



Controlling size and shape of Zn-Al-PAB layered double hydroxide

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ABSTRACT

In the recent years nanosize layered double hydroxide materials have been extensively prepared and studied for many future applications. In this contribution, Zn-Al-PAB layered double hydroxide (PAB=para amino benzoate) with wide range particle size and various shape is reported. Para amino benzoate acid is one of the sunscreen compounds. Zn-Al-PAB with particle size in the range of 100-200 nm and spherical shape can be prepared using reactants of zinc chloride, aluminium chloride and sodium para amino benzoate. Zn-Al-PAB that has larger particle size of 300-500 nm with cubic shape is obtained when zinc nitrate and aluminium nitrate are used. If zinc sulphate and aluminium sulphate are used, much larger particle size of 700-900 nm with turbine-like shape is yielded. During the nucleation process, chloride, nitrate and sulphate in the solution help control the shape and size of Zn-Al-PAB LDH. Hydration number of the anions is believed to be responsible for the growth of the Zn-Al-PAB LDH aggregate that will affect the size. Large hydration number of anion will set barrier for Zn-Al-PAB to grow bigger.

Keywords: Layered double hydroxide, para amino benzoate, nanoparticle, anion effect

INTRODUCTION

Layered double hydroxides (LDHs), also known as hydrotalcites, anionic clays, and mixed metal hydroxides consist of $M^{II}(\text{OH})_6$ and $M^{III}(\text{OH})_6$ edge-sharing octahedrons forming sheets similar to those of brucite, $\text{Mg}(\text{OH})_2$ [1]. The overall positive charges on the octahedral sheets are balanced by anions occupying the interlayer space which are exchangeable [2-5]. The naturally present mineral known as hydrotalcite is a Mg-Al LDH in which CO_3^{2-} is charge balancing anions and is formulated as $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\cdot\text{CO}_3\cdot 4\text{H}_2\text{O}$ [4-5]. LDHs have been studied extensively for many possible applications mainly for anion exchangers, acid scavengers, polymer additives, battery cathodes, catalysts, catalyst supports, and electrode modifiers [6-12].

In the recent years, layered double hydroxides have been studied extensively because of possible application in drug delivery system, organic-inorganic composite materials, and cathode materials [1]. We have reported previously that para amino benzoic acid (PABA) can be inserted into the interlayer space of Zn-Al-CI LDH to balance the positive charge of octahedral sheet as para amino benzoic (PAB) anion to produce organic-inorganic sunscreen [13]. PABA is an ingredient of sunscreen lotion approved by US Food and Drug Administration (FDA), and it can be added up to 15% by weight. Most organic sunscreens consist of benzene ring as main chromophore subunit and other functional groups such as carbonyl and ether. In this contribution we would like to report on the effect of starting salts on the size and morphology of Zn-Al-PAB. The counter anions of the starting salts to be studied are chloride,

nitrate, and sulphate. The shape and the size of Zn-Al-PAB crystallite are found to be dependent on the type of the counter anions.

EXPERIMENTAL

Zinc chloride, zinc nitrate, zinc sulphate, aluminium chloride, aluminium nitrate, aluminium sulphate, and para amino benzoic acid (PABA) were supplied by Merck and were of analytical grade chemicals and used without further purification. Other chemicals were also obtained from Merck used as received.

Zn-Al-CI LDH was prepared according procedure in the literature [13]. Synthesis of the Zn-Al-PAB from zinc and aluminium chlorides was performed in a three-necked round flask. A 25.0 mL aqueous solution of 0.60 M (15.0 mmol) was mixed with 25.0 mL aqueous solution of 0.20 M (5.0 mmol) aluminium chloride and stirred quickly at about 1000 rpm using a magnetic stirrer. To this mixture, a 50.0 mL solution containing 10.0-mmol sodium para amino benzoate (Na-PAB) was added using a funnel and stirred quickly. Na-PAB was prepared prior to the mixing by stoichiometric reaction of PABA with NaOH. It took about 2 minutes to complete the addition of Na-PAB solution.

The suspension was hydrothermally heated in a PTFE bottle at 100°C for 15 hours. The product was separated using a centrifuge and washed three times using double distilled water. The collected solid was dried in an oven at 70 °C for 48 h. After being dried, its layered structure was confirmed using X-ray Diffraction (XRD) on Shimadzu 6000 series. The metal contents

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were determined using atomic absorption spectrometry (AAS) using appropriate standard solution. The amount of water is determined by gravimetric method using porcelain crucible container after the sample was heated at 180 °C for 3 h. The PAB in the interlayer space was recovered by reaction the solid with dilute nitric acid. PABA was separated as precipitate since other metal components were dissolved. The results of the elemental analysis were used to determine the structural formulae of the product [6]. Similar procedure was applied to prepare Zn-Al-PAB from corresponding nitrate and sulphate salts.

