the hexagonal cell of the space group in rhombohedral symmetry from the positions of the (003), (006) and (009) diffraction lines:

$$c=[d(003)+2d(006)+3d(009)].$$

The value of c parameter for HTC is equal to 22.95 Å and corresponds to a gallery height of 2.85 Å, assuming 4.8 Å for the thickness of the brucite-like sheets [15].
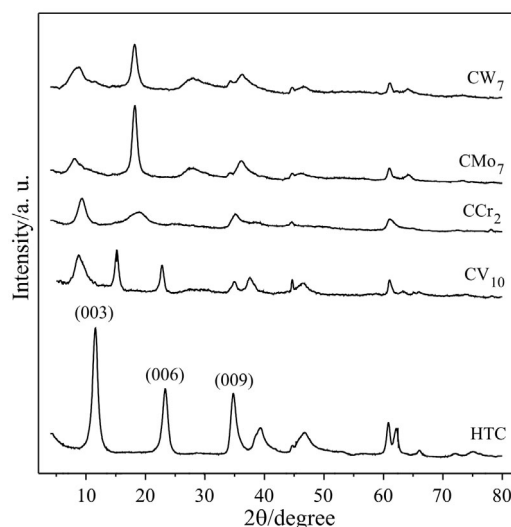

Fig. 1 XRD patterns of the as-synthesized samples

This is in a good agreement with literature data for carbonate-containing hydrotalcites [1, 6].

The XRD patterns for the samples after the ion-exchange procedure reveal that the hydrotalcite structure is the only crystalline phase present in the synthesized materials. However, the shift of the (00l) reflections towards lower values of 2θ angles is observed. This effect can be attributed to an increase in the interlayer distance. It can be therefore assumed that the intercalation of the parent hydrotalcite with polyoxometalate anions has been successful. The values of the c parameter for the intercalated samples can be calculated from the positions of the (006) and (009) peaks:

$$c = 3\frac{2d(006) + 3d(009)}{2}$$

In this calculation d_{003} is omitted due to fact that broad reflections present at 9.90 Å (for CV_{10}), 10.38 Å (for CW_7) and 10.76 Å (for CMo_{10}) result from overlapping the (003) reflection and the diffraction lines which are ascribed to magnesium and aluminum salts of polyoxometalates [16]. The values of the c parameter calculated for the CV_{10} and CCr_2 hydrotalcites (35.04 and 28.55 Å, respectively) are entirely correlated with the size of $V_{10}O_{28}^{6-}$, and $Cr_2O_7^{2-}$ anions [17, 18], whereas both polymolybdate and polytungstate exchanged samples are characterized by lower c parameter (both 29.22 Å) than that supposed taking into account the size of $W_7O_{24}^{6-}$ or $Mo_7O_{24}^{6-}$ ions [19]. This fact should be explained by a partial depolymerization of $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$ anions that could occur at pH and reactants concentration used during the ion-exchange procedure.

The content of metals in the samples was determined by X-ray fluorescence, whereas the amounts of C, N and H were found by elemental analysis. The results, obtained as the molar ratios of Mg/Al and Al/Me (where Me=V, Mo, W or Cr) as well as mass% of C, N and H, are comparatively presented in Table 1. The measured molar ratio of Mg/Al in the parent hydrotalcite is essentially in an accordance with the intended one. The HTC sample contains a small amount of N apart from C and H. The detected traces of nitrogen are attributed to the interlayer NO_3^- anions incorporated into the crystal structure from the solution of Mg and Al nitrates used for the preparation of the parent hydrotalcite. Taking into account the measured contents of elements the chemical formula of HTC can be described as

$$[Mg_{0.641}Al_{0.359}(OH)_2](CO_3)_{0.178}(NO_3)_{0.002} \cdot 0.70H_2O.$$

During the ion-exchange procedure, performed at acidic conditions, the interlayer nitrates were entirely replaced with polyoxometalate anions. However, the intercalated hydrotalcites contain a small amount of carbonates. It is most likely that the presence of impurities of CO_3^{2-} is a result of incomplete exchange of carbonate anions with polyoxometalate species. It should be noticed that the higher amount of carbonates was detected in the Cr- and W-containing samples. These materials were prepared at milder acidic conditions (pH=5.5) than the other samples. Probably the relatively high level of pH caused a slight stabilization of CO_3^{2-} in the interlayer space of the $Cr_2O_7^{2-}$ and $W_7O_{24}^{6-}$-exchanged hydrotalcites. Moreover, an interaction of atmospheric CO_2 with a strong basic surface of layered double hydroxide cannot be ex-

