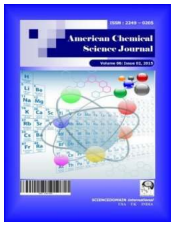

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The Influence on Synthetising Mg-Al Hydrotalcite by Using Different Mg and Al Sources as the Precursors

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

In this paper, Mg-Al hydrotalcite crystals were synthesized using the different Mg sources and Al sources as the precursor via hydrothermal method. The effects of different Mg and Al sources on the microstructure and the growth of LDHs were investigated by the X-ray diffraction (XRD), scanning election microscopy (SEM) and energy dispersive spectrometer (EDS), simultaneity. Besides, according to the ligand theory, its growth mechanism was discussed. The research indicated that the better LDHs crystal could been prepared under the condition of pH=12, hydrothermal temperature of 120℃ and time of 12 h. The different Mg and Al sources combination had certain influence on the phase, dispersion, regularity, ratio of thickness, purity, size and microstructure of LDHs products. When the Mg sources was fixed for $MgCl_2$, choosing Al_2O_3, $Al(NO_3)_3$ and $AlCl_3$ as Al sources respectively, the obtained LDHs with poor purity, regularity dispersion and crystallinity were synthesized when Al_2O_3 was used as Al sources; but the LDHs had better regularity, dispersion, crystalline and purity when $Al(NO_3)_3$ and $AlCl_3$ were chosed as Al sources. The reason could be that the different solubility and polarity of anion caused the slight variation of products microstructure. Compared to $MgCl_2$ with high dissolvability, when the Mg

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sources was fixed for $Mg(NO_3)_2$, choosing $Al(NO_3)_3$ and $AlCl_3$ as Al sources respectively, it is more advantageous to getting LDHs with better crystalline, regularity, and smaller in size. When both Mg sources and Al sources had higher solubility, the synthesized LDHs were with higher crystalline and regularity. The EDS analysis results showed that the purity of LDHs synthesized with Al_2O_3 had poor solubility. In addition, LDHs prepared by Mg sources and Al sources with higher solubility do not contain any other anionic impurities, and the average ratio of Mg/Al is about 3, which is very close to the theoretical value.

Keywords: Different precursor; Mg-Al hydrotalcite; crystal structure; hydrothermal method; growth mechanism.

1. INTRODUCTION

Hydrotalcite compound type also called layered double hydroxides is a kind of important inorganic functional materials [1]. Hydrotalcite compound type with special anionic layered structure has many characteristics, such as alkaline, cation on layer board can allocate, interlayer anionic exchangeability. Therefore, It has widely potential applications in many fields [2,3], such as catalysts, ion exchange and adsorption, medicine, functional polymer materials, flame retardant additives and papermaking. In recent years, with hydrotalcite as object of study mainly focused on the synthesis of various types of hydrotalcite, adsorption and catalytic properties [4-6], and in hydrotalcite layered compounds "matrix" of magnesium aluminum preparation methods of hydrotalcite, the influence of process conditions on the crystal microstructure of the research is relatively small, because of the material microstructure determines the macro physical and chemical properties of the material. Therefore, it is very important to study and discuss the influence of different factors on the phase and microstructure of the product, which has very important practical significance.

The ideal Mg-Al-LDHs crystal is a typical layered structure with D_{3d} symmetry, which belongs to R-3 m space group L^6PC space group. And, the intercalated anion in the interlayer of Mg-Al-LHDs is carbonate ion. In practical applications, the Mg-Al-LDHs has a direct impact on the physical and chemical properties of different particle size, crystalline phase and layer spacing. Therefore, the research and preparation of Mg Al hydrotalcite crystal with controllable morphology and size is very necessary. At present, there are many methods for the preparation of Mg-Al-LDHs and the structural control methods, such as liquid phase precipitation method, sol-gel method and hydrothermal method, etc. And the different preparation methods, precursors and synthesis conditions have great influence on the formation of Mg-Al-LDHs crystals. The hydrothermal method is carried out under a high temperature, high pressure, low saturation water solution reaction environment and reaction temperature is relatively low, easy to grow high quality crystals, especially in the growth process of little influence from the outside world, by changing the system temperature, pH value, crystallization temperature, crystallization time and different forequarters and concentration to control crystal growth [7,8]. So it is widely used in of inorganic functional materials. In the previous study, the effects of different reaction temperature, pH, reaction time and concentration on the phase and microstructure of Mg-Al-LDHs were systematically investigated. On this basis, this paper selects relatively cheap price of the chemical raw materials, examined and compared the different magnesium sources and aluminum sources as the precursor under hydrothermal conditions on the synthesis of Mg-Al-LDHs materials facies and micro structure of the influence, and the growth mechanism were discussed.

