



Synthesis and thermal properties of ZnAl layered double hydroxide by urea hydrolysis



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ABSTRACT

The synthetic zinc aluminum layered double hydroxide (LDH) with Zn/Al molar ratios of 0.25–8 was synthesized by the urea method. The structure, composition and morphological properties were investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscope (SEM). Pure layered double hydroxide phase was obtained when the Zn/Al ratios are 0.5, 1 and 2. The lower (0.25 and 0.33) and higher (3, 4, 6 and 8) initial Zn/Al molar ratios resulted in the formation of ZnAl–CO₃–LDH with AlOOH and Zn₄(CO₃)(OH)₆·nH₂O, respectively. The thermal properties of these LDHs were studied by the thermogravimetric and differential thermal analysis (TG–DTA). The XRD patterns of the calcined products at 900 °C showed that the LDHs prepared at different Zn/Al molar ratios can be used as good precursors for preparing mixed oxide or spinel.

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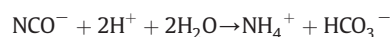
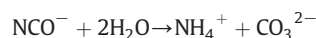
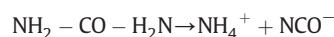
1. Introduction

Layered double hydroxide (LDH) is a class of two-dimensional anionic clays which is composed of an ionic lamellar solid that contains positively charged brucite-type layers and exchangeable hydrate gallery anions. The ability of LDHs to intercalate anions makes them useful as catalysts, catalyst supports, anion exchangers, adsorbents, electrochemical reactions and bioactive nanocomposites [1–6]. The general formula of LDH is $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}] \cdot mH_2O$, where M^{II} and M^{III} are metals in the oxidation states +2 and +3, respectively; Aⁿ⁻ is the interlayer anion of charge *n* that leads to the electro-neutrality of the LDH; and the coefficient *x* is the molar ratio of M^{II}/(M^{II} + M^{III}). They are structurally similar to the mineral brucite [Mg(OH)₂] with a fraction of M^{II} ions replaced by M^{III} ions [7]. Due to uniform distribution of cations in the brucite layer, the LDH is an excellent precursor for preparing spinels or mixed oxides [8,9]. These calcined products are useful solids that found potential applications in areas such as catalysis, lithium-ion batteries and solar cells because of their superior electrochemical performance [10–13].

Hitherto, several synthesis methods to synthesize LDH of different metal cations have been reported by early researchers. Co-precipitation is the most widely used method to prepare LDH [14]. The drawback of the method is that, no matter how fast the stirring speed is, the instantaneous pH value is certainly different in different parts of the slurry. As a result, it is very difficult to obtain LDH with high crystallinity. And this method often results in strong agglomeration of primary particles in aggregates with very broad size distributions. Such morphology leads

to very low specific surface areas and porosity that may adversely affect the catalytic properties of LDH. Moreover, once the aggregates are formed they are very stable and resistant to de-cohesion even under powerful ultrasonic treatments [15]. To predict the behavior of LDHs in the applications, the control and reproducibility of their crystal and particle properties is important and a high crystallinity is necessary. The urea hydrolysis method introduced by Costantino et al. was an important advancement in this regard [16].

The urea method utilizes urea instead of NaOH as the precipitating agent. The advantage of using urea is that the urea hydrolysis progresses slowly which leads to a low degree of super saturation during precipitation. Urea is a weak Bronsted base (*p*K_b = 13.8). It is highly soluble in water and its controlled hydrolysis in aqueous solutions can yield ammonium cyanate or its ionic form (NH₄⁺, NCO⁻). Prolonged hydrolysis results in either CO₂ in an acidic medium or CO₃²⁻ in a basic environment as shown below [17–19].



A reaction temperature above 60 °C produces the progressive decomposition of urea in ammonium hydroxide leading to a homogeneous precipitation. This method has been already employed for the synthesis of well crystallized [MAI–CO₃–LDH] (M = Li, Mg, Ni, Co),

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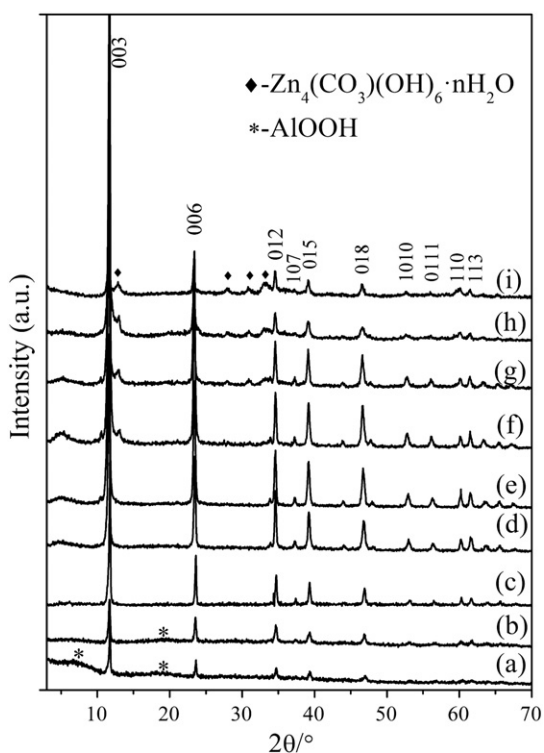


Fig. 1. XRD patterns of samples (a) $Zn_{0.25}Al$, (b) $Zn_{0.33}Al$, (c) $Zn_{0.5}Al$, (d) Zn_1Al , (e) Zn_2Al , (f) Zn_3Al , (g) Zn_4Al , (h) Zn_6Al , and (i) Zn_8Al .

