SHORT COMMUNICATION

Kinetics on Dehydration Reaction during Thermal Treatment of MgAl-CO₃-LDHs

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Abstract−Kinetics on the dehydration reaction of interlayer water during the thermal treatment of synthetic LDHs was studied. LDHs with different layer charges such as Mg_8Al_2-CO_3-LDH, Mg_6Al_2-CO_3-LDH and Mg_4Al_2-CO_3-LDH were used. The powder X-ray diffraction patterns and TGA diagrams of synthetic LDHs show the typical structural and thermal properties of MgAl-LDHs intercalated with carbonate. The non-isothermal kinetics for the loss of interlayer water molecules was investigated by the TGA diagrams. The water molecules dehydrated from interlayer of LDHs with similar activation energies of 106, 105 and 107 kJ mol^{-1} for the Mg_8Al_2-CO_3-LDH, Mg_6Al_2-CO_3-LDH and Mg_4Al_2-CO_3-LDH at each inflection point of TGA curves, respectively. The dehydration reactions were controlled by the diffusion of water molecules through two-dimensional interlayers, and the frequency factors were 5.78×10^{11}, 5.68×10^{10} and 4.66×10^{10} min^{-1} for the Mg_8Al_2-CO_3-LDH, Mg_6Al_2-CO_3-LDH and Mg_4Al_2-CO_3-LDH, respectively.

Key words: Layered Double Hydroxide, Non-isothermal Kinetics, Dehydration, Thermogravimetric Analysis (TGA)

INTRODUCTION

Hydrotalcite-like compounds (HTlcs), which are also called layered double hydroxides (LDHs) are a family of interesting materials with many practical applications as catalytic materials, ceramic precursors, medicine stabilizers, ion-exchangers/adsorbents, and composite materials [Bruce and O'Hare, 1996; Cavani et al., 1991; Ogawa and Kuroda, 1995; Vaccari, 1995]. In this class of materials, the isomorphous substitution of M(III) ion for M(II) ion of M(II)(OH)₂ (brucite-like compounds) generates positively charged layers and the net positive charge is compensated by intercalated anions (inorganic/organic) to maintain charge neutrality, and the water of crystallization also finds a place in the free space of interlayer [Allmann, 1968; Taylor, 1973]. These materials could be formulated as M(II)$_{1-x}$M(III)$_x$(OH)$_2$(A^{m-})$_{x/m}$·nH₂O; M(II)=Mg, Ni, Zn; M(III)= Al, Cr, Fe; A^{m-} is exchangeable anion with charge −m; 0.20≤x≤ 0.33 [Cavani et al., 1991]. The value of x is the contents of M(III) to the total metal, which means charge density of the interlayer. A wide range of derivatives containing various combinations of M(II), M(III), and A^{m-} ions can be readily synthesized under laboratory conditions [Chibwe and Jones, 1989; Miyata, 1980; Taylor, 1973]. These basic materials have a relatively large surface area of 20-120 m²g^{-1} and anion-exchange capacity of 2-5 meqg^{-1} [Miyata, 1983].

The thermal treatment of LDHs results in the destruction of layered structure and then the formation of catalytically active mixed metal oxides (MMOs) [Reichle, 1986; Sato et al., 1986a]. The dehydration reaction and decomposition occur by thermal treatment. But the layered structure is reconstructed with anionic species such as Cl$^-$, OH$^-$, CrO₄$^{2-}$, and PO₄$^{3-}$ when the MMOs are reacted with aqueous anions [Constantino and Pinnavaia, 1995; Sato et al., 1986b]. The reconstruction of interlayer of LDHs is referred the rehydra-

tion reaction. This reconstruction property of MMOs proves it to be useful for removing anionic species from industrial wastes [Parker et al., 1995; Sato et al., 1986b]. The sorption behavior of aqueous TcO₄$^-$, I$^-$, and CrO₄$^{2-}$ on MMO of MgAl-CO₃-LDH have already been investigated [Kang et al., 1996, 2001; Rhee et al., 1997]. The ion-exchange reactions were proposed and equilibrium constants were also calculated.

Investigation of the thermal decomposition of LDHs has been an active field and many studies have been reported for the effective methods to obtain well-dispersed homogeneous MMOs [Barriga et al., 1996; Chibwe and Jones, 1989; Reichle et al., 1986; Rives, 1999; Sato et al., 1986; Velu et al., 1997; Yun and Pinnavaia, 1995]. The thermal behavior of LDHs intercalated with carbonate ion is generally characterized by two steps [Brindley and Kikkawa, 1980; Yun and Pinnavaia, 1995]. The first one is an endothermic process at lower temperatures where weight losses are caused by the removal of surface water and interlayer water. This is the dehydration reaction of LDHs. This process is reversible, reabsorbing water molecules from aqueous solution or air. The second one is also an endothermic process at higher temperatures, the transition of which is due to the losses of water from hydroxyl groups of brucite-like layer and carbon dioxide from carbonate ion. As a result, the layered structure is destroyed.

