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Preparation of Zn/Ga-layered Double Hydroxide and Its Thermal Decomposition Behavior

Kiyoshi FUDA, Noboru KUDO, Shinji KAWAI, and Toshiaki MATSUNAGA
Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Akita 010

A Zn/Ga-layered double hydroxide (LDH) with CO_3^{2-} ions was prepared by coprecipitation method. The well crystallized powder was obtained and analyzed by XRD and FT-IR. Its thermal decomposition behavior studied by TG-GC system indicated that almost half of CO_3^{2-} ions remained in the poorly crystallized oxide matrix even at 773 K.

Mixed metal layered double hydroxides (LDHs; $M^{2+}_{1-x}M^{3+}_x(OH)_2(CO_3)_{x/2}nH_2O$) have been utilized for many uses such as anion exchange materials, precursors of catalysts and anion sorbents.1) Recently a variety of LDHs containing different di- and trivalent cations have been prepared.2) However, the knowledge of a LDH containing Zn^{2+} and Ga^{3+} is very little in literature.3) Here we wish to demonstrate that a well-crystallized hydrotalcite phase can be obtained by coprecipitation method and that CO_3^{2-} ions adsorbed in the interlayer are tightly bonded to the poorly crystallized oxide matrix even at 773 K when thermally decomposed.

Mixed solutions of $ZnCl_2$ and $GaCl_3$, having total cation concentration of 0.2 M, were prepared with cation molar ratio, $x=Ga^{3+}/(Zn^{2+}+Ga^{3+})$, 0.33. The mixed cation solution was dropped slowly into 0.1 M Na_2CO_3 aqueous solution with vigorous stirring, and the pH of the solution was kept at 10.0 by addition of 2 M NaOH during precipitation. The obtained suspension was further aged at 333 K for 18 hours. The powder was separated centrifugally and washed repeatedly with deionized water, and then dried in vacuo at 318 K. The chemical formula of the sample determined by atomic absorption and gravimetric analyses was $Zn_{0.7}Ga_{0.3}(OH)_2(CO_3)_{0.16}0.66H_2O$.

The XRD measurement was performed by Rigaku RAD-C diffractometer. The XRD pattern of the sample showed sharp and symmetrical peaks characteristic of well-crystallized hydrotalcite-type phase, which were indexed in rhombohedral symmetry (the $R\bar{3}m$ space group). Figure. 1 shows the patterns of the original sample (a) and the samples calcined at elevated temperatures (b-f). The pattern of the original sample is quite similar to that of Zn/Al-LDH reported by Thevenot et al.[4] The lattice parameters were calculated by using a least square fitting program: a_0=0.3112 nm and c_0=2.299 nm. From patterns of the calcined samples, it is found that the layer structure is destroyed at 473 K and poorly crystallized phase appears up to 1073 K and crystallized phases are clearly observed at 1273 K including mainly ZnO, $ZnGa_2O_4$ and some Ga oxide phases.

Infrared analysis was performed using KBr pellets. Sample was run on a Perkin-Elmer 1640 model FT-IR spectrometer. In Fig.2, the spectra of the original sample and the sample calcined at 673 K are shown. In the IR pattern of the original sample a relatively sharp and strong line at 1360 cm^{-1} is observed, which is assigned to ν_3 (asymmetric stretching) vibration mode of a carbonate ion. If the carbonate ion lies in a site of lower symmetry, e.g. C2v, than the unperturbed carbonate, D3h, the line will be resolved into two lines due to removal of degeneracy of ν_3-vibration, and ν_1 (1095 cm^{-1}) will become infrared active. However, both of splitting of ν_3 and absorption corresponding to ν_1 are not observed in this sample. This fact indicates that the carbonate ion lies in a symmetrical site between two adjacent brucite layers in parallel direction. On the contrary, broadened and doubly splitted absorption lines of ν_3 appear in the spectra of the sample calcined at 673 K as is shown

