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THERMAL ANALYSIS ON THE KINETICS OF MAGNESIUM-ALUMINUM LAYERED DOUBLE HYDROXIDES IN DIFFERENT HEATING RATES

ANALIZA TERMICZNA KINETYKI ROZKŁADU WARSTWOWEGO PODWÓJNEGO WODOROTLENKU MAGNEZU ALUMINIUM PRZY RÓŻNYCH SZYBKOŚCIACH GRZANIA

The thermal decomposition of magnesium-aluminum layered double hydroxides (LDHs) was investigated by thermogravimetry analysis and differential scanning calorimetry (DSC) methods in argon environment. The influence of heating rates (including 2.5, 5, 10, 15 and 20K/min) on the thermal behavior of LDHs was revealed. By the methods of Kissinger and Flynn-Wall-Ozawa, the thermal kinetic parameters of activation energy and pre-exponential factor for the exothermic processes under non-isothermal conditions were calculated using the analysis of corresponding DSC curves.

Keywords: Layered double hydroxides, Thermal analysis, Kinetic

1. Introduction

Layered double hydroxides(LDHs), also known as hydrotalcite (HT)-like materials, are a class of synthetic two-dimensional nanostructured anionic clays whose structure can be described as containing brucite-like layers[1,2], where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been replaced isomorphously by trivalent cations[3], giving positively charged layers with charge-balancing anions between them; some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region. LDHs are promising materials for a large number of practical applications in catalysis, adsorption, pharmaceuticals, photochemistry, electrochemistry and so on[4,5].

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 mixed metal oxides (MMOs). The thermal behavior of LDHs intercalated with carbonate ion is generally characterized by two steps. The first one is an endothermic process at lower temperature where weight losses are caused by the removal of surface water and interlayer water[6-8]. 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 temperature, the transition of which is due to the losses of water form hydroxyl groups of brucite-like layer and carbon dioxide from carbonate ion. As a result, the layered structure is destroyed [9-11].

2. Experimental

2.1. Synthesis

MgAl-CO₃-LDHs were prepared by similar method reported preciously. In mechanochemical synthesis, the mixtures of aluminum hydroxide, magnesium hydroxide, and sodium hydrogen carbonate were used. The magnesium to aluminum molar ratio was 2:1, and the aluminum hydroxide to sodium hydrogen carbonate molar ratio was maintained constant at 1:0.5. The mixtures were mechanically activated in an AGO-II planetary mill at 10 g for 15 min, and the ball-to powder weight ratio was 30:1. The milled product was subsequently heated in hot deionized water at 90° for 12h, separated in centrifugal separator and dried in air at ambient temperature for 24h.

2.2. Characterization

The analyses by TG and DSC of LDHs were carried out with STA449F3 of NETZSCH thermal analysis instruments. Thermal properties were examined by TG-DSC methods under argon atmosphere, and which was purged with a gas flow rate of 20mL/min. The measurements were carried out from 303K to 900K at five different heating rates of 2.5, 5, 10, 15, 20K/min. Approximate 10mg of the sample was placed in an aluminum pan and Al₂O₃ was selected as the reference material.

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The phase compositions of the samples were determined by an X-ray diffraction (XRD) meter (Model D/max-3B, Rigaku) equipped with a graphite monochromator under Cu K_{α} radiation ($\lambda = 0.15406\text{nm}$), operating at 40kV and 20mA over a 2θ range from 5° to 75° .

3. Results and discussion

3.1. Mechanochemical synthesis and product characterization

The TG-DSC profiles of LDHs at different heating rates after thermal decomposition were presented in Fig. 1. As shown in Fig. 1, the thermal decomposition processes of LDHs could be revealed basically by two maximum processes in the TG-DSC profiles, which therefore strongly suggested the degradation of LDHs could be mediated by two mass-loss stages.

