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Direct Observation of a Metastable Solid Phase of $Mg/Al/CO_3$-Layered Double Hydroxide by Means of High Temperature *in Situ* Powder XRD and DTA/TG

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Introduction

Mg/Al-layered double hydroxide (Mg/Al-LDH) has a hydrotalcite-like layered structure in which some anions are located at the interlayer region between positively charged layers of the double hydroxides.[1] The layers have a brucite-like structure, although a part of octahedral Mg^{2+} sites are replaced by Al^{3+} and the resulting excess positive charges are located in the layers. This compound has the general formula $Mg_xAl_y(OH)_{2(x+y)}A_zB_{(y-z)/2}\cdot nH_2O$ (A and B are mono- and divalent intercalating anions, respectively) and shows basal spacing $d = 7.6-7.8$ Å in powder X-ray diffraction (XRD) patterns when A and B are small inorganic anions.[1,2] It has been reported recently that some aromatic compounds with anionic substituents are intercalated thereby enhancing the interlayer distance in LDH.[3−7]

A popular method of preparing these intercalated products is mixing calcined powder of LDH with aqueous solutions of anions to be intercalated. Although the original hydrotalcite-like layered structure at room temperature is lost after LDH is calcined at 400−500 °C, the structure is recovered when the calcined LDH is rehydrolyzed. Anions in the solution are taken into the interlayer region on that occasion. In spite of the usefulness of calcined LDH in the synthesis of intercalated products, changes in the layered structure of LDH through the calcination has rarely been studied so far.[8,9] Thermally metastable phases are sometimes missed in conventional XRD measurements because the measurements are done after samples are heated and then cooled outside XRD sample chambers. Therefore, in order to detect metastable phases, *in situ* high-temperature powder X-ray diffraction (HTXRD) measurements are necessary through which measurement the temperature of samples is kept constant. In particular, detailed examination below 400 °C is essential since some thermal events have been observed in this temperature region of differential thermal analysis/thermal gravimetry (DTA/TG).[4,5] In this study, Mg/Al-LDH with interlayer carbonate ($Mg/Al/CO_3$-LDH) is synthesized with different atomic ratio Mg/Al in the layer and change in the layered structure of $Mg/Al/CO_3$-LDH associated with elevating temperature below 1000 °C is investigated by means of *in situ* HTXRD with the aid of DTA/TG and X-ray photoelectron spectroscopy (XPS).

Table 1. Chemical Composition of the Solids Synthesized with Different Mg/Al Atomic Ratios

Mg/Al[a]	formulae	Mg/Al[b]
2.0	$Mg_{0.65}Al_{0.35}(OH)_{2.00}(CO_3)_{0.17}\cdot 0.42H_2O$	1.9
3.0	$Mg_{0.72}Al_{0.28}(OH)_{1.98}(CO_3)_{0.15}\cdot 0.48H_2O$	2.6
4.0	$Mg_{0.76}Al_{0.24}(OH)_{1.91}(CO_3)_{0.17}\cdot 0.42H_2O$	3.2

[a] In preparation. [b] In analysis.

Experimental Section

The synthesis and analysis of $Mg/Al/CO_3$-LDH has been described previously.[1,4] A mixture of aqueous solutions of $MgCl_2$ (0.28 mol/dm^3) and $AlCl_3$ (0.07 mol/dm^3) was added dropwise with vigorous stirring to an aqueous solution of Na_2CO_3 (0.25 mol/dm^3); the reaction mixture was at room temperature in air, and the pH was kept at 10−11 by using NaOH, followed by aging for 42 h at 73−74 °C. After washing until a test for Cl^- with Ag^+ in the filtrate was negative, the white precipitate of $Mg/Al/CO_3$-LDH was dried overnight at 80 °C before measurement and analysis. Two metal components were separated by using a cation-exchange resin, followed by chelatometric titration.[10] Table 1 lists the result of chemical analysis where the atomic ratio of two metal components was varied a Mg/Al = 2,3, and 4 in the sample preparation with other synthetic conditions unchanged.

Measurement of *in situ* HTXRD was carried out in the temperature range 30−1000 °C in air by using a Rigaku Rint 2500 X-ray diffractometer equipped with a high-temperature attachment, with conditions of sequential temperature increase (5 °C/min) and of temperature holding time (15 min) before each measurement. The Cu Kα line was used for the X-ray source, with a monochromator positioned in front of a scintillation detector. DTA/TG was done by using a Shimadzu TA-50 Thermoanalyzer between room temperature and 1000 °C with temperature rising rate of 2 °C/min and with air flow. Under the reduced pressure (0.1−1 μPa), a Shimadzu ESCA-1000 with a Mg cathode ($h\nu = 1253.6$ eV; 10 kV/30 mA) was used for measuring of XPS with a C 1s electron as an energy reference (285.0 eV).[11]