The microscopic view of the solid was pictured using scanning electron microscope (SEM). The interlayer organic anion was confirmed using FTIR.

RESULTS AND DISCUSSION

Table 1 shows the formula of Zn-Al-PAB prepared using different salts. During the preparation of the solid, after nucleation process was done at room temperature, hydrothermal treatment was performed at 100 °C for 18 h. Metals were determined using atomic absorption spectrometry (AAS) and interlayer water was determined gravimetrically after heating at 180°C for 3 h. The formulae are fit to the general structure of layered double hydroxide of $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^-_{z1}A^{2-}_{z2}\cdot mH_2O]$. It is expected that the structural formula is very close to the ideal structure of hydrotalcite. In most cases, PABA content was slightly higher, meaning that some non structural (free) PAB may be included. Ideally, the number of moles of PAB should equal to that of the number of moles of aluminium. The excess in the positive charge of the layered double hydroxide sheet has to match the number of moles of charge balancing anion.

Figure 1 depicts the XRD pattern of Zn-Al-PAB prepared using zinc nitrate and aluminium nitrate. Note that similar XRD pattern was observed with other zinc chloride and aluminium chloride [13] as well as zinc sulphate and aluminium sulphate. The basal spacing of Zn-Al-Cl LDH is 7.60 Å [7]. The increase in the basal spacing to 10.85 Å (corresponding to $2\theta=8.14^\circ$) strongly suggests that interlayer anion has been replaced by para amino benzoic. However the native Zn-Al-NO₃ is still present as revealed by the existence of basal spacing 7.60 Å. Complete replacement of nitrate anion by para amino benzoic anion seems impossible as it was reported for replacement of chloride by ferrocyanide [8]. We also observed similar pattern for other Zn-Al-PAB synthesized using zinc chloride and aluminium chloride [13] as well as zinc sulphate and aluminium sulphate.

Figure 2 shows FTIR spectra of Zn-Al-PAB synthesized using zinc nitrate and aluminium nitrate. We have reported earlier the FTIR spectra of Zn-Al-Cl LDH without para amino benzoic acid earlier [13]. In

Table 1. Structural formulae of Zn-Al-PAB prepared using different initial counter anion of the salts. Nucleation was done at room temperature and hydrothermal treatment was performed following the nucleation.

Compound	Counter Anion	Structure
Zn-Al-PAB	Cl ⁻	$Zn_{0.745}Al_{0.254}(OH)_{1.650}(PAB)_{0.349}\cdot 0.684H_2O$
Zn-Al-PAB	NO ₃ ⁻	$Zn_{0.768}Al_{0.232}(OH)_{1.652}(PAB)_{0.348}\cdot 0.652H_2O$
Zn-Al-PAB	SO ₄ ²⁻	$Zn_{0.727}Al_{0.273}(OH)_{1.684}(PAB)_{0.316}\cdot 0.727H_2O$

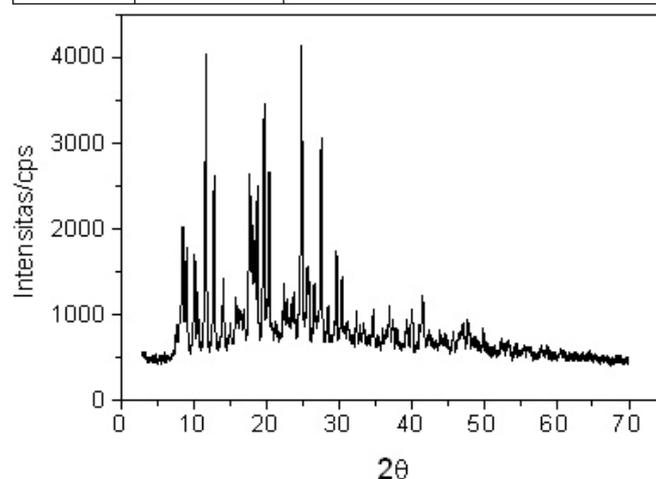


Figure 1. XRD pattern of Zn-Al-PAB prepared using zinc nitrate and aluminium nitrate. This XRD pattern was very similar to that obtained using zinc chloride and aluminium chloride.