[NiFe–CO₃-LDH], [CoTi–CO₃-LDH] and even three-component LDH with large particle sizes [20–25]. With the different formation mechanism, unlike in the co-precipitation method, Mg/Al ratio of 1:1 was successfully prepared by the urea method [17]. The urea method was also used to prepare ZnAl-LDH with an initial Zn/Al = 2 [26]. Except for the carbonate containing LDHs which were always synthesized by urea method, a nitrate containing ZnAl-LDH (Zn/Al = 2) was successfully directly synthesized in this way [27]. In our previous studies, a novel Zn–Al layered double hydroxide (LDH) with a composition of $[ZnAl_2(OH)_6]CO_3 \cdot nH_2O$ was prepared by the urea method and could be a new precursor for preparing zinc aluminate spinel [28]. In this paper, a further study about the preparation of ZnAl–CO₃-LDH with different Zn/Al molar ratios (0.25–8) was discussed and the formation mechanism of ZnAl–CO₃-LDH by the urea method was preliminarily explored. Furthermore, the products of calcined LDH at 900 °C were investigated by XRD.

2. Experimental

2.1. Materials

The chemicals used in this study were of analytical grade and were purchased from Sinopharm Group Co. Ltd. All of the chemicals were used without further purification. Deionized water was used as a solvent throughout this study.

Table 1

The indexing of XRD for the ZnAl–CO₃-LDH with different Zn/Al molar ratios at 0.25–8.

Parameter (nm)	$Zn_{0.25}Al$	$Zn_{0.33}Al$	$Zn_{0.5}Al$	Zn_1Al	Zn_2Al	Zn_3Al	Zn_4Al	Zn_6Al	Zn_8Al
d_{003}	0.75193	0.75270	0.75317	0.76026	0.76026	0.76027	0.76222	0.76353	0.76159
d_{006}	0.37621	0.37746	0.37636	0.37873	0.37985	0.38080	0.38097	0.38177	0.38130
d_{110}	0.15286	0.15308	0.15320	0.15339	0.15364	0.15363	0.15365	0.15365	0.15364
Lattice parameter a	0.30572	0.30616	0.30640	0.30678	0.30728	0.30726	0.30730	0.30730	0.30728
Lattice parameter c	2.25653	2.26143	2.25884	2.27658	2.27994	2.28280	2.28624	2.29061	2.28629

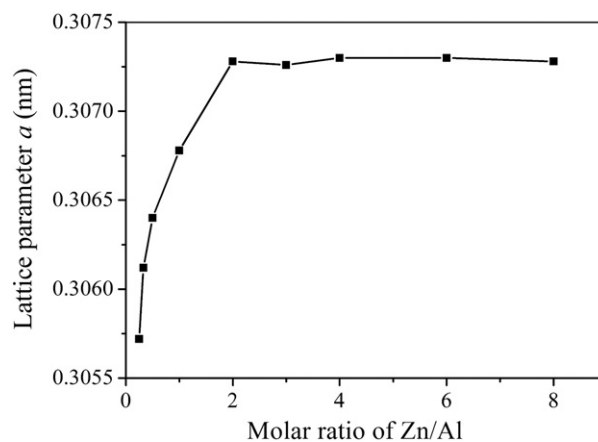


Fig. 2. The a value plotted versus the Zn/Al molar ratio.

2.2. Synthesis

The urea method was used to prepare ZnAl–CO₃-LDH with a concentration of $Zn^{2+} + Al^{3+} = 0.15$ M. $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water in a three-neck flask. Urea ([urea]/[NO₃[−]] molar ratio of 3) was dissolved in the above solution. The flask was soaked in an oil bath preheated at 100 °C to start the hydrolysis reaction. The solutions were maintained at 100 °C for 24 h under stirring. The formed solids were collected by filtration, washed with deionized water and subsequently dried at 60 °C for 24 h. The samples with different Zn/Al molar ratios of 0.25, 0.33, 0.5, 1.0, 2.0, 3.0, 4.0, 6.0 and 8.0 were designated as $Zn_{0.25}Al$, $Zn_{0.33}Al$, $Zn_{0.5}Al$, Zn_1Al , Zn_2Al , Zn_3Al , Zn_4Al , Zn_6Al and Zn_8Al , respectively. The numbers indicate the Zn/Al molar ratios. The calcined products were obtained by placing ZnAl–CO₃-LDH in a muffle furnace at 900 °C for 1 h in air. After calcination, the powders were removed from the furnace and characterized.

2.3. Characterizations

The powder X-ray diffraction (XRD) patterns of all samples were determined on a Rigaku D/MAX-rA X-ray diffractometer with Cu K_α radiation ($\gamma = 0.15418$ nm). The sample were scanned for 2θ values ranging from 3 to 70° with a scan speed of 1°/min. Fourier transform infrared spectroscopy (FT-IR) spectra of samples were collected in KBr pellets on a VERTEX-70 Fourier transformation infrared spectroscope in reflectance mode, at the range of 400–4000 cm^{−1} and with a resolution of 1.43 cm^{−1}. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out in air using a SDTQ600 comprehensive thermal analyzer with a heating rate of 10 °C/min. Micro-morphology was obtained with an S-4800 high resolution scanning electron microscope (SEM).

3. Results and discussion

The XRD patterns of ZnAl–CO₃-LDH prepared at different Zn/Al molar ratios were shown in Fig. 1. The diffraction peaks for (003) and (006) crystal planes, as well as the peaks for (012), (015) and (018) crystal planes, indicate the well-formed crystalline layered structure.

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