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Microanalysis Study on Hydrothermal Synthesis of Mg, Al-Hydrotalcite

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In this study, the reactants are $Al(NO_3)_3$, $Mg(NO_3)_2$, Na_2CO_3 and precipitant is NaOH. The Mg, Al-hydrotalcite (Mg-Al-LDH) crystals is prepared by hydrothermal method. The products are investigated by X-ray diffraction, scanning electron microscope and X-ray energy dispersive spectrometer. The influences of Mg-Al-LDH crystals micro-structure and growth are systematic researched in different conditions of pH values, hydrothermal temperature and reaction time. At the same time, we discussed the growth mechanism. The results indicated that the systematic pH value has great influence on growth of Mg-Al-LDH. The growth units $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6^-]^{3-}$ can not form when the pH value is lower, so the product is not Mg-Al-LDH. While when pH=12, the formation of the ligand tend to stabilize and the hexagon Mg-Al-LDH has good crystalline and regularity. Keeping pH value at 12 and increasing the temperature, the crystals size tends to increase. When the temperature reached 160 °C, the product size is stable and is about 230-300 nm. When the system is in the optimum conditions of pH value and temperature, the reaction time has hardly any influence on crystals growth. As long as hydrothermal system is balanced for a certain time, the good crystalline Mg-Al-LDH crystals can be prepared but increasing time is only in favor of the crystals growth and regularity. The energy dispersive spectrometer analysis result verified that the Mg/Al is about 3 which approached to the theoretical value.

Keywords: Hydrothermal method, Mg, Al-hydrotalcite, Microanalysis, Growth mechanism.

INTRODUCTION

Hydrotalcite-like compounds, also called layered double hydroxide (LDH), are a class of an important inorganic functional material[1]. Because of its special anionic layer structure, it has alkaline, cation allocation in the layers, anionic exchangeability in the interlayer and so on. Therefore, layered double hydroxides have great important application potential in catalyst, ion exchange and adsorption, medicine, functional polymer material, flame retardant additive and papermaking, *etc.*[2,3]. In recent years, the researches of layered double hydroxides focused on synthesis, adsorption and catalytic performance. While the preparation method and technological conditions influenced on the crystal micro-structure were relatively less. Micro structure of materials determines the macroscopic physical and chemical properties. So it's important to research and discuss the different influence factors which affect the product phase and micro structure in the preparation process and it has crucial practical significance.

At present, there are many preparation methods of layered double hydroxide, such as liquid phase precipitation method, sol-gel method and hydrothermal method, *etc.*[4-7]. Among these ones, the hydrothermal method is reacting at the conditions of high temperature, high pressure, low saturability and sealed reaction environment. The reaction temperature is relative lower and it's easy to form high quality crystallites. Especially, the outside condition can hardly influence the system in reaction process. So we can control the growth of crystallities by changing the temperature, pH value, crystallization temperature, crystallization time and the different reactant and concentration[8]. Hence, this method is widely used in the preparation of inorganic functional material. In this work, the reactants are $Al(NO_3)_3$, $Mg(NO_3)_2$, Na_2CO_3 and precipitant is NaOH. We systematic studied different conditions such as reaction temperature, pH value, reaction time impacted on synthesizing layered double hydroxide phase and microstructure. And the crystal growth mechanism in the hydrothermal environment has been discussed. Consequently, it can provide a good experimental foundation to prepare size controllability, high stability, good dispersibility, high purity layered double hydroxide and composite material.

EXPERIMENTAL

$Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, Na_2CO_3 and NaOH, all of these are analytically pure.

Y-2000 Automatic X-ray diffraction, Dandong Radiative Instrument Group Co. Ltd. JSM-7500F field emission scanning electron microscope with the resolution at 1 nm, JEOL LTD. JAPAN (X-ray energy dispersive spectrometer, American Noran Co.). VERTEX70 Fourier infrared spectrometer (Germany, Bruker)).

