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SYNTHESIS OF MAGNESIUM-ALUMINUM LAYERED DOUBLE HYDROXIDES BY MECHANOCHEMICAL METHOD AND ITS SOLID STATE REACTION KINETICS

MECHANICZNO-CHEMICZNA SYNTEZA WARSTWOWEGO PODWÓJNEGO WODOROTLENKU MAGNEZU ALUMINIUM I KINETYKA REAKCJI W STANIE STAŁYM

AbstractŁş A mechanochemical method is developed in preparing magnesium-aluminum-layered double hydroxides (MgAl-LDHs). This approach includes activation process and diffusion process. In order to verify the LDHs structure and study the reaction kinetics, X-ray diffraction (XRD) patterns, inductively coupled plasma(ICP) and physical adsorption instrument were characterized. The results show that activation time can change the surface of particles and affect the reaction grade. During the diffusion process, reaction time is the most important factor. The reaction energy (ΔQ) was calculated that is 6kJ/mol.

Keywords: Layered double hydroxides, Mechanochemical method, Kinetic

1. Introduction

Layered double hydroxides (LDHs) are a class of anionic layered clay, with interlayer ion exchangeable and grain size distribution can be controlled. In recent years, LDHs have aroused increasing attention due to their existing and potential applications such as catalysis, catalysis supports, flame retardant, additives and pharmaceutical, ion exchange and adsorption, and so on[1,2]. LDHs can generally be prepared by precipitation, hydrothermal, Sol-gel method and ion exchange method[3-6]. In this paper, LDHs was prepared by solid state reaction, namely the mechanochemical method. And it was discussed about the solid reaction kinetics.

The traditional kinetic model of mechanochemical processes was proposed by F.Kh. Urakaev and V.V. Boldyrev[7,8]. The feature of this model is that time factor is separated from other influence factors during mechanochemical processes. It can be expressed in Eq.(1).

$$\alpha = \alpha(\omega_k, N, R/I_m, X)\,\alpha(t) = K\alpha(t) \tag{1}$$

According to it, A.A.Politov[9] put forward the concept of smart grinding, that is to fully consider the mechanism of mechanical reaction in the study of mechanical, and the material morphology and chemical properties are also important. The reaction rate equation is reformulated as Eq.(2).

$$\alpha = SK[As] \tag{2}$$

The synthetic process of LDHs by mechanochemical method includes activation and diffusion. The speed of diffusion process is slower than activation process, so the reaction speed is dominated by diffusion process. The reaction interface constantly changed during the reaction process. The synthesis kinetics will base on the diffusion kinetics of ГИНСЛИНГ equation.

2. Experimental

2.1. Synthesis

Analytically grade $Mg(OH)_2$, $NaHCO_3$ and $Al(OH)_3$ were used for the synthesis of LDHs. The R (Mg/Al molar ratio) was 2:1. The mixtures were mechanically activated in an AGO-II planetary mill at an acceleration of 20g for 5 to 20 minutes. The grinding media was 8 mm stainless steel ball, and the ball to powder weight ratio was 30:1. After grinding, the powder was leached in hot deionized water for 12h, then separated in centrifugal separator and dried in air at ambient temperature for 24h.

2.2. Characterization

The X-ray diffraction (XRD) patterns were obtained with a D/max-3B X-ray power diffractometer (Rigaku Co.), using Cu K_α radiation (λ =0.15406nm) from 5 to 75 at a scanning rate of 3.6° /min. A model J-A1100 (Jarrell-Ash Co. USA) inductively coupled plasma (ICP) atomic emission spectrometer was employed for metal element analysis. The surface area of sample was measured on a NOVA 4000(Conta Co. USA) physical adsorption instrument.

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3. Results and discussion

3.1. Mechanochemical synthesis and product characterization

The XRD spectra of mixtures with different milling time are presented in Fig. 1. As shown in Fig. 1, with the increasing of milling time, the intensity of the starting material's diffraction peak become weaken, and the diffraction peak become wide. Mechanical milling caused the smaller article size and bigger specific surface area. During the milling process, $Mg(OH)_2$ is relatively stable. Even if the milling time increased 20min, $Mg(OH)_2$ still kept the crystal morphology exists. After grinding the powders were leached in water at 90° with 12 hours. According to XRD patterns of the samples (Fig. 2), these sharp and symmetric peaks demonstrate the formation of a single well crystallized LDHs.

