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# Studies on Synthesis and Properties of Mg-Al-nitrate Layered Double Hydroxides

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**Abstract:** A positive Mg-Al-nitrate layered double hydroxides (LDHs) has been synthesized using a non-steady coprecipitation method. The shape, size, chemical composition, electrical property and anion exchange property of the positive nanoparticle were studied by SEM, XRD, FTIR, chemical analysis, spectroanalysis and measuring of electrophoretic mobilities. Preliminary results show the positive nanoparticle is a promising precursor of polymer/LDHs nanocomposite.

**Keywords:** Layered double hydroxide, nanoparticle, synthesis, positive.

Layered double hydroxides (LDHs), or the so-called hydrotalcite-like compounds, are important clay materials owing to their intercalation ability of anionic species and other physicochemical properties for application as anion adsorbents, medicine stabilizers, ion-exchangers, ionic conductors, catalysts and catalyst supports [1-2]. The general formula is, $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{m-}_{x/m} \cdot nH_2O]^{x-}$, abbreviated by: $[M^{II}\text{-}M^{III}\text{-}X]$. The net positive charge, due to substitution of trivalent by divalent metal ions, is compensated by an equal negative charge of the interlayer solvated anions. The hydrated anions in the interlayer spaces can be replaced almost with any desired anions, organic or inorganic, by utilizing ion exchange methods. For simple inorganic anions the exchange facility is decreased in the order [3] $NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$.

A large number of applications of LDHs based on the intercalation or exchange of specific guests have been described[1, 4]. The insertion of guests is limited by the guest's size because during exchange, the layers must be forced to dispart. An alternative approach to insert guests would be *via* exfoliation of the LDHs followed by condensation of the layers in the presence of guests. Exfoliation, however, is difficult for LDHs because of the high charge density on the layers. For the [Mg-Al-$NO_3$], the $NO_3^-$ has strong exchange capacity and bigger basal spacing, so in many literatures, [Mg-Al-$NO_3$] has been selected to be a precursor of polymer/LDHs nanocomposite[5,6].

In the early report[7], [Mg-Al-$NO_3$] was prepared by steady coprecipitation method. In the procession of reaction, the pH of the slurry needed to keep at 10. After the addition was completed, the slurry needed to hold at 65°C for a period of 16 days. In the present study, a non-steady coprecipitation method was used to get [Mg-Al-$NO_3$]. This method showed a different reaction mechanism and shorter reaction time comparing

with the steady coprecipitation method[8].

Under a $N_2$ atmosphere, a mixed solution of magnesium and aluminum nitrate was prepared in the molar ratio of 1:1, or 2:1, or 3:1. Then diluted ammonia water (5:1(V/V)) was added to the solution at a speed of 50 mL/min. The final pH value was 10.0. A given amount of $NaNO_3$ was added. The precipitate was aged for 1 h. at room temperature, and then washed with deionized water. After that, the filter cake was peptized at 80°C, forming the positive sol. It was dried at 60°C to get LDHs nanoparticle. To exchange the interlayer nitrate ions, [Mg-Al-$NO_3$] was reacted with 0.04 mol/L aqueous solutions of benzoate and 0.02 mol/L aqueous solution of sodium dodecylbenzenesulphonic acid (SDB), respectively. Reaction were held at 65°C for 3 days with occasional shaking, then washed three times with water, and dried in air at 60°C, so [Mg-Al-(Benzoate)] and [Mg-Al-(SDB)] were got.

Scanning electron microscopy (SEM) used a HITACHI S-530 scanning electron microscope. Powder X-ray diffraction (XRD) patterns were recorded using D/max-YB diffractometer with Cu Ka radiation. The $\zeta$ potential of nanoparticle was measured by DXD-I microelectrophoresis instrument. The contents of magnesium and aluminum in the precipitate were measured by electron spectroscopy for chemical analysis of JXA-840 scanning electron micrograph. FTIR spectra were recorded in the region 4000-400 $cm^{-1}$ on a Nicolet 50X infrared spectrophotometer.

**Table 1** shows that the chemical composition of particles are dependent on the composition of the raw material, when the ratios of Mg/Al in the raw material are 1:1, 2:1, 3:1, the ratios of Mg/Al in the products are 1:1, 2:1, 3:1, respectively. The basal spacing of particles are dependent on the composition of the raw material, the biggest base spacing can be get when Mg/Al molar ratio is 2:1.