In spite of a great deal of research on the thermal behavior of LDHs, however, few kinetic studies for the dehydration of interlayer water molecules and decomposition of layers for the LDHs have been reported up to now. The only related study was reported by Velu et al., who investigated the decomposition kinetics of ZnAl-X-LDHs (X=Cl$^-$, NO₃$^-$, CO₃$^{2-}$, and SO₄$^{2-}$) and mentioned the correlation between the activation energy and interlayer anions [Velu et al., 1997]. According to their result, hydrogen bonding between water molecules and anions might play a key role for determining the activation energy. There, however, remain some factors to be considered such as metal composition and charge density of posi-

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tive hydroxide layer, grain size of LDHs, and dimension and charge of interlayer anions.

In this work, we describe the kinetic behaviors of interlayer water molecules in the synthetic MgAl-CO$_3$-LDHs with different Mg/Al ratio (x values) in the layer and evaluate the non-isothermal kinetics parameters such as the activation energy and frequency factor for the dehydration reaction investigated by means of TGA. In addition, we report the effect of charge density of the hydroxide layer on the dehydration reaction process. It would be valuable to understand the dehydration /rehydration reaction kinetics of interlayer water molecules in LDHs because this work becomes a good model study for the diffusion of small molecules into or out of two-dimensional layered catalyst such as polyoxometallate (POM)-pillared clay minerals.

EXPERIMENTAL

MgAl-CO$_3$-LDHs were prepared by similar method reported previously [Rhee et al., 1995]. To an aqueous solution containing MgCl$_2$· 6H$_2$O and AlCl$_3$·6H$_2$O with Mg/Al ratios of 2, 3, and 4, a mixed solution of 2 M NaOH and 0.2 M Na$_2$CO$_3$ was slowly added under continuous stirring at pH 10 and 40 °C. White precipitates of LDHs were separated from the mixtures by centrifugation, washed with deionized water and dried at 60 °C. The final dried white powders were sieved through a 250 μm mesh.

The contents of C and H of the synthetic LDHs were analyzed by using a Carlo Erba 1106 elemental analyzer, and the contents of metals were determined by using ICP-AES at Korea Basic Science Institute. Powder X-ray diffraction patterns were obtained by a Rigaku D/MAX-IIIC diffractometer using nickel-filtered Cu Kα radiation (1.5418 Å) with a graphite monochromater at rate 2θ=4° min^{-1} and with a range 2θ=5-65 degrees. The crystallite size was calculated by Scherrer's equation using half-maximum width of the diffraction peaks. Thermogravimetric analyses for LDHs were recorded on a DuPont 2050 TGA instrument from room temperature to 1,000 °C at different heating rate of 1.25, 2.50, 5.00 and 10.0 °C min^{-1} under N$_2$ gas flow 10 cm^3 min^{-1}. Equal masses of test sam-
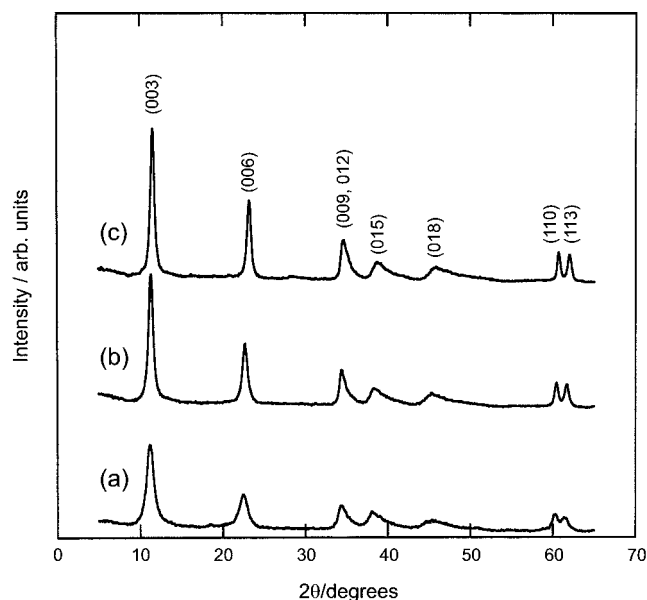

Fig. 1. Powder X-ray diffraction patterns of Mg$_8$Al$_2$-CO$_3$-LDH (a), Mg$_6$Al$_2$-CO$_3$-LDH (b), Mg$_4$Al$_2$-CO$_3$-LDH (c).

ple (~30 mg) were used in TGA measurements.