2. EXPERIMENTAL

2.1 Reagent and Instrument

Main reagents: magnesium ($Mg(NO_3)_2•6H_2O$), magnesium chloride ($MgCl_2$), aluminum nitrate ($Al(NO_3)_3•9H_2O$), alumina (Al_2O_3), aluminum chloride ($AlCl_3$), anhydrous sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were analytical reagents.

Main instruments: Y-2000 Automatic X-ray diffraction (Dandong Radiative Instrument Group Co. Ltd); JSM-7500F field emission scanning electron microscope (Japanese electronics, resolution is 1 nm (with X ray spectrometer,

American Noran company, lithium drift silicon detector, detecting element range B-U, detector resolution 132eV)).

2.2 Preparation of Sample

According to the stoichiometric ratio of Mg-Al hydrotalcite, we can configure the water solution of different magnesium and aluminum sources, putting it into the beaker with magnetic stirring to mix evenly; the pH value of the mixed solution was adjusted by means of sodium hydroxide and sodium carbonate. In accordance with our exploration of research and related literature, the pH value of the mixed solution was adjusted as 12. After mixing evenly, we should add it into the Teflon reactor, which is placed inside the oven temperature programmed to 120 degrees. After 18 hours of the constant temperature, naturally cooling to room temperature, the final product is obtained by filtering, washing, drying, grinding the synthetic product. Then, layered double hydroxide crystals were characterized by the X ray diffraction (XRD) and scanning election microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 XRD Analysis of Different Precursor Products

In the same experimental conditions, the XRD of different magnesium sources and aluminum sources precursors in combination with the products are shown in Fig 1. In Fig. 1,after the peak searching by computer, the diffraction peaks of 2θ = 11.2°,22.8°,34.4°,38.4°,45.3°,60.4°, etc. all belong to the characteristic peaks of Mg-Al Hydrotalcite (standard PDF card number: 22-700), corresponding to the crystal plane respectively (003), (006), (009), (015), (018), (110) surface. And, there is no obvious impurity peaks. It shows that the different magnesium sources and aluminum sources precursors can synthesis magnesium aluminum hydrotalcite crystals. In addition, it also can be seen from Fig. 1, With the $MgCl_2$ as the magnesium sources, the intensity, width and background of the diffraction peak of the synthesized product exists large differences because of the precursor of the aluminum changed to Al_2O_3, Al $(NO_3)_3$, $AlCl_3$. With the Al_2O_3 as the aluminum sources in Fig. 1(a), there has been a characteristic diffraction peaks of Mg-Al hydrotalcite, but the diffraction peak is wide and the diffraction intensity is low. This shows that under the hydrothermal conditions, the synthesis of LDHs is poorer, and the crystal growth is not complete. With the $Al(NO_3)_3$ as the aluminum sources in Fig. 1(c), the XRD peak's back is relatively high, the peak is high and narrow. It shows that the crystallinity of the product is higher and the crystal growth is relatively complete. With the $AlCl_3$ as the aluminum sources in Fig. 1(e), it can be seen that the (003) and (006) peak of the obtained product is highest, narrow and sharp. This shows that the crystallinity of the Synthetic product under this condition is optimal. With the $Mg(NO_3)_2$ as the magnesium sources in Fig. 1(b) and (d), aluminum sources for $Al(NO_3)_3$ than $AlCl_3$ to obtain a product of the XRD peak intensity is relatively higher, which says the regularity and crystallinity are better. In this study, characteristic diffraction peaks of a different precursor influenced by a combination of product, we believe that is mainly related to the hydrothermal system of initial pH value, the solubility of the precursor and the combination of different anionic polar (electronegativity) related. Because they affect the concentration of magnesium and aluminum ion in the system, which results the construction of LDHs ionic ligand structure changed in the hydrothermal system, thus affecting the formation of crystal nucleus and the crystallization of LDHs, the specific reason and reaction mechanism needs further research.

3.2 The Micro Analysis Study of the Products

Fig. 2 shows the SEM graph of LDHs prepared with different precursors, which were combined by magnesium and aluminum sources.