Results and Discussion

Figure 1 shows a general view of the HTXRD patterns of $Mg/Al/CO_3$-LDH synthesized with the ratio Mg/Al = 3 in the whole temperature range. There are three temperature regions which are classified by the common HTXRD pattern in each region: $30 \le T \le 180$ °C, $180 \le T \le 380$ °C, and $380 \le T \le 1000$ °C. Sharp and intense patterns are observed in the former two temperature regions. The pattern in the first region, where all the diffraction lines are due to the well-known hydrotalcite-like layered structure of $Mg/Al/CO_3$-LDH (Phase I), agrees with that reported by many authors.[1,2,4] This structure becomes obscure at 180 °C, and another new phase (Phase II) appears at this temperature. Phase II grows at 200−260 °C and diminishes completely at 380 °C. Three major points are observed in the HTXRD pattern of Phase II when the pattern is compared with

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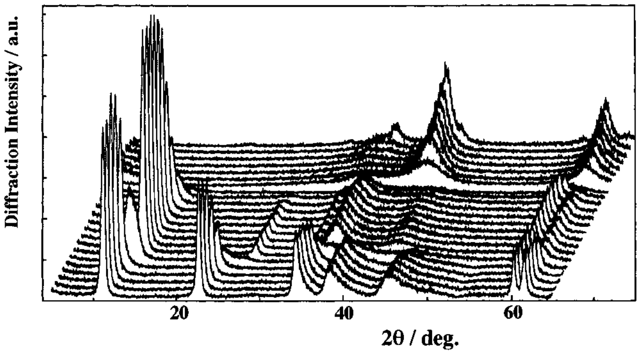

Figure 1. *In situ* HTXRD patterns of Mg/Al/CO_3-LDH (Mg/Al = 3) at different temperatures (°C) from bottom to top: 30, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 320, 340, 360, 380, 400, 500, 600, 700, 800, 900, and 1000.

that of Phase I. First, the most intense line of Phase II lies at $2\theta = 13.4°$, larger by 2.2° than the most intense line of Phase I. Second, the pattern at high 2θ region is different from that of Phase I. Third, the pattern at around $2\theta = 60°$ resembles that in both phases. In the third temperature region, MgO appears at above 400 °C, and finally a spinel phase ($MgAl_2O_4$) appears near 1000 °C.[8] These solid phases result from the dehydroxylation of the double hydroxides when the layer structure collapses. The HTXRD pattern at 1000 °C remains unchanged after the sample in the XRD chamber is cooled down to room temperature and then ground in an agate mortar, although a small shift of the 2θ angle is observed owing to the thermal contraction.

The HTXRD pattern of Phase II at 300 °C can be indexed as 2θ (*hkl*) = 13.40° (001), 26.96° (002), 33.86° (100), 36.40° (101), 43.74° (102), 60.24° (110), and 61.90° (111), assuming a hexagonal lattice with unit cell dimensions $a_0 = 3.070$ Å and $c_0 = 6.592$ Å. Only two 00*l*-type lines are observed in this indexing, which is in good contrast to the XRD pattern of Phase I where several intense 00*l*-type diffraction lines are observed. Considering that a developed layered structure along the *c* axis in Phase I gives the extensive 00*l*-type lines,[1,2,4] the extent of layer stacking in the crystal structure of Phase II is relatively small. The basal spacing of Phase I is equal to the sum of the thickness of one layer of Mg/Al-double hydroxides (4.8 Å) and the interlayer distance (3.0 Å).[1] The interlayer distance of the latter phase is determined by the dimensions of the interlayer carbonate dianions, which are located with their molecular planes parallel to the internal surface of the layer.[1] On the other hand, the interlayer distance of Phase II is calculated to be 1.8 Å with the same assumption for the thickness of one double hydroxide layer as that of Phase I.

Among three solid samples of different atomic ratio Mg/Al in Table 1, the temperature at which Phase II appears in HTXRD depends on the ratio although the XRD pattern of this phase is common. In the HTXRD pattern of Mg/Al/CO_3-LDH synthesized with atomic ratio Mg/Al = 3, Phase II appears at 180 °C and disappears at 380 °C (Figure 1). In the pattern of the solid sample synthesized with the ratio Mg/Al = 2, Phase II appears at 200 °C and disappears at 380 °C whereas in the pattern of the sample synthesized with the ratio Mg/Al = 4, these temperatures are 160 and 380 °C, respectively. In other words, the transition temperature from Phase I to Phase II decreases with increasing the atomic ratio Mg/Al of samples and the temperature from Phase II to MgO/$MgAl_2O_4$ is unchanged among three samples. The former result indicates that the Al^{3+} thermally stabilizes the hydrotalcite-like layered structure of Mg/Al/CO_3-LDH. This is partly elucidated as the increased electrostatic attraction between the excess positive charge on this metal cation and the interlayer carbonate contributes to the thermal stability of the Phase I. An exhaustive study would be necessary in order to obtain a more definite and total view of the effect of the atomic ratio Mg/Al on the thermal stability of Phase I.