Table 1 Chemical composition of the as-synthesized samples

Sample	Molar ratio		Content/mass%		
	Mg/Al	Al/Me[*]	C	N	H
HTC	1.79	–	2.49	0.03	4.12
CV$_{10}$	1.66	0.94	0.10	0.00	2.70
CMo$_7$	1.96	0.39	0.15	0.00	2.60
CW$_7$	1.50	0.52	0.38	0.00	2.58
CCr$_2$	1.65	1.02	0.40	0.00	3.56

[*]*Me* =V, Mo, W or Cr

cluded. Nevertheless, there is no doubt that the prepared hydrotalcites contain the polyoxometalate guests as dominant interlayer anions.

The results of TG-DTA analysis for the parent hydrotalcite is shown in Fig. 2a, while the evolved gas mass spectrometric curves are presented in Fig. 2b. The carbonate-containing Mg–Al layered double hydroxide decomposes in three main stages with a total mass loss amounting to 44.7% (46.7% was expected). The endothermic pro-
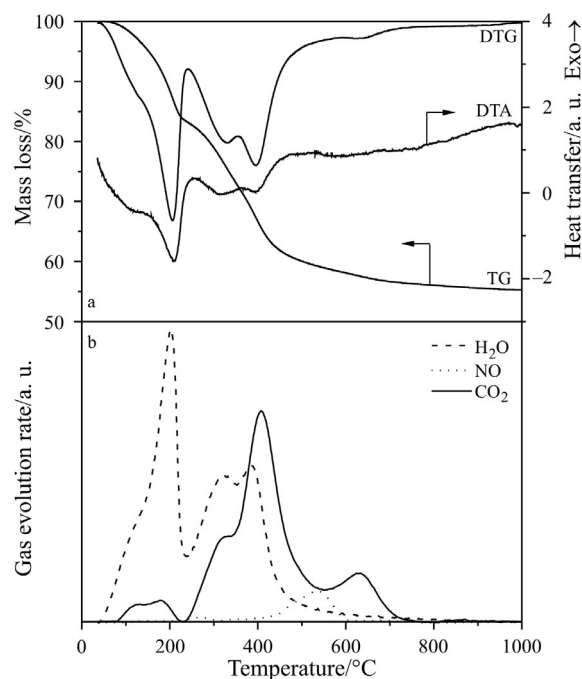
Fig. 2 Results of a – TG-DTA analysis and b – MS of the evolved gases for the HTC sample

cesses of removal of the interlayer water, as well as H_2O and CO_2 weakly adsorbed on the external surface of the sample, take place in the temperature range of 30–240°C. The second step shows two unresolved endothermic peaks (at 325 and 395°C) assigned to the decomposition of the brucite-like sheets and the interlayer anions. Water vapour formed in dehydroxylation process and CO_2 originated from decarboxylation are the main gaseous products of thermal decomposition in this temperature region. Additionally, small quantities of NO that appear in the temperature range from 435 to 605°C are attributed to the decomposition of the interlayer NO_3^- anions. At still higher temperature the elimination of CO_3^{2-} residues occurs. This final stage of the hydrotalcite decomposition proceeds with the maximum rate at 630°C.