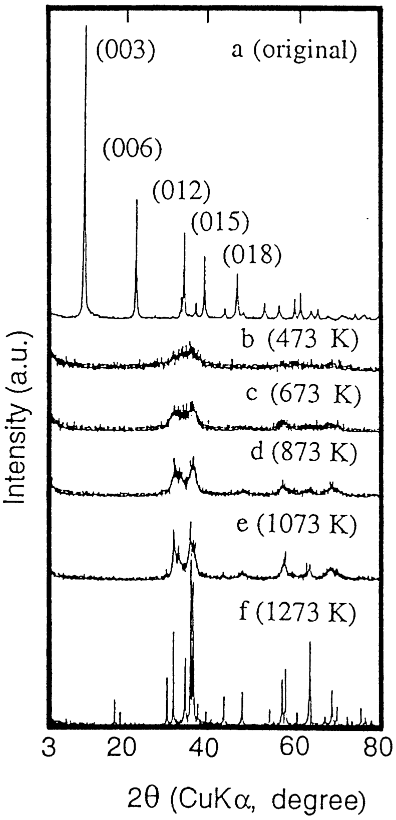

Fig. 1. XRD patterns of Zn/Ga-LDH (a) and of the calcined samples (b-f).

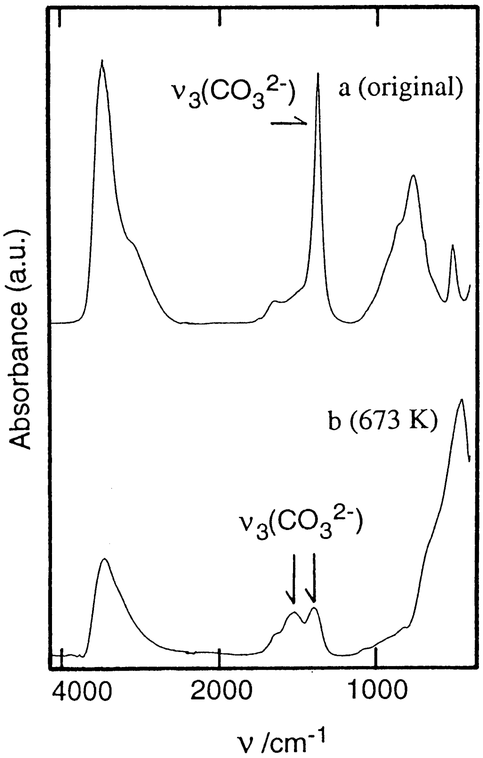

Fig. 2. FT-IR spectra of Zn/Ga-LDH (a) and of the sample calcined at 673 K (b).

at the bottom of the figure. This indicates that although significant amounts of CO_3^{2-} reside in the sample, the symmetric feature of the CO_3^{2-}site was lost in the calcined sample. In addition, a broad absorption band at around 3400 cm^{-1}, which is assigned to the stretching vibration of OH, was also remained in the spectra. This indicates that hydroxyls also reside in significant amounts.

Thermal decomposition behavior was observed by a gas-flow type TG (Shimazu TG-30 model), which was equipped with GC (active carbon column). The temperature programmed decomposition (TPD) profile for CO_3^{2-} was obtained by periodic monitoring of the CO_2 gas evolution from the sample by GC. The heating rate and gas flow rate were 5 K min^{-1} and 50 ml min^{-1}, respectively. The result of the sample is shown in Fig. 3. In the TG line the first step of the relatively large loss of weight is observed between 373 K and 473 K and is mainly attributed to the loss of interlayered water molecules and partial decomposition of the hydroxyls. A rather moderate loss of weight followed up to 623 K, which corresponds to the first evolution of CO_2 peaked at 513 K as is shown at the bottom of the figure. This process is attributed to the loss of both water from structural hydroxyls and CO_2. The third gradual loss of weight observed over 623 K, corresponding to the second peak of CO_2 evolution centered at about 853 K. The amount of the CO_2 evolved in this temperature range calculated using the TPD profile was 0.86 mmol g^{-1}, which contributes 3.8 % to the weight loss. On the other hand, the weight loss in this temperature range was estimated as 5.4 % from the TG analysis. The difference can be