Preparation of Mg, Al-hydrotalcite: The aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ was prepared respectively according to the stoichiometric ratio of Mg, Al-hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) and mixed uniformity in the beaker under stirring. A certain amount of aqueous solution of Na_2CO_3 was added. Respectively, adjust pH value of mixed solution to 6, 8, 10, 12 by NaOH. Then put it to the polytef autoclave after stirring uniformity. According to our study and pertinent literature[9], put the autoclave into oven with temperature programming to 120 °C and maintaining 18 h in constant temperature. Turn off the power and cooled to room temperature. After the filter, washing, drying and grinding, the layered double hydroxide was obtained. Layered double hydroxide crystals were characterized by the X ray diffraction (XRD) and scanning election microscopy (SEM), then picked out the optimal pH value and remain unchanged. Changing the hydrothermal temperature and reaction time respectively and prepare the samples of these conditions.

RESULTS AND DISCUSSION

Effect of different pH values on product phase and microstructure: Fig. 1 is XRD patterns of products with different pH values in 120 °C and 18 h. As can be seen from Fig. 1, the change of pH value has great influence on the phase formation. When the pH=6 (Fig. 1a), the diffraction characteristic peaks didn't appear. It illustrates that the product didn't crystallize in this condition. When the pH=8, the diffraction peaks appeared obviously in the region of 2θ = 10.37°, 20.03°, 61.005°. But the peak shape is wide and peak to background ratio is lower. It showed that the product was compose of multiphases using computer peak searching analyzing. The main components are scarbroite (PDF#: 14-0828) and magnesium carbonate phases. It indicated that this condition is not benefit to prepare layered double hydroxide crystals.

When pH value increased to 10, the layered double hydroxide diffraction peaks appeared at 2θ = 11.2°, 22.8°, 34.4°, 38.4°, 45.3° and 60.4° and the crystal planes correspond, respectively (003), (006), (009), (015), (018), (110). But 2θ angles were slightly increased than the standard layered double hydroxide. At the same time, $MgCO_3$ diffraction peaks appeared obviously at 2θ = 32.3° (Fig. 1c). It showed that not only the layered double hydroxide product had difference with stoichiometric ratio, but also contained other impurity phases. As pH value increased to 12, the layered double hydroxide diffraction peaks were all appeared and corresponded to the standard PDF card (PDF#22-700). It has good symmetry and the peak pattern is sharp and no impurity peaks as well. The peak to background ratio was increasing compared with (Fig. 1c). It declared that the higher purity layered double hydroxide can be synthesized in the hydrothermal environment condition of pH=12.