The TG and DTA profiles for the $V_{10}O_{28}^{6-}$, $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$-intercalated samples are shown in Fig. 3. Generally, the total mass losses for the $V_{10}O_{28}^{6-}$, $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$-containing hydrotalcites are lower than for HTC due to the high molecular mass of metal atoms constituting polyoxometalate anions remaining in the sample in the course of thermal treatment. The experimentally measured mass losses are: 24.6% for CV_{10}, 24.8% for CMo_7 and 23.8% for CW_7. The observed thermogravimetric curves are essentially similar to that recorded for the parent material. However, all the decomposition peaks are shifted to lower temperatures. The loss of the interlayer and surface water occurs at temperatures lower than 210°C with maximum rates of H_2O evolution at 100–140°C (CMo_7), 150°C (CV_{10}) and 185°C (CW_7).
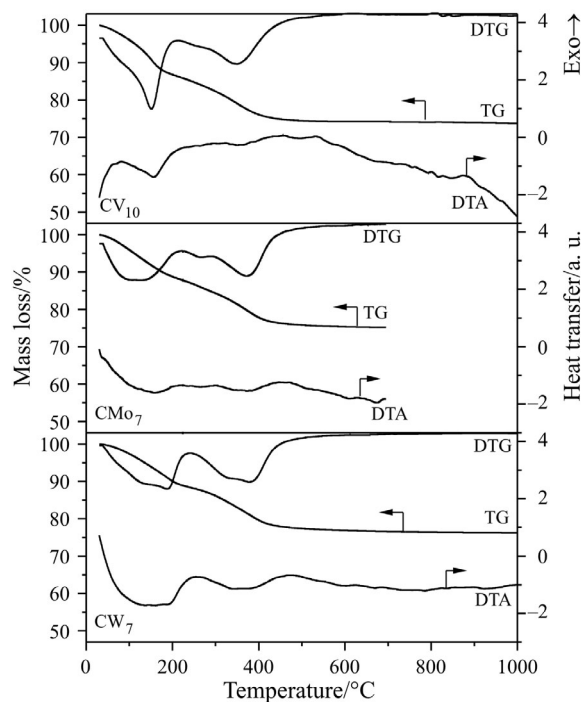

Fig. 3 Results of TG-DTA analysis of the CV_{10}, CMo_7 and CW_7 hydrotalcites

Dehydroxylation of the brucite-like layers proceeds above 240°C and is manifested by two peaks centered at 270 and 370°C (CMo_7), 255 and 350°C (CV_{10}), 330 and 380°C (CW_7). It should be therefore concluded that the intercalation of the HTC sample with isopolymetalate anions results in a slight decrease of thermal stability of hydrotalcite structure. No high-temperature decomposition of carbonates is observed for the polyoxometalate-pillared hydrotalcites.

The thermal behavior of the dichromate-pillared hydrotalcite is illustrated in Figs 4a (TG and DTA profiles) and 4b (MS of the evolved gases). The total mass loss is in this case equal to 36.4%. The sample loses interlayer and surface water at temperature below 250°C. The maximum rate of this endothermic process is found at 170°C. The decomposition of the hydroxyl groups forming the brucite-like sheets as well as small amount of carbonates present in the interlayer space is represented by the asymmetric DTG peak centered at 445°C. Moreover, the dichromate-containing hydrotalcite shows a peculiarity during the thermal treatment differing it from the other studied polyoxometalate-pillared samples. The mass loss correlated with the emission of oxygen is observed over 430°C. This effect could be attributed to the thermal reduction of Cr^{6+} ions. A similar phenomenon was found previously for the Cu-containing hydrotalcites [8].

XRD patterns of the samples calcined at 700°C (Fig. 5) show that during the thermal treatment the hydrotalcite structure is transformed into mixed metal oxides. For the parent hydrotalcite the reflections observed at $2\theta \approx 43$ and $2\theta \approx 63°$ correspond to a MgO-like phase (periclase) or rather to the magnesia-alumina solid solution [5, 18].
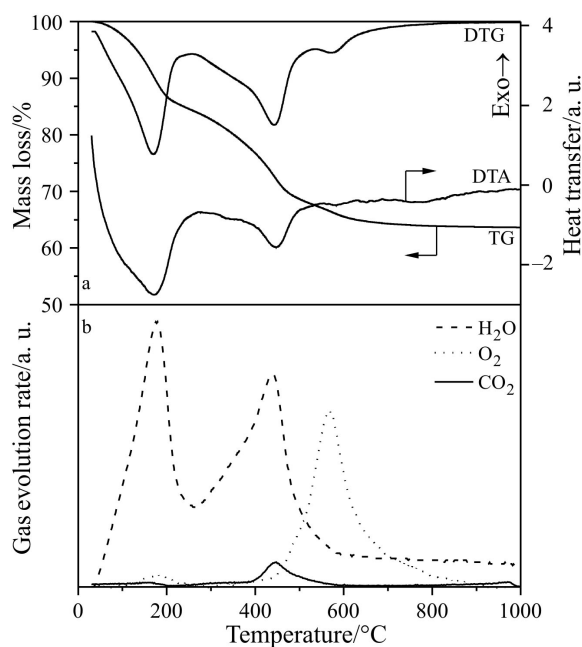