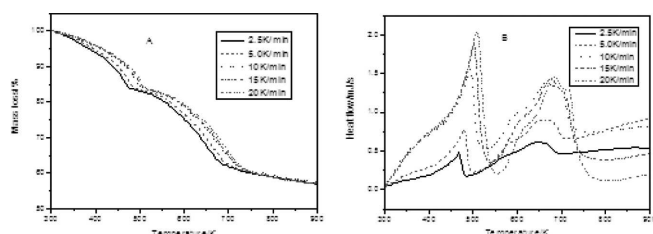
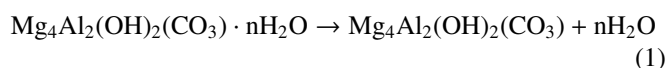


Fig. 1. The TG(A) and DSC(B) curves of LDHs under argon at the heating rates of 2.5, 5, 10, 15, 20K/min

The first stage is the thermal dehydration of interlayer water molecules of LDHs. This can be expressed by the simple chemical Eq.(1). It is centered at a low temperature around 480K.



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^[11]: 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.

The second stage ends at a higher temperature around 750K due to evolution of carbon dioxide from interlayer carbonate ion and elimination of water from condensation of lattice hydroxide. In the second transition, the weight losses of $\text{Mg}_4\text{Al}_2\text{CO}_3$ -LDHs are divided into two stages, while those of the others are overlapped. These two transitions depend on many factors such as drying conditions quantitatively and qualitatively. With the increasing of heating rate, the results indicated that there was an upward shift in the peak temperature of the exothermic peak.

The powder XRD for LDHs calcined at different temperatures are shown in Fig. 2. Sharp, intense peaks at low diffraction angles and broad, less intense peaks at higher angles confirm the presence of LDHs with 3R packing of layers.

The heating rate was $5^{\circ}/\text{min}$ while LDHs was calcined and keep 3 hours. When the temperature is 200° , the basal peaks at low angles become lower and weaker, suggesting a decrease in the crystallization of the solids. At the same time a clear decrease in the orderliness of the layer is noted, as indicated by both the decrease in intensity and sharpness of the (110) plane reflections observed around 60° . When the temperature is 600° , the layer structure of LDHs is destroyed completely and solid became MgAl_2O_4 and MgO . The Fig. 2 also can verify the decomposition process of LDHs with the increasing of temperature.

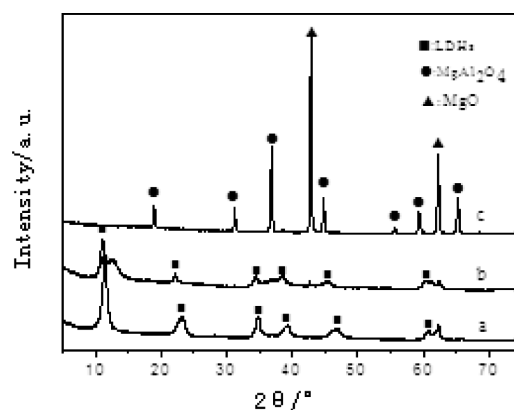


Fig. 2. X-ray diffraction patterns of LDHs powder calaed at different temperature:(a)LDHs, (b)200°, (c)600°

3.2. Thermal decomposition Kinetics

In order to obtain the thermal kinetic parameters, e.g., the activation energy, E and the pre-exponential factor, A of the exothermic decomposition of LDHs, the methods of multiple heating rates, namely Kissinger method and Flynn-Wall-Ozawa method, were employed. These “model-free” methods are multi-rate methods and free from kinetic model, which could allow the activation to be obtained independently. The relevant equations are as follows[12]:

$$\text{Kissinger equation} : \ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (2)$$

Where β is the heating rate, T_p is the maximum peak temperature of a DSC scan at that rate, and R is the gas constant of 8.314J/mol.

Flynn-Wall-Ozawa equation:

$$\log \beta = \log \frac{AE}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E}{RT_p} \quad (3)$$

Where $g(\alpha)$ is the integral function of conversion[13].