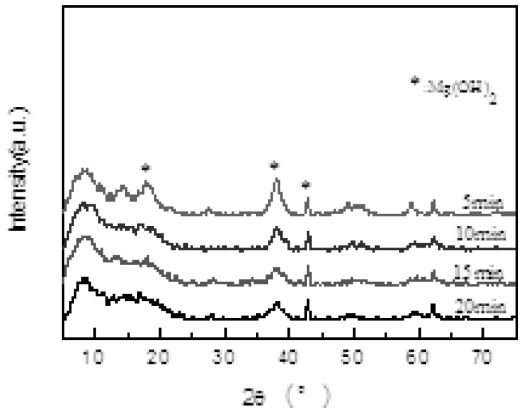

Fig. 1. XRD patterns of the ground mixtures at different milling time

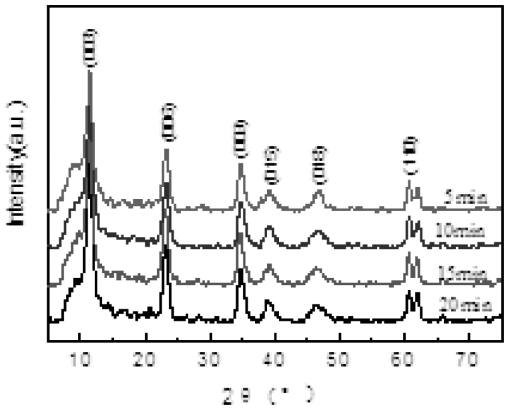

Fig. 2. XRD patterns of the ground mixtures at different milling time after leaching

The surface areas of the mixtures with different grinding time were shown in Fig. 3. After fitting index, the relationship between surface area and the grinding time can be illustrated with Eq.(3), the correlation coefficient was 0.99686. In the grinding process, the specific surface area and the grinding time were not a simple linear relationship. The specific surface area changed very little when the grinding time was over 10 minutes.

$$S = 1.971 + 237.83 \exp\left(-\frac{t}{1.5591}\right) \qquad (3)$$

During the diffusion process the reaction temperature is a greater impact on the reaction rate. When the milling time was 5min, the XRD spectrums of samples with different temperature were shown in Fig. 4. It can be seen from the graph with the increasing of water temperature, the diffraction peaks intensity increase gradually, the regularity of the crystal is getting better and better. From the TABLE 1 it is visible that $d003$, $d110$ decreased with increasing temperature, and Mg/Al molar ratio was closer to the feed ratio. This shows that there was more Al^{3+} to replace Mg^{2+} board. Because the ion radius of Al^{3+} is smaller than Mg^{2+}, the atomic spacing becomes smaller. At the same time, the charge density and ions force between layers increased.