RESULTS AND DISCUSSION

The powder X-ray diffraction spectra for LDHs synthesized are shown in Fig. 1. These patterns are in good agreement with other synthetic hydrotalcite [Powder Diffraction Files, 1986a] and natural hydrotalcite [Powder Diffraction Files, 1986b]. The chemical compositions and structural parameters of the prepared LDHs are summarized in Table 1. The LDHs with Mg/Al ratios of 4, 3 and 2 will be described as Mg$_8$Al$_2$-CO$_3$-LDH, Mg$_6$Al$_2$-CO$_3$-LDH and Mg$_4$Al$_2$-CO$_3$-LDH, respectively. Chemical analyses results indicated that the molar ratios of Mg to Al in the solid products were close to those of the starting aqueous reaction mixtures. The lattice param-

Table 1. The chemical compositions, structural parameters, crystallite sizes and kinetic parameters of synthetic LDHs

	Mg$_8$Al$_2$-CO$_3$-LDH	Mg$_6$Al$_2$-CO$_3$-LDH	Mg$_4$Al$_2$-CO$_3$-LDH
Mg/%[a]	25.36	22.69	19.77
Al/%[a]	6.86	8.40	10.61
x[b]	0.196	0.250	0.326
Interlayer water/%[c]	15.3	16.3	16.7
Unit cell a/Å	3.07	3.06	3.05
Basal spacing/Å	7.90	7.82	7.65
Crystallite size/Å[d]			
(110) direction	79.2	129	167
(003) direction	65.4	101	131
E_a/kJ mol^{-1}	106	105	107
Z/min^{-1}	5.78×10^{11}	5.68×10^{10}	4.66×10^{10}

[a]Weight percent.

[b]The value of [Al]/([Mg]+[Al]) in solid products.

[c]Weight loss of the first transition on the basis of TGA curves.

[d]Calculated by Scherrer's equation using half-maximum width of the X-ray diffraction peaks.
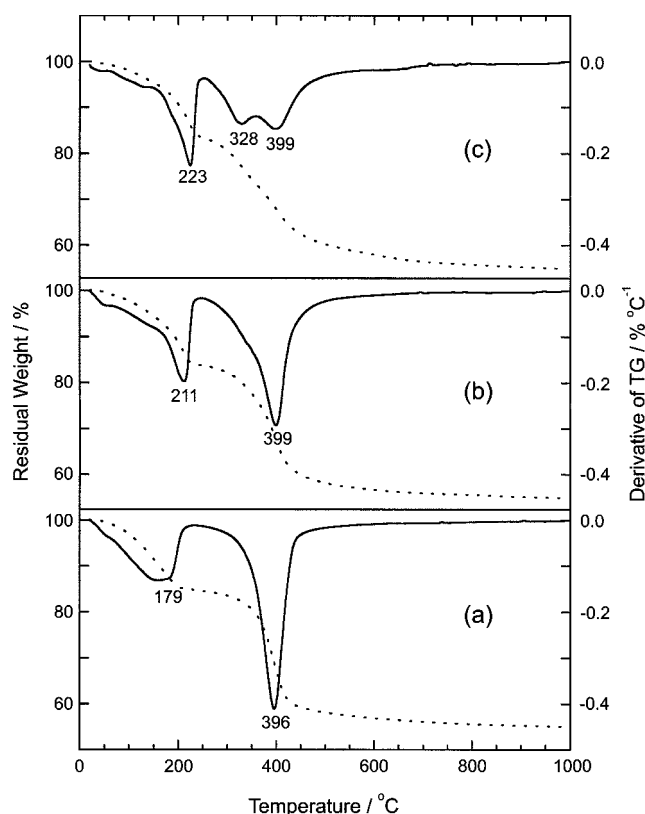
$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O \leftrightarrows Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} + nH_2O(g)$$

Fig. 2. Thermogravimetric analysis (dotted line) and derivative of TG (dTG) (solid line) diagrams of Mg₈Al₂-CO₃-LDH (a), Mg₆Al₂-CO₃-LDH (b), Mg₄Al₂-CO₃-LDH (c). Heating rate is 10.0 °C min⁻¹.

eter a value decreased with increasing the content of Al. The basal spacing of Mg₈Al₂-CO₃-LDH, Mg₆Al₂-CO₃-LDH and Mg₄Al₂-CO₃-LDH were 7.90 Å, 7.82 Å and 7.65 Å, respectively. The basal spacings also decreased with increasing the content of Al due to the increase of Coulombic attractive force between the positively charged brucite-like layers and the negatively charged interlayer anions [Yun and Pinnavaia, 1995]. The intensity of all the PXRD patterns for the prepared materials increased with the content of Al as shown in Fig. 1, which results from the increase of crystallite sizes in the direction of both the (003) and (110) faces.