As shown in Fig. 2, when the pH value, hydrothermal temperature and reaction temperature were fixed in the hydrothermal system and magnesium sources was fixed to $MgCl_2$, the microstructure of LDHs would be directly influenced by the different aluminum sources precursors. Fig. 2(a) was the SEM graph of LDHs prepared with insoluble Al_2O_3. It can be found that the product without apparent hexagonal structure takes on incomplete flake structure and agglomeration phenomena. Besides, some amorphous materials with lower grain are absorbed on its surface, which reflects the uniformity and regularity of the product are comparatively poor. By using the point analysis function of X-ray energy disperse spectroscopy (EDS), it has been confirmed that aluminum contents of amorphous particles is high, from which the particles were inferred as the

intermediate generated by Al_2O_3 and alkali reaction. Fig. 2(b) and Fig. 2(c) are the SEM graph of products prepared with $Al(NO_3)_3$ and $AlCl_3$ respectively as aluminum sources precursors. Compared with Fig. 2(a), they take on apparent hexagonal structure and the uniformity and regularity are better. However, its grain sizes and thickness has subtle differences. The former grain size is 90-250 nm and its thickness is about 30 nm. Compared with that in Fig. 2(b), the particle size in Fig. 2(c) with 40 nm thickness is bigger, which is about 100-340 nm. When magnesium sources was fixed to $Mg(NO_3)_2$ and aluminum sources was respectively fixed to $AlCl_3$ and $Al(NO_3)_3$, the grain sizes of the products were reduced evidently (Fig.(d) and (e)) and the crystallinity, uniformity and regularity are about the same as that in Fig, 2(b) and (c). When $AlCl_3$ is as aluminum sources precursors, the grain size and thickness of LDHs crystal is respectively 90-150 nm and 30 nm. However, when $Al(NO_3)_3$ is as aluminum sources precursors, its grain size is about 100-150 nm.

In addition, the LDHs prepared in different conditions were investigated via X-ray Energy Disperse Spectroscopy (XREDS). Through the analysis of point and irregular schistous grain from point to line in Fig. 2(a), it was proved that the aluminum contents of particles is relatively high and average Mg/Al ratio of the products is about 2.5, which illustrates Al_2O_3 is not advantage for the preparation of LDHs. By the EDS analysis of LDHs prepared in other reaction system, its average Mg/Al ratio is about 3, which is very close to the theoretical value and other anion impurities are not contained. The typical graph can be seen in Fig. 3.

In the hydrothermal environment, the formation of the product mainly includes nucleation and growth process. The morphology of the crystal is mainly determined by the internal structure of the crystal, and is influenced by the other conditions [9]. At present, there are many mechanism of hydrotalcite formation. Anion coordination polyhedron theory, which combines the growth law of the crystal structure with the growth environment and the organic combination of the crystal structure from the formation of the growth units, the adsorption and crystallization of the interfacen [10,11], can achieve the purpose of reasonable explanation. Hydrotalcite laminates with D_{3d} symmetry, the macroscopic symmetry elements in crystallography belongs to the $P\bar{3}m_1$ space group $\bar{3}m$. The layer of hydrotalcite is a eight-plane structure with metal ion as the center, and its growth units mainly consisted of $[Mg^{-}(OH)_6]^{4-}$ and $[Al^{-}(OH)_6]^{3-}$. In the hydrothermal system, the hydrotalcite is mainly formed by the process of bonding of growth units. Effects of different hydrothermal environments and conditions affect method of crystal superposition

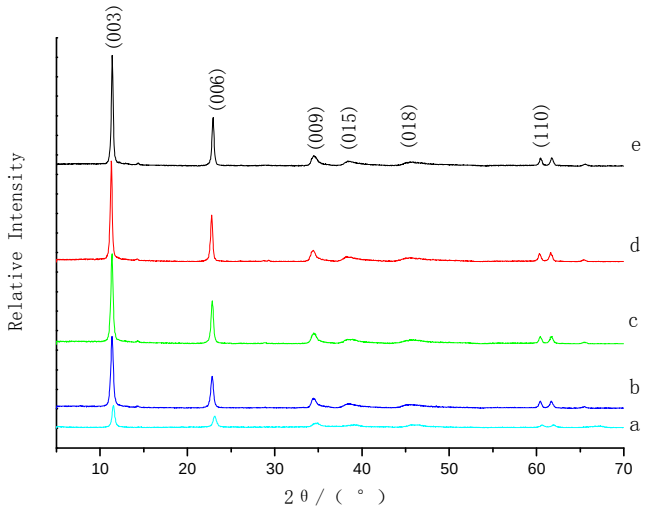

Fig. 1. XRD diagram of synthesis products of different precursors

a:MgCl2+Al2O3; b:Mg(NO3)2+AlCl3; c:MgCl2+Al(NO3)3;d: Mg(NO3)2+ Al(NO3)3； e:MgCl2+AlCl3.