Fig. 4 Results of a – TG-DTA analysis and b – MS of the evolved gases for the CCr_2 sample
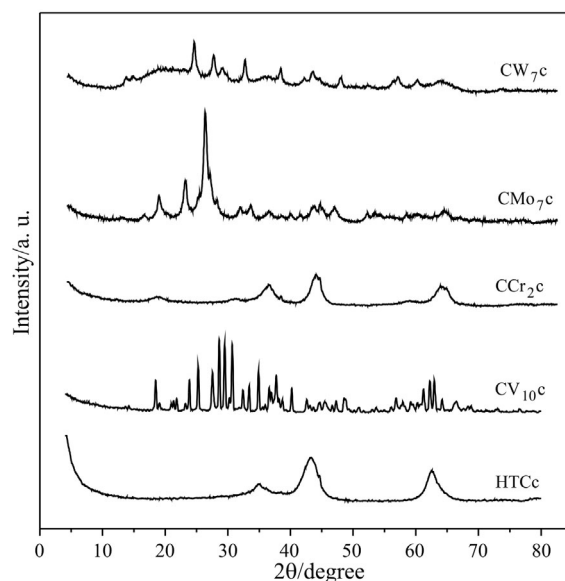
Fig. 5 XRD patterns of the studied hydrotalcites calcined at 700°C

The presence of transition metal in the polyoxometalate-pillared materials causes that the magnesium vanadate (α-$Mg_2V_2O_7$), magnesium molybdate ($MgMoO_4$) and magnesium tungstate ($MgWO_4$) become the dominant phases for the calcined CV_{10}, CMo_7 and CW_7 samples, respectively. The lack of a separate heat effect in DTA curves recorded for the intercalated hydrotalcites suggests that the mentioned above phases have to be formed in the course of dehydroxylation of the brucite-like layers. High dispersion of polyoxometalate anions localized between the brucite-like sheets undoubtedly promotes the solid-state reaction resulting in an appearance of magnesium metalates. The results of X-ray diffraction obtained for CCr_2 confirm the fact that this sample undergoes thermal reduction at high temperature. Besides MgO phase also $MgAlCrO_4$ spinel is observed in the CCr_2 hydrotalcite calcined at 700°C. Thus, the reduction of Cr^{6+} to Cr^{3+} ions proceeds.

Conclusions

Hydrotalcites containing magnesium and aluminum in the brucite-like sheets and carbonate or polyoxometalate ($V_{10}O_{28}^{6-}$, $Cr_2O_7^{2-}$, $W_7O_{24}^{6-}$ or $Mo_7O_{24}^{6-}$) anions in the interlayers were prepared. The introduction of pillars into the interlayer space was confirmed by powder X-ray diffraction and chemical analysis. An increase in the basal spacing was observed for the parent sample exchanged with isopolymetalate anions. The calculated c parameter rose as follows:

$$HTC < CCr_2 < CMo_7 = CW_7 < CV_{10},$$

which corresponded to the size of the introduced anions.

The thermal behavior of the synthesized hydrotalcites was studied by TG/DTA/EGA and XRD measurements. Three essential steps of the decomposition process of HTC were observed. Dehydration of the parent hydrotalcite was complete below 240°C. Dehydroxylation of the brucite-like layers and the decomposition of the interlayer anions (CO_3^{2-} and NO_3^-) occurred in the temperature range of 240–550°C. Finally, decarboxylation started and reached the maximum rate at 630°C. For the polyoxometalate-intercalated hydrotalcites this high-temperature stage of decomposition disappeared due to the absence of residual carbonates. The transition metal containing samples under study were found to be less thermally stable than the parent material. The only hydrotalcite pillared with dichromate anions showed the high-temperature effect of decomposition attributed to the thermal reduction of Cr^{6+} to Cr^{3+}. The samples calcined at 700°C consisted of mixed metal oxide phases. This fact allows assuming that in the final stage of dehydroxylation process the components of layers reacted with the interlayer species forming magnesium metalates.

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