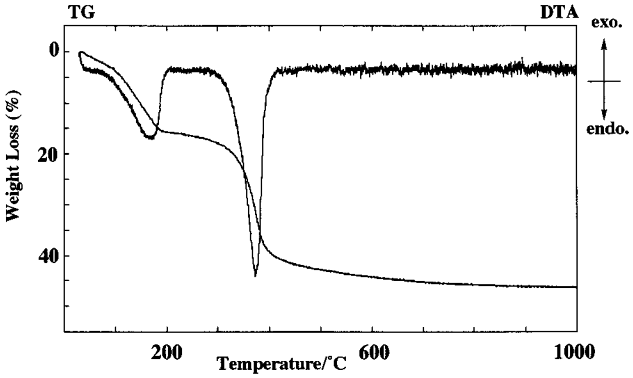

Figure 2. TG/DTA curves of Mg/Al/CO_3-LDH synthesized with the atomic ratio Mg/Al = 4.

Figure 2 illustrates the DTA/TG curves of Mg/Al/CO_3-LDH synthesized with the ratio Mg/Al = 4. Two endothermic peaks appear at 160 °C (endotherm A), and the other is at 374 °C (endotherm B). Total weight loss of sample mass throughout the temperature range in the TG curve agrees well with the summation of all volatile components (H_2O and CO_2) in the chemical formula in Table 1. It should be noted that the temperatures of endotherms A and B agree with those of formation and degradation of Phase II in HTXRD pattern of this solid sample, respectively. This agreement is observed in two other samples of different atomic ratio Mg/Al. Although a quantitative elemental (C, H) analysis of Phase II never gives a reproducible carbon content, the content is always in the trace order. Since the HTXRD pattern of Phase II indicates that the layered structure is still maintained in this phase, it is reasonable to assume that the weight loss at endotherm A in the TG curve is due to elimination of interlayer carbonate and water which appears as nH_2O in the formula in Table 1. When Phase II is formed at the temperature of endotherm A, it is reasonable to suppose that the interlayer carbonates react with interlayer water molecules producing hydroxyl anions at the interlayer gallery of this phase. The less bulky nature of the interlayer hydroxyl anion compared to the carbonate explains the reduction of the interlayer distance in XRD patterns from 3.0 Å (Phase I) to 1.8 Å (Phase II). Since no LDH with interlayer hydroxyl anion has been reported so far for any combination of metal cations in the layer, it is safe to conclude that the resulting layer structure in Phase II is not stable. The instability of Phase II is verified by the observation that the XRD intensity of Phase II decreases slowly when the sample calcined at 300 °C in an electric furnace is stored at room temperature in an air-tight silica gel desiccator. The decrease of XRD intensity becomes significant after 56 days in the desiccator, indicating that Phase II is also metastable at room temperature and degrades slowly to an XRD-silent amorphous phase in a dry condition. Furthermore, when the Phase II sample is placed in a humid atmosphere at room temperature, Phase I becomes predominant in the XRD pattern in a day. It is well-known that the interlayer carbonate of Phase I is stable against anion exchange reactions at room temperature in aqueous solutions.[1] The presence of metastable Phase II well explains the fact that Mg/Al/CO_3-LDH must be calcined at the temperature as high as 400 °C when the calcined powder is used for the intercalation of desired anionic species in aqueous solution. The calcination is necessary in order to eliminate stable CO_3^{2-} from the interlayer gallery.

XP spectra of Mg/Al/CO_3-LDH show several photoelectron peaks which are assigned to core level electrons emitted from Mg, Al, C, and O atoms of the solid compound.[12] Since Al^{3+} ions occupy the octahedral (O_h) Mg^{2+} sites isomorphously, the coordination number of Al^{3+} in the layers of Phase I is six (O_h Al^{3+}). The binding energy of an Al 2p electron has been reported for O_h Al^{3+} and T_d Al^{3+}.[13,14] Barr et al. have analyzed the XPS spectra of YAG and have reported that the binding energy of O_h Al^{3+} is larger than that of T_d Al^{3+}. In this study, the binding energy of an Al 2p electron for Phase II is 73.8 eV and no significant shoulder in the lower energy side is observed. This value is equal to the binding energy of Phase I (73.6 eV)[4] when a bandwidth of ±0.5 eV is considered. Therefore, it is concluded that Phase II also has octahedral Al^{3+} in the layer.

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