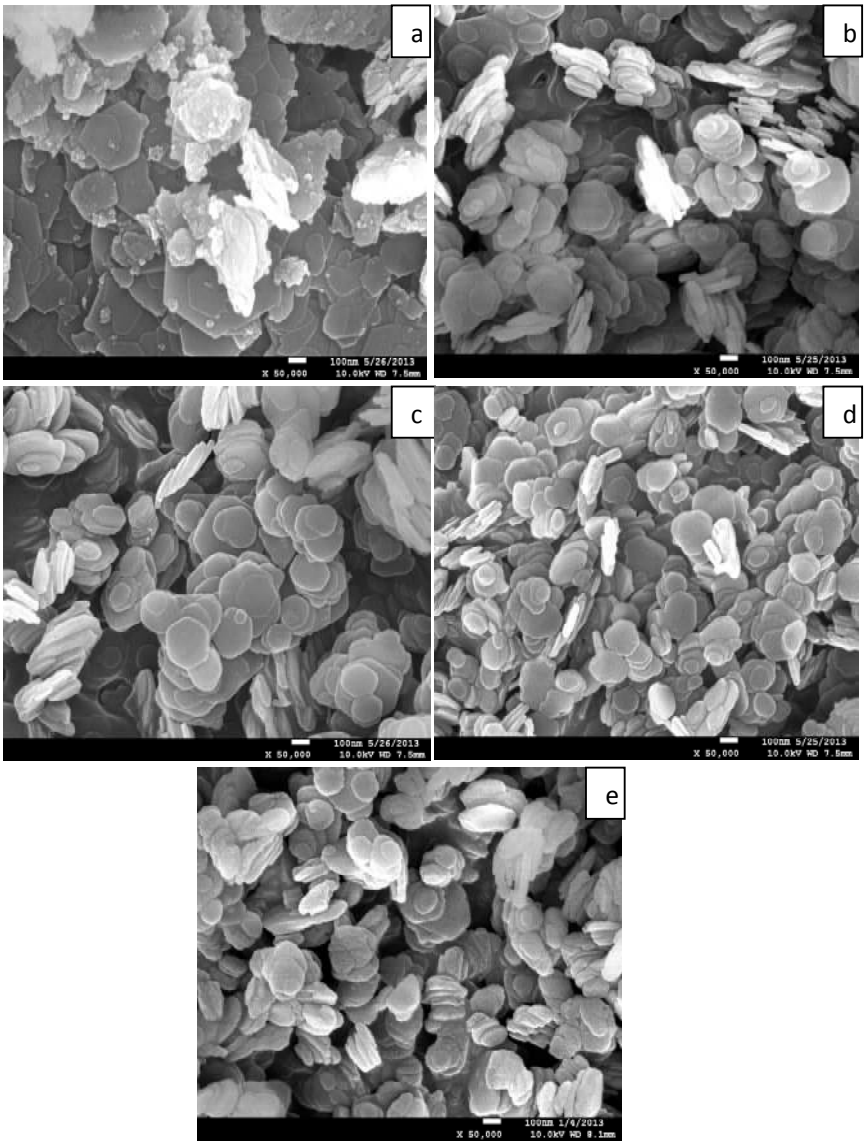

Fig. 2. SEM diagram of the products prepared by different precursors

a:$MgCl_2$+Al_2O_3; b:$MgCl_2$+$Al(NO_3)_3$; c: $MgCl_2$+$AlCl_3$; d: $Mg(NO_3)_2$+$AlCl_3$; e: $Mg(NO_3)_2$+$Al(NO_3)_3$;