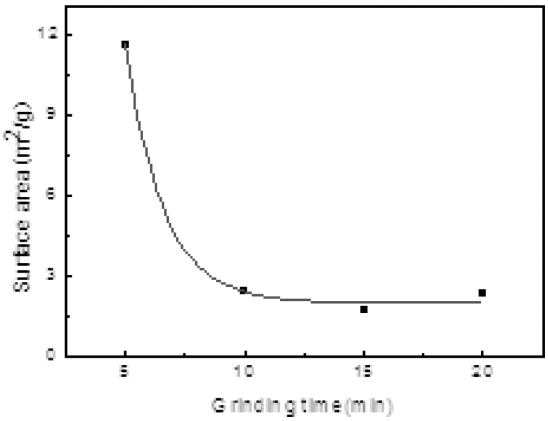

Fig. 3. The surface area of ground mixtures with different grinding time

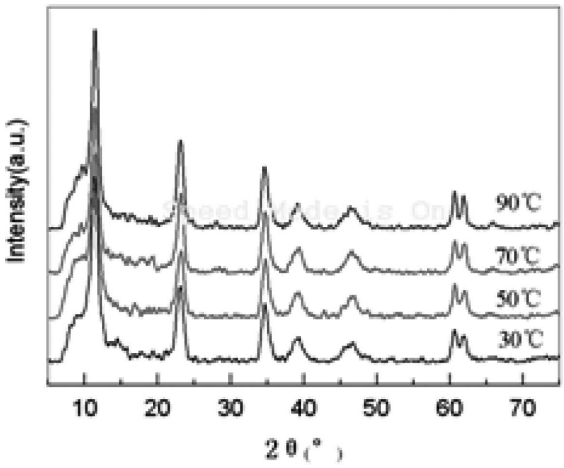

Fig. 4. XRD patterns of different leaching temperature

TABLE 1
XRD structural parameters and ICP results of the solid products at different temperature

Temperature	30°	50°	70°	90°
d003/nm	0.78377	0.78284	0.77284	0.77149
d110/nm	0.15296	0.15295	0.15286	0.15278
R(Mg/Al)	2.47	2.44	2.30	2.20

3.2. Solid State Reaction Kinetics

This reaction is controlled by diffraction process, so the following equation can be employed to present the experimental data.

$$F_K(G) = 1 - \frac{2}{3}G - (1-G)^{2/3} = \frac{2DN\mu C_0}{R_0^2 \rho n} t = K_K t \quad (4)$$

When G is the fraction converted, K_k is the kinetic constant, t is the reaction time. According to the Arrhenius equation, $K = A\exp\left(-\frac{\Delta Q}{RT}\right)$. The Eq.(4) can be expressed as Eq.(5) after logarithmic transformation.

$$\ln\left[1 - \frac{2}{3}G - (1-G)^{2/3}\right] = B - \frac{\Delta Q}{R} \cdot \frac{1}{T} \quad (5)$$

The reaction grade can be determined with Mg/Al molar ratio of sample compared with feed ratio. The data obtained are shown in TABLE 2. Because the diffraction reaction controls the rate, the relation between the left side of Eq.(5) and 1/T must be linear. According to the slope of this line ΔQ can be got. A good linear fit was observed in Fig. 5, with regression coefficient(r) was 0.969. It was calculated that ΔQ=6kJ/mol, A=1.36.

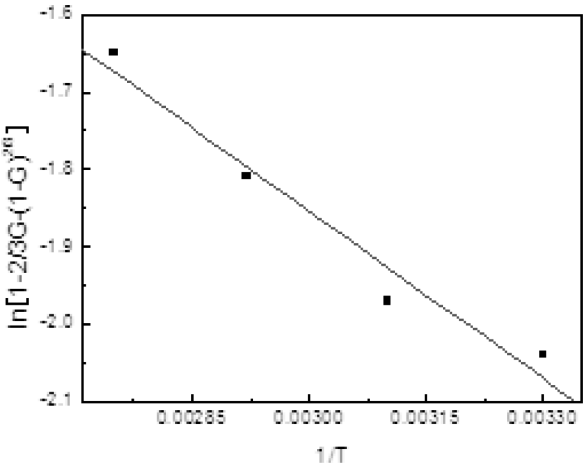

Fig. 5. The regression curve of ln[1-2/3G-(1-G)$^{2/3}$]-1/T

According to Eq. 2, the Kinetic equation of the reaction can be shown as the following formula.

$$\alpha(t) = [A_s]\left[0.37 + 44.24exp\left(-\frac{t}{1.56}\right)\right] \quad (6)$$

In the formula, t is the activation time; [As] is structure factor associated with material morphology and properties.

TABLE 2
The degree of reaction data prepared LDHs by mechanochemistry

Temperature/°	Reaction grade G(t=12h)/%	1/T	ln[1-2/3G-(1-G)$^{2/3}$]
30	0.81	3.30×10^{-3}	-2.04
50	0.82	3.10×10^{-3}	-1.97
70	0.87	2.92×10^{-3}	-1.81
90	0.91	2.75×10^{-3}	-1.65

4. Conclusions

MgAl LDHs was successfully synthesized by mechanochemical method. During the activation process, the mixture got enough energy and decreased the activation energy of diffusion reaction. ΔQ was calculated that is 6kJ/mol. According to the intelligent grinding model, the kinetic equation can be expressed by Eq.(6).

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