The thermal analysis profiles of three LDHs are shown in Fig. 2. Two weight losses are observed [del Arco et al., 1993]; the first one is centered at a low temperature around 200 °C due to removal of water molecules from interlayer space, and the second one, which ends at a high temperature around 600 °C due to evolution of carbon dioxide from interlayer carbonate ion and elimination of water from condensation of lattice hydroxide. A further, small weight loss is observed at higher temperatures. In the second transition, the weight losses of Mg₄Al₂-CO₃-LDH are divided into two stages, while those of the others are overlapped. These two transitions depend on many factors such as x values, hydrothermal treatments, and drying conditions quantitatively and qualitatively.

The first stage is the thermal dehydration of interlayer water molecules of LDHs, which process is a reversible process [Brindley and Kikkawa, 1980; Yun and Pinnavaia, 1995]. This can be expressed by the simple equation.
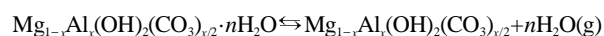
When the water molecules are dehydrated, the layered structure of LDHs is not destroyed, but basal spacing is slightly decreased. The dehydration process may involve several stages: the breaking of bonds among brucite-layers, anions and water molecules; the slight deformation of initial crystal lattice; the formation of new crystal lattice; the adsorption and desorption of gaseous water; water diffusion; heat transfer. The rate of thermal dehydration is determined by the rate of one or more of these stages.

Inflection temperatures, which correspond to the temperature of maximum weight loss, were obtained from derivatives of TGA (dTG) diagrams. It was found that inflection temperatures were shifted toward higher region as the content of Al of LDHs increased [Miyata, 1980; Mascolo and Marino, 1980]. By pretreatment of sample at 60 °C for 100 h, it is known that there is no interparticle pore water [Yun and Pinnavaia, 1995], wherein the water is condensed between aggregated crystal plates. No dTG data corresponds to the interparticle pore water. Therefore, the first transition of weight loss in TGA diagrams corresponds to the dehydration reaction of interlayer water molecules in the LDHs. Because the concentration of carbonate in interlayer was diluted at very low charge density of LDH, water molecules might be movable more easily than in the interlayer of higher charged LDH. Since a different extent of hydrogen bondings could exist between water molecules and carbonate ions and brucite-like layers in the interlayer, dehydration of water molecules could be influenced by layer charge.

The usual method for obtaining kinetics data involves a series of experiments under isothermal conditions at different temperatures. Under isothermal conditions the reaction rate of thermal decomposition is generally expressed by $d\alpha/dt = kf(\alpha)$, where α stands for the fraction of material reacted, t reaction time, k rate constant. The $f(\alpha)$ is a certain function of α, which depends on the reaction mechanism. The temperature dependence of k is expressed by Arrhenius equation $k = Ze^{-Ea/RT}$, where E_a is the activation energy and Z frequency factor. Non-isothermal kinetic methods enable one to conduct a series of experiments quickly at a range of temperature [Brown and Phillpotts, 1978; Horowitz and Metzger, 1963; Kim and Chun, 1995; Zsakó, 1968].