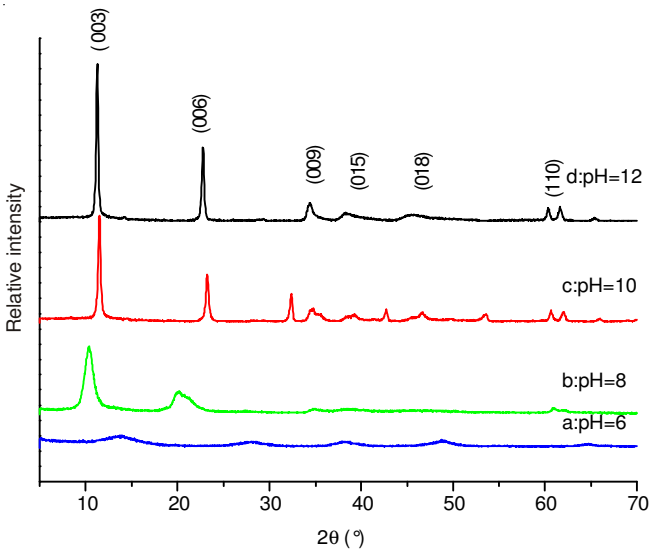

Fig. 1. XRD patterns of different pH value

Fig. 2 is SEM images of products in the condition of different pH values. Fig. 2 suggests that the product has not crystallized at pH=6. As pH value increased to 8, the crystalline state and layer structure appeared and the dispersity gradually increased. When pH=10, the hexagon layered structure of layered double hydroxide became obvious, but the regularity, dispersity and homogeneity were not as good as pH=12 (Fig. 2d). Its size is 150-180 nm and thickness is about 50 nm. The reason is that the concentration of OH^-, H^+, Al^{3+}, Mg^{2+}, CO_3^{2-} were caused by the different pH values in the hydrothermal environment. Consequently, ion ligand structure has changed in the hydrothermal system. The growth unit of layered double hydroxide crystalline belongs to ion ligand structure and there are

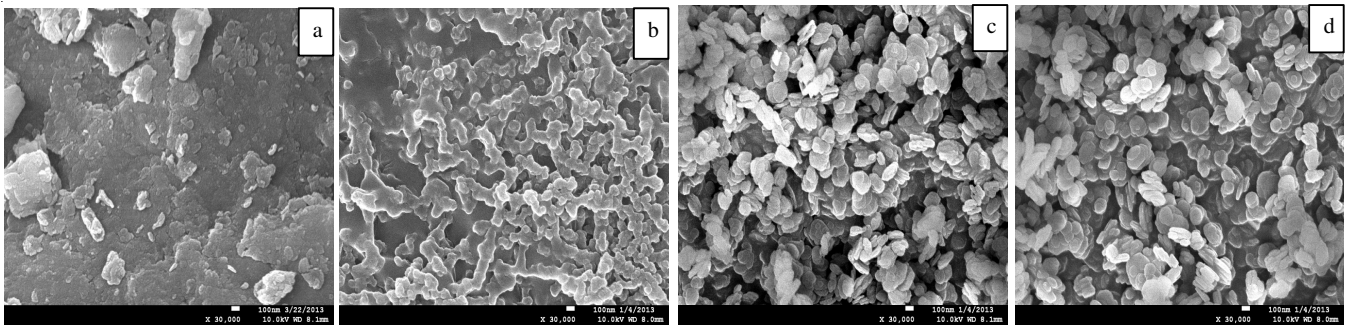

Fig. 2. SEM images of different pH value; (a) pH=6; (b) pH=8; (c) pH=10; (d) pH=12

$[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6^-]^{3-}$ in the system. $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6^-]^{3-}$ can not form when the pH value is lower, so the product is not layered double hydroxide. As pH value increased, the ligand tended to stabilization and the growth units began to superimpose. The process are dehydration between the hydroxyls (-OH) and combination of octahedron coarris. The base layer $[Mg_6A_{l2}(OH)_{16}]^{2+}$ is forming. In order to balance the electrovalence, CO_3^{2-} and $4H_2O$ entered into the base layers. So the layered layered double hydroxide crystals have formed. Even so, because the layered double hydroxide crystal phase transition is complex in the hydrothermal system, the formation mechanism of layered structure will be researched further[10-12].

Effect of different hydrothermal temperatures on the product phase and microstructure: The layered double hydroxide crystals can be prepared when pH value greater than or equal to 12. Fig. 3 is XRD patterns of different temperatures in the condition of keeping pH value and reaction time unchanged. As we can see from Fig. 3, when the temperature is in the range of 100-160 °C, the diffraction peaks of layered double hydroxide are all appeared. The main peaks patterns are sharp and have not other impurity peaks. It illustrates that the products have good crystal and all of these are layered double hydroxide. As the hydrothermal temperature elevated, the relative intensity of (003) and (006) tended to increase and then decrease later. When the temperature is 120 °C, the peak to background ratio is maximum; but the temperature increased, the ratio is minish; when to 160 °C, the ratio became minimum, while the other peaks intensity changed unconspicuous. It declared that the temperature is the important factor of (003) and (006) growth. Furthermore, from Fig. 3, the half-width of XRD characteristic peaks have distinctions at different temperatures. The reason may be the size of layered double hydroxide crystals.