The values of $\ln \frac{\beta}{T_p^2}$ or $\log \beta$ were plotted against the values of $1/T_p$. A straight line through the data points was obtained by linear regression. The activation energy, E , was determined from the slope, and the pre-exponential factor, A , was determined from the Eq.(2) and (3). The typical kinetic plots by Kissinger and Flynn-Wall-Ozawa methods for LDHs in Ar are shown in Fig. 3.

TABLE 1

The kinetic parameters for the degradation of LDHs using the methods of Kissinger and Flynnner-Wall-Ozawa

Methods	Process I			Process II		
	$E/\text{kJ}\cdot\text{mol}^{-1}$	A/min^{-1}	R^2	$E/\text{kJ}\cdot\text{mol}^{-1}$	A/min^{-1}	R^2
Kissinger	90.24	5.96×10^{10}	0.99	245.19	8.71×10^{18}	0.93
Flynnner-Wall-Ozawa	94.28	5.69×10^{10}	0.99	244.67	8.38×10^{18}	0.94
Average	92.26	5.82×10^{10}		244.93	8.54×10^{18}	

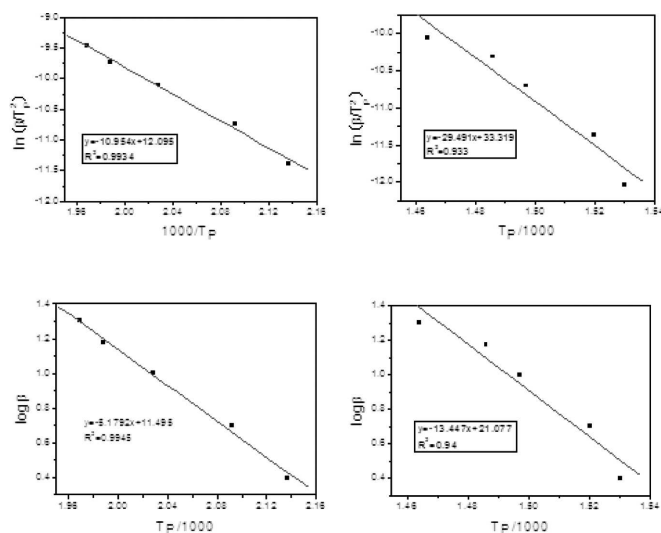


Fig. 3. The plots of $\ln \frac{\beta}{T_p^2}$ and $\log \beta$ versus $1/T_p$ for LDHs using the methods of Kissinger and Flynnner-Wall-Ozawa

The kinetic parameters for the degradation are listed in TABLE 1. The type of reaction, shape and crystallite size of LDHs particles and the steric constraint of interlayer anions are considerable factors in determining the pre-exponential factor. It is well known that the water molecules of the interlayer diffuse two-dimensionally, and the second stage diffusion is three-dimensionally.

From the results of TABLE 1, the values of E and A obtained using Kissinger method were 90.24, 245.19 kJ/mol and 5.96×10^{10} , $8.71\times 10^{18} \text{min}^{-1}$ respectively. Meanwhile, the values of E and A obtained by Flynnner-Wall-Ozawa method were 94.28, 244.67 kJ/mol and 5.69×10^{10} , $8.38\times 10^{18} \text{min}^{-1}$, respectively. The results of Kissinger method and Flynnner-Wall-Ozawa method were confirmed without a significant difference, which indicated that LDHs should have good thermal stability.

4. Conclusions

The thermal behavior and decompositions of LDHs, studied using TG and DSC in different heating rates. The results

demonstrated that there are two weight losses: dehydration of interlayer water and decomposition of layer and interlayer anions, respectively.

The values of the kinetic parameters obtained by Kissinger and Flynnner-Wall-Ozawa methods for LDHs have a good correlation. The average activation energies of first stage and second stage are 92.26, 244.93 kJ/mol respectively.

Acknowledgements

The authors thank Prof. Politov A. of institute of solid state chemistry and mechanochemistry SB RAS for his comment on this manuscript. This study was supported by the Liaoning department of education scientific research project (No.L2011074).

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