These involve the continuous measurement of a change of physical properties of sample which is increased with a constant heating rate. Using several non-isothermal runs at different heating rates, $q_1, q_2, \ldots, q_n$, at common value of conversion $\alpha = \alpha_i$, at $T = T_1$ in run 1, at $T = T_2$ in run 2, and $T = T_n$ in run n, the activation energy of reaction can be calculated. The derivatives of TGA with heating rates $q_1 = 1.25$, $q_2 = 2.50$, $q_3 = 5.00$ and $q_4 = 10.0$ °C min⁻¹ of Mg₆Al₂-CO₃-LDH are shown in Fig. 3. The temperature range of dehydration reaction is shifted to high temperature as the heating rate is increased. The activation energies of LDHs obtained from the four runs at inflection temperatures are shown in Table 1. The interlayer water of Mg₈Al₂-CO₃-LDH, Mg₆Al₂-CO₃-LDH and Mg₄Al₂-CO₃-LDH was dehydrated with activation energy 106, 105 and 107 kJ mol⁻¹, respectively. It is quite interesting that the activation energies of interlayer water for three MgAl-CO₃-LDHs are very close to each other in spite of their different layer charge densities. The activation energy might be affected by the extent of hydrogen bondings between water molecules and interlayer anions and brucite-like lay-
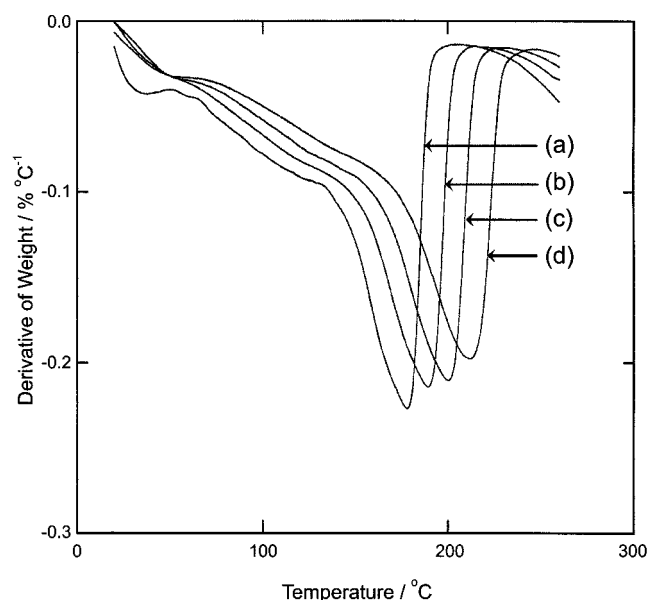
Fig. 3. Derivative of TG diagrams of Mg₆Al₂-CO₃-LDH with various heating rates: (a) 1.25, (b) 2.50, (c) 5.00 and (d) 10.0 °C min⁻¹.

ers. The hydrogen bondings of water molecules in LDHs may be affected by many factors such as the charges and compositions of layers, and the dimensions and shapes of interlayer anions. The activation energies of three LDHs, however, are the same magnitude.

The rate constant of the dehydration reaction is also influenced by frequency factor, Z. The type of reaction, shape and crystallite size of LDH particles and the steric constraint of interlayer anions are considerable factors in determining the frequency factor [Yun and Pinnavaia, 1995]. It is well known that the dehydration of LDH is a topotactic reaction without cracking. The reaction is controlled by the diffusion of water molecules or geometric factors of LDH. Because the LDH crystallized with hexagonal unit cell and reported SEM image indicated that apparent shape seemed to be a hexagon, the shape can be simplified to a cylindrical one [Cavani et al., 1991]. The water molecules of the interlayer diffuse two-dimensionally (D_2 mechanism) [Pesic et al., 1992]. The frequency factors were 5.78×10^{11}, 5.68×10^{10} and 4.66×10^{10} min⁻¹ for the Mg_8Al_2-CO₃-LDH, Mg_6Al_2-CO₃-LDH and Mg_4Al_2-CO₃-LDH, respectively. The increase of the Al content induces the crowdedness of the interlayer due to more carbonate ions. Therefore, the steric constraint is increased and frequency factor Z is decreased. Kinetic parameters are summarized Table 1.

CONCLUSION

In summary, three synthetic MgAl-CO₃-LDHs with different Mg/Al ratio are all typical layer-structured materials and have a linear variation of the a and c parameters with layer charge.

Well-known two weight losses were observed in TGA diagrams of LDHs: dehydration of interlayer water and decomposition of layer and interlayer anions, respectively. Adopting heterogeneous nonisothermal decomposition kinetic method, the activation energy and frequency factor for the loss of interlayer water molecules at inflection temperature were investigated by the TGA diagrams obtained

at different heating rates. Inflection temperature shifts towards higher region. The activation energies of the interlayer water for Mg_8Al_2-CO₃-LDH, Mg_6Al_2-CO₃-LDH and Mg_4Al_2-CO₃-LDH are nearly the same value of about 106 kJ mol⁻¹. The frequency factors decreased with increasing Al contents indicating the steric constraint of carbonate ions. The dehydration reaction is controlled by the diffusion of water molecules and the frequency factor is more important than activation energy factor.

The effects of metal composition, particle size and interlayer anions of LDHs are objectives for future work. It would be meaningful to elucidate the dehydration reaction process completely, which would provide a great deal of information for the diffusion of small molecules into interlayer of LDHs.

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