**Table 1** Chemical formulas and basal spacing of [Mg-Al-$NO_3$] for various Mg/Al ratios

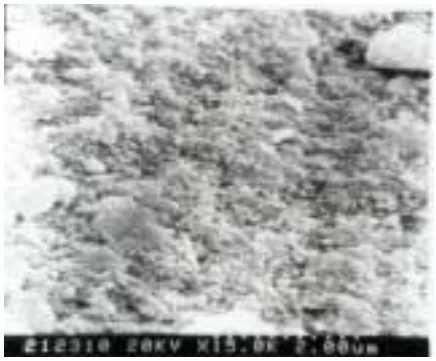
| Sample | Mg/Al molar ratio | Chemical formula | Basal spacing (Å) |
|---|---|---|---|
| 1 | 1:1 | $[Mg_{0.48}Al_{0.52}(OH)_2](NO_3)_{0.52}\ 1.15H_2O$ | 8.3 |
| 2 | 2:1 | $[Mg_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}\ 0.66H_2O$ | 8.9 |
| 3 | 3:1 | $[Mg_{0.75}Al_{0.25}(OH)_2](NO_3)_{0.25}\ 0.68H_2O$ | 7.8 |

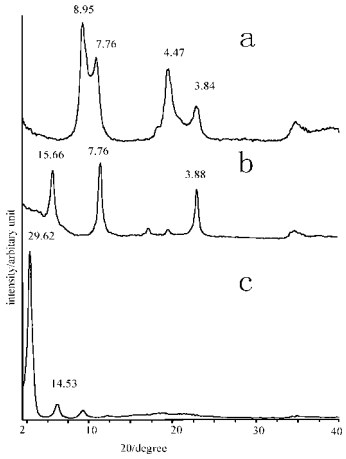
**Figure 1** shows the SEM image of the precipitated [Mg-Al-$NO_3$]. The morphology is markedly thin, plate-like particle. The particle size is about 300 nm.

The XRD data for the LDHs samples containing nitrate, benzoate, SDB interlayer species are shown in **Figure 2**. The peak which occurred at approximately 10° (2 $\theta$) for [Mg-Al-$NO_3$] was attributed to the reflections from the (003) family of crystallographic planes. Benzoate and SDBS insertion into the LDHs gallery resulted in a shift of the $d_{003}$ reflection from 8.95 Å for [Mg-Al-$NO_3$] to 15.7Å and 29.6 Å for [Mg-Al-(Benzoate)] and [Mg-Al-(SDB)], respectively.

**Figure 1** SEM image of [Mg-Al-$NO_3$]

**Figure 2** XRD patterns of a) [Mg-Al-$NO_3$], b) [Mg-Al-(Benzoate)], c) [Mg-Al-(SDB)]






The ζ potential of nanoparticle increased with increasing the contents of magnesium in precipitate [8]. When the ratios of Mg/Al in the raw material are 1:1, 2:1, 3:1, the ζ potential of particle is 36.87, 41.30, 42.31 mV, respectively.

**Figure 3** FTIR spectra of a) [Mg-Al-$NO_3$], b) [Mg-Al-(Benzoate)], c) [Mg-Al-(SDB)]

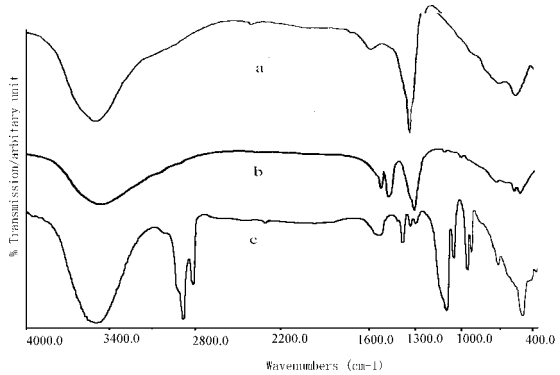



**Figure 3** shows the FTIR spectrum of [Mg-Al-$NO_3$]. The absorption band at around 3500$cm^{-1}$ was attributed to OH stretching. A strong absorption band at 1385 $cm^{-1}$ was due to the presence of nitrates. The anion exchange reactions were also confirmed by FTIR spectroscopy (**Figure 3**). Of significant difference for FTIR spectra in **Figure 3** was the very low intensity of the absorption band around 1385 $cm^{-1}$ for [Mg-Al-(Benzoate)] and [Mg-Al-(SDB)]. At the same time the bands at around 2850-2950 $cm^{-1}$ and 1210-1240 $cm^{-1}$ became more prominent. It showed that the organic anions had been exchanged with the nitrates in the gallery of LDHs. FTIR and XRD results showed that the [Mg-Al-$NO_3$] could accommodate the benzoate and SDB

anions in the intergallery to get a bigger basal spacing. So polymer could be easily intercalated into the benzoate-LDH or SDB-LDH to obtain polymer / LDHs nanocomposite.

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