Fig. 4 is the SEM images of different temperatures. The crystals are all hexagon layered structure. The change of temperature has influenced on integrity, homogeneity and size of layered double hydroxide. When the temperature is lower (Fig. 4a), the size of product is small about 80-170 nm. When to 120 °C, the size tended to be increased and the integrity and homogeneity enhanced obviously. When to 140 °C, the crystal size increased suddenly and became big and thin. Heating up to 160 °C, the size increased inconspicuously and about 230-300 nm. It stated that temperature affects the layered double hydroxide crystallization, but there is optimum temperature range for the different reactants in the hydrothermal system[13,14].

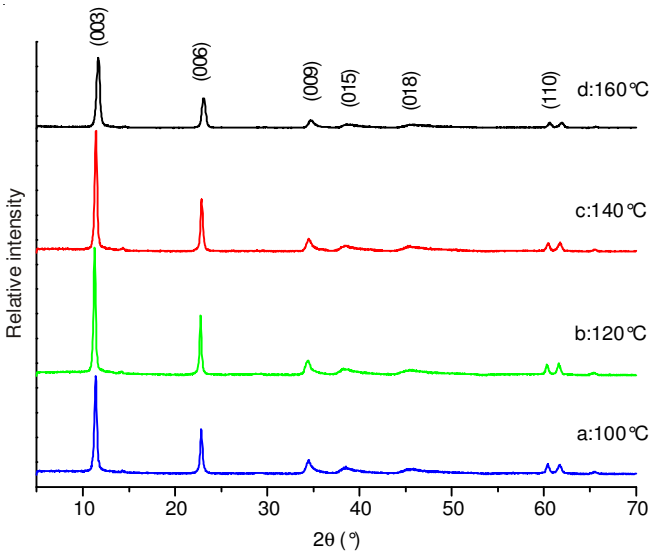

Fig. 3. XRD patterns of different temperatures

After achieve the optimum value, there is hardly influence on morphology of layered double hydroxide as the temperature increasing. The main reason is that the temperature affected the solubility product and system surface free energy of the reactants and mid-precipitate product. So the concentration of Mg^{2+} and Al^{3+} are changed in this system. At the same pH value, the construction speed and superimposition speed of anion coordination octahedron $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)^{6-}]^{3-}$ are changed. The transformation of temperature leaded to the change of growth units combining means and orientation. As the temperature increasing, the layered double hydroxide crystal grew faster relatively along a-axis but grew slower along c-axis. Therefore, the crystal morphology is tended to completeness. But when the temperature reached optimal value, a large number of configurational ions closely packed nucleation and the atomic arrangement became tightness. On the contrary the interlayer spacing reduced, but had little influenced to the crystal morphology. In addition, the transform of temperature also affected nucleate and surface free energy of crystals. When the temperature reached a certain value, the stable crystals can grow after the embryo reached the critical particle size in the system[15-17]. Overall consideration, we consider that the optimal hydrothermal temperature is 120 °C and this result is as same as the XRD.

Effect of different reaction times on the product phase and microstructure: The effect of synthetic product in the different reaction times is studied in the condition of pH=12