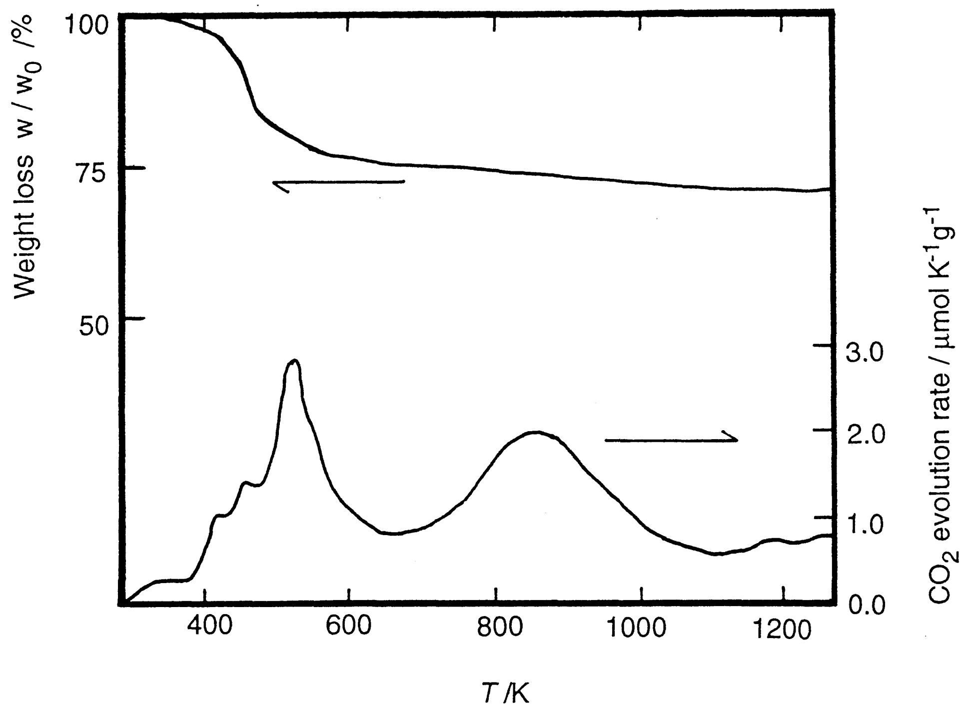

Fig. 3. TG and TPD profiles of Zn/Ga-LDH.

assigned to the decomposition of the residual hydroxyls mentioned above. Considering relatively slow heating rate and high gas flow, it is likely that this doubly peaked and widely spreading process of CO_3^{2-} decomposition is genuine of the present system.

From the above results, the feature of thermal decomposition of the Zn/Ga-LDH can be summarized as follows: (1) Decomposition of hydroxyls occurs in the temperature range from 373 to 623 K. (2) The layer structure is destroyed at about 473 K, resulting in a poorly crystallized oxide and/or hydroxide phase up to 1027 K. (3) The decomposition of CO_3^{2-} ions proceeds over wide temperature range with two peaks at 513 and 853 K. In case of Mg/Al-LDH, it has been reported that two steps of weight loss are observed at 513 and 693 K, being attributed to the loss of the interlayer water molecules, and the sum of decompositions of structural hydroxyls and CO_3^{2-} ions, respectively.5) From the TPD profile, it is found that almost half of the CO_3^{2-} ions which originally adsorbed in the interlayer of the Zn/Ga-LDH remained in the poorly crystallized phase at 773 K. In this sense, it can be said that the CO_3^{2-} ions are more tightly bonded to the solid phase when thermally decompsed in comparison with the other LDH systems.

References

1) S. Miyata, *Gypsum Lime*, **187**, 47(1983).
2) W. T. Reichle, *Solid State Ionics*, **22**, 135(1986).
3) K. A. Carrado, A. Kostapapas, and S. L. Suib, *Solid State Ionics*, **26**, 77, (1988).
4) F. Thevenot, R. Szymanski, and P. Chaumette, *Clays Clay Miner.*, **37**, 396(1989).
5) T. Sato, T. Wakabayashi, and M. Shimada, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 89(1986).

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