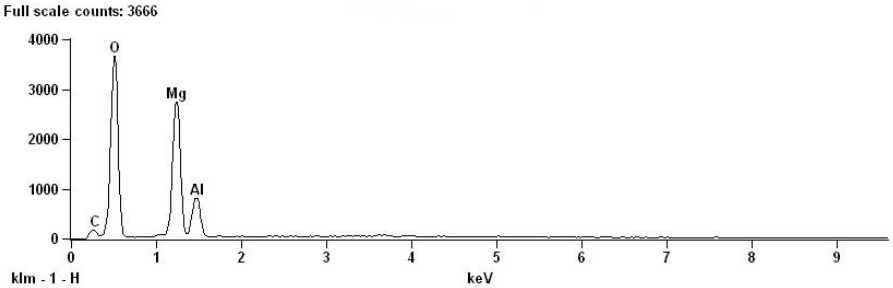

Fig. 3. The EDS spectrum of LDHs

and bonding speed of growth units [12,13]. In previous studies, we using magnesium nitrate and aluminum nitrate as precursors, confirmed that in the hydrothermal system only when the

pH is greater than or equal to 12, can we succeed to prepare a structure to a single and complete hydrotalcite [14]. The temperature mainly influences the hydrotalcite lateral growth, but when it reaches a certain temperature, the change in temperature of Mg-Al hydrotalcite crystal morphology has small impact. The reaction time has little effect on the crystal growth change, but beneficial to the improvement of the crystal growth and regularity. In this study, the reason why the different precursor combinations can affect the microstructure of the product, we think it is mainly related to the initial pH value of hydrothermal system, the solubility of precursors and the anion polarity of magnesium and aluminum ions. With the $MgCl_2$ as the magnesium sources, the solubility of aluminum sources precursors is Al_2O_3>$AlCl_3$ >$Al(NO_3)_3$. At the same pH conditions, the insoluble Al_2O_3 with the alkali gradually generates AlO^{2-} to provide aluminum source, which makes the precipitation rate of Mg^{2+} and Al^{3+} not synchronized. This not only affects the change of the pH value of the system, but also affects the formation speed and integrity the hydrotalcite crystal growth unit $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6]^{3-}$. Because composite process is a primitive hydroxyl [-(OH)] of mutual dehydration and octahedral combined process of edges, which influences the formation of the basic layer of positively charged $[Mg_6Al_2(OH)_{16}]^{2+}$ leaving the synthesis of crystalline, homogeneity and purity is relatively poor. With the $Al(NO_3)_3$ and $AlCl_3$ as the aluminum sources, although there are some differences between the solubility of the two, they all belong to the soluble better material, which has a relatively small effect on ion concentration of OH^- and H^+ in hydrothermal system and the growth units of hydrotalcite crystal phase transition process. However, due to the differences of the polarity of chloride and nitrate ions [15], this leads to a slight difference in the microstructure of the product. Similarly, in the system of the better solubility of $Mg(NO_3)_2$ as the magnesium sources and the $Al(NO_3)_3$ and $AlCl_3$ as the aluminum sources, it is easier to form a stable negative ion coordination eight surface $[Mg\text{-}(OH)_6]^{4-}$ growth units. However, for the differences between the solubility and anionic polarity of $Al(NO_3)_3$ and $AlCl_3$, affecting the formation and growth speed of $[Al\text{-}(OH)_6]^{3-}$, which makes the connection mode and orientation of the growth elements both change. It eventually led to Mg-Al hydrotalcite crystal along the a-axis growth superimposed rate affected, so the morphology appears as differences of crystal micro structure.

4. CONCLUSIONS

(1) The crystal phase transition of Mg-Al hydrotalcite was influenced by the selection of precursors, pH value, hydrothermal temperature and reaction time in the hydrothermal system. When the pH value, hydrothermal temperature, reaction time and other conditions were fixed and invariable. There were some effects of different magnesium and aluminum sources in combination on the synthesis of combinations of hydrotalcite crystal microstructure and its crystal growth. The uniformity, dispersion, crystal regularity and the ratio between diameter and thickness of obtained products were affected by the insoluble or less soluble precursors directly.

(2) Compared with the less soluble magnesium sources precursor ($MgCl_2$), the one ($Mg(NO_3)_2$) with high solubility is more conducive to prepare the smaller size Mg-Al-LDHs crystal with better crystallinity and regularity.

(3) The magnesium and aluminum sources precursors with different solubility and anion polarity have influence on the construction speed and integrity of growth units $[Mg\text{-}(OH)_6]^{4-}$ and $[Al\text{-}(OH)_6]^{3-}$, which furtherly results in slight change in connection mode, composite rate and azimuth of growth units in the process of phase transition of LDHs. Therefore, the different precursor combinations of magnesium and aluminum sources create different microstructure of obtained products.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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