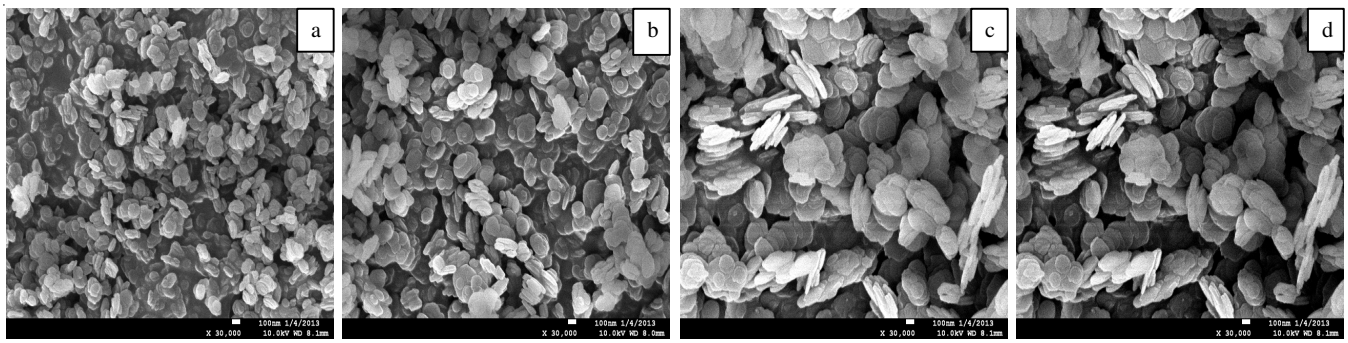

Fig. 4. SEM images of different temperatures; (a) 100 °C; (b) 120 °C ; (c) 140 °C; (d) 160 °C

and 120 °C. Fig. 5 is the XRD patterns of products that treated by hydrothermal for 3, 6, 12, 18 and 24 h, respectively.

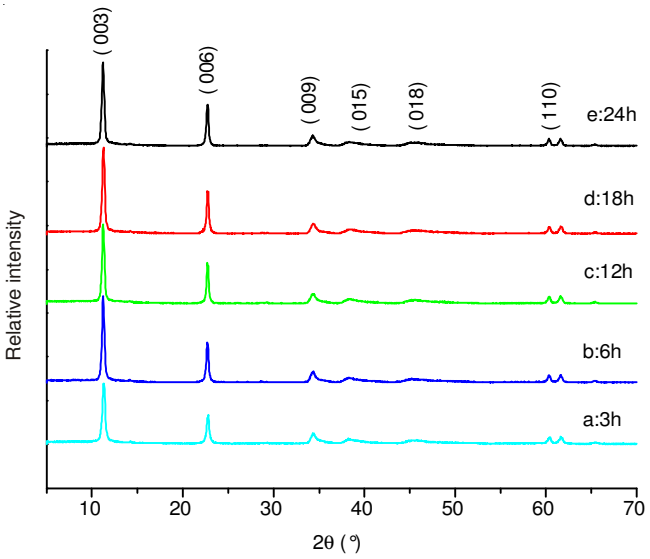

Fig. 5. XRD patterns of different hydrothermal reaction time

From Fig. 5, it is seen that the layered double hydroxide characteristic diffraction peaks had appeared when the reaction time is 3 h. The relative intensity of layered double hydroxide peaks had increased as the time prolonged. But the distinction of XRD patterns isn't obvious. This implies the reaction time have little influence to the growth of crystals at the optimal pH value and temperature. The hydrothermal time is only benefit to enhance the crystal growth and the regularity. The good layered double hydroxide crystals can be prepared if only assuring the time can make the system balance.

Fig. 6 is the SEM images of different times. The synthetic products is hexagon and layered layered double hydroxide crystal when the reaction time is 6 h. The crystals have good regularity, uniformity and dispersity and its size is about 90-270 nm and thickness is 50 nm (Fig. 6a). When the time increased, the size and morphology changed unconspicuous, it only enhanced the regularity and homogeneity of layered double hydroxide (Fig. 6 bcd). The reason is that the system degree of supersaturation is related to the crystal growth rate[18-20]. When reached the optimum time, the hydrothermal system is balanced and prolong the time is only in favour of integrality of crystals. But it have not advantage of the anion coordination octahedral superimposition speed and the generate speed of growth units $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6]^{3-}$. Consequently, to study the optimum hydrothermal time of different systems have some function of he integrality and the morphology.

In addition, the X-ray spectroscopy of scanning electron microscope (EDS) is used to analyse for different conditions (Fig.7). From Fig. 7, the synthetic layered double hydroxide is not containing any impurities and the Mg/Al is about 3 which very approached the layered double hydroxide theoretical value.