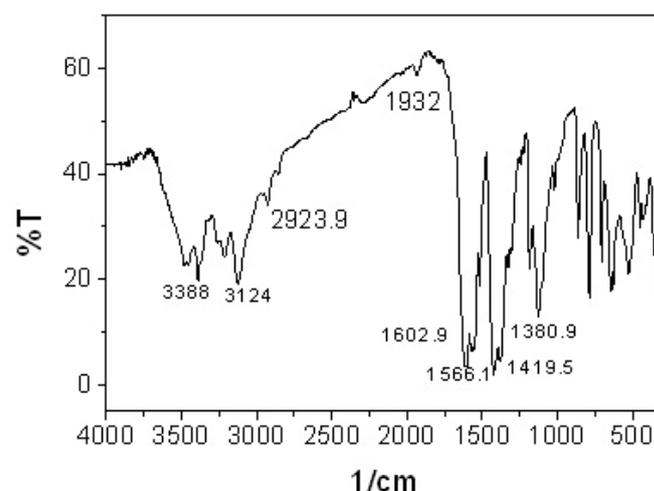


Figure 2. FTIR spectra of the Zn-Al-PAB prepared using zinc nitrate and aluminium nitrate.

Figure 2, a band of O-H stretching is seen at 3552 cm^{-1} . The corresponding O-H bending at 1630 cm^{-1} is not observed probably overshadowed by other bands. The N-H stretching is very close to O-H stretching, which is observed at 3213 cm^{-1} and C-H stretching of the aromatic ring can be confirmed with the band at 3124

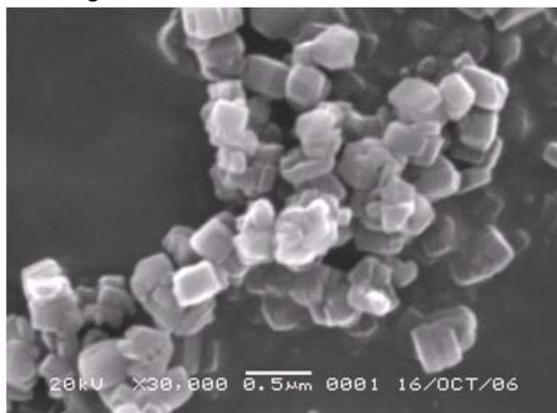


Figure 3. SEM image of the Zn-Al-PAB prepared using zinc nitrate and aluminium nitrate at 30,000 magnification. The estimated crystallite was 200-300 nm.



Figure 4. SEM image of Zn-Al-PAB prepared using zinc chloride and aluminium chloride at 20,000 magnification. The estimated crystallite was 300-500 nm.



Figure 5. SEM image of Zn-Al-PAB prepared using zinc sulphate and aluminium sulphate at 20,000 magnification. The estimated crystallite was 700-900 nm.

cm^{-1} . The C=C vibration of the benzene ring is also supported by the vibration at 1419 cm^{-1} and 1566 cm^{-1} , respectively. The band near 1608 cm^{-1} corresponds to the C=O vibration mode. In addition, the C-H bending of aromatic ring is also clearly recorded at 710 cm^{-1} . From the FTIR spectra, it is not ambiguous to conclude that para amino benzoic acid has been inserted into the interlayer space of the host.

Figure 3 shows the SEM image of Zn-Al-PAB synthesized using SEM image of Zn-Al-PAB prepared using zinc nitrate and aluminium nitrate at magnification of 30,000X. It can be estimated that crystallite size is in the range of 200-300 nm. The shape of the crystallite is spherical and is very homogeneous. Spherical crystallite of Zn-Al-PAB could be prepared only by using zinc nitrate and aluminium nitrate.

When zinc chloride and aluminium chloride was used as starting salts, the size of the crystallite is much bigger (Figure 4). The particle size of this Zn-Al-PAB is in the range of 300-500 nm slightly bigger than prepared using chloride salts. The crystallite has cubic shape. Larger particulate of Zn-Al-PAB about 700-900 nm in diameter is obtained when zinc sulphate and aluminium sulphate are used. Interestingly, the shape of the material looks like turbine as presented in Figure 5.

In general, nanosize LDH prepared in this work is slightly bigger than that of Mg-Al LDH prepared using hydrothermal treatment at boiling temperature [14, 15]. Mild hydrothermal condition and slow crystal growth seem to result in larger particulate of Zn-Al-PAB. The difference in the hydration number of the anions, in this case chloride, nitrate, and sulphate, is believed to be responsible for the shape and size of the Zn-Al-PAB particulates.

CONCLUSIONS

The counter anions of the salts affect size and the shape of Zn-Al-PAB crystallite. Small crystallite of Zn-Al-PAB of only 100-200 nm with spherical shape can be prepared using zinc nitrate and aluminium nitrate as starting materials. A bigger crystallite of 700-900 nm with turbine-like shape is obtained from zinc sulphate and aluminium sulphate. An intermediate size of Zn-Al-PAB crystallite of about 300-500 nm is obtained when nitrate salts are used. These suggest that nanosize crystallite of Zn-Al-PAB could be designated when certain salts are used in synthesis. In the future it is expected that preparation of nanosize layered metal oxides has to consider starting salts as well as their charge balancing anions.

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