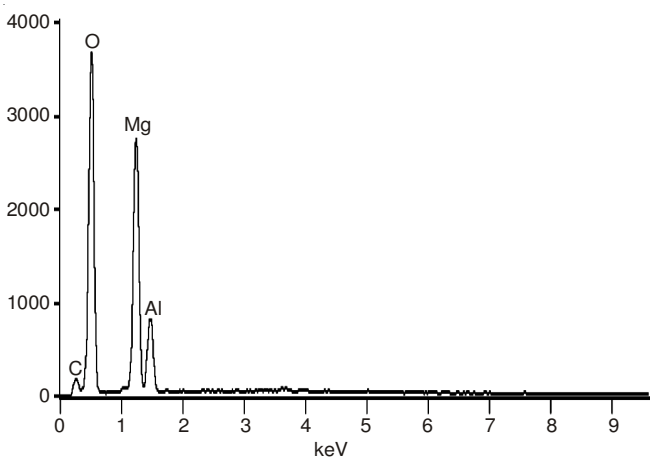

Fig. 7. Energy dispersive spectrometer spectrum of layered double hydroxide

Conclusion

The reactant are $Al(NO_3)_3$, $Mg(NO_3)_2$, Na_2CO_3 and precipitant is NaOH. The layered Mg, Al-hydrotalcite (Mg-Al-LDH) crystals is prepared by hydrothermal method. The systematic pH value has great influence on growth of Mg-Al-LDH. When the pH value is lower, The growth units $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)^{6-}]^{3-}$ can not form, so the product is not Mg-Al-LDH. While when pH=12, the formation of the ligand tend to stabilize and the hexagon Mg-Al-LDH has good crystalline and regularity. When the temperature reached 160 °C, the product size is stabilization and is about 230-300 nm. When the system is in the optimum conditions of pH value and temperature, the reaction time has hardly influence on crystals growth. As long as hydrothermal system is balance in a certain time, the good crystalline Mg-Al-LDH crystals can be prepared but increasing time is only in favor of the crystals growth and regularity. In addition, the energy dispersive spectrometer analysis result verified that the Mg/Al is about 3 which very approached the theoretical value.

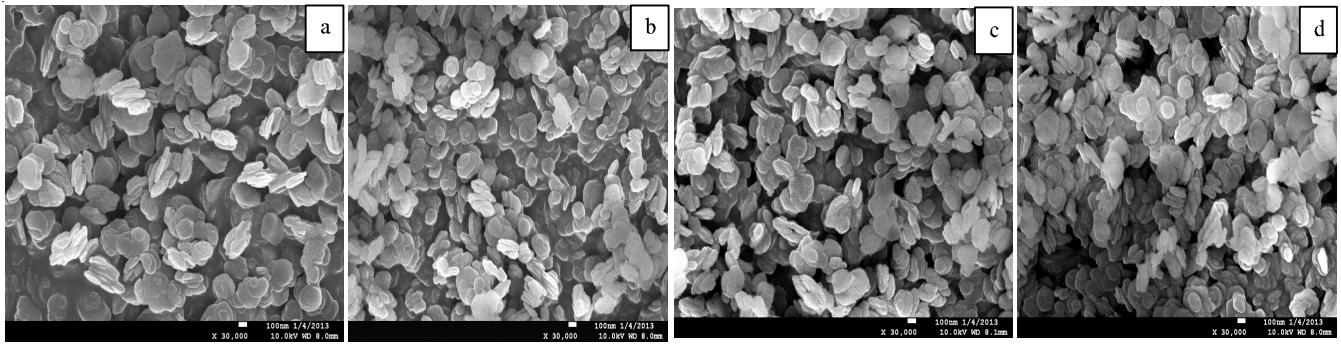

Fig. 6. SEM images of different times; (a) 6 h; (b) 12 h; (c) 18 h; (d) 24 h

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