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Synthesis and Characterization of Hydrotalcite at Different Mg/Al Molar Ratios

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Abstract

Synthesis and characterization of Mg-Al hydrotalcite have been studied. Synthesis of Mg-Al hydrotalcite was carried out using co-precipitation method at constant pH followed by hydrothermal treatment at 110°C for 12 hours. The effect of Mg/Al molar ratios 2:1 and 3:1 was investigated by using XRD, FTIR, and SEM-EDX. The results showed that these synthesized samples were identical to hydrotalcite materials based on X-ray diffractogram and FTIR spectra. The XRD patterns exhibit sharp reflection with high intensity with characteristic basal spacing at 11-23°, broad and asymmetric peaks at 34-66°. The FTIR spectra for the synthesized samples are in good agreement with slight shifting peaks at certain wavenumber characteristic of hydrotalcite. The morphologies of synthesized samples were shown by SEM and particles were formed as an accumulation of primary nanoparticles. Meanwhile chemical composition of the final products showed that Mg/Al ratio didn't meet the theoretical value because the reaction under optimum pH. In general it is showed that molar ratio affected on the structure and material properties of synthesized hydrotalcite.

Keywords: co-precipitation, hydrotalcite, molar ratio

1. Introduction

Hydrotalcite is also known as layered double hydroxide in which divalent cations within brucite-like layers are replaced by trivalent cations. Positive charge in the interlayer space between two brucite sheets is compensated by hydrated anions. Introducing different anions in the interlayer regions and variation of cations during synthesis is the way to modify the surface properties of the minerals. Due to the complex layered structure, wide range of chemical compositions, high ion exchange capacity, reactive surface and the interlayer space making hydrotalcite great focus of material.

The huge interest of hydrotalcite make a good potential in variety applications as ion exchangers, absorbents, CO₂ capture, carrier of bioactive molecules, catalyst, and catalyst support due to their high surface area, structural stability, and phase purity¹. However there are restricted of natural hydrotalcite application owing to the low crystalline, high impurity content, and unstable crystal structure.

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The study on synthesis of hydrotalcite has received considerable attention and up to date, several synthesis methods including co-precipitation², sol gel³, ion exchange⁴, and hydrothermal treatment⁵.

However the physicochemical properties of hydrotalcite are affected by several parameters during synthesis process. In this paper, we would like to study the effect of molar ratio on the structure, morphology, chemical composition, as well as elemental analysis of prepared hydrotalcites.

2. Material and Methods

2.1 Materials

Reagents used all were analytical grade. Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3) were used for synthesis of hydrotalcite in p.a. grade from Merck, Germany and deionized water.

2.2. Preparation of hydrotalcite

Mg/Al hydrotalcite with different molar ratio were prepared by co-precipitation following the procedure described by Zhao *et al.* (2003)⁶. The first solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in deionized water at Mg/Al molar ratio of 2:1 and 3:1. The second solution containing appropriate amounts of NaOH - Na_2CO_3 was added on a certain ratio so that the final $\text{Al}/\text{CO}_3^{2-}$ molar ratio equals to 1.33 and the pH of the final solution was $8,5 \pm 0,5$ with a speed rate 4 mL/minute under vigorous stirring. The mother solution was poured into a closed vessel with inner liner of teflon and aged at 110°C for 12 hours. The precipitate then was separated by filtering and washed with deionized water and dried 120°C overnight. The synthesized material was assigned as HT1 and HT2.

2.3. Characterization of hydrotalcite

Hydrotalcites were characterized by a number of methods including X-ray diffraction using Philips X-Pert Powder Diffractometer to identify structure identification, FTIR spectrophotometer 8201PC Shimadzu to analyze functional group, and SEM-EDX ZEISS EVO ® MA-10 to characterize morphology of material.

3. Results and Discussion

3.1. Synthesis of Mg/Al hydrotalcite

In this study, Mg/Al hydrotalcite were synthesized by co-precipitating an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a highly basic carbonate solution. Sodium hydroxide was added to magnesium and aluminum salt solution formed a white colloidal, whereas the adding of sodium hydroxide need to be quickly due to precipitation of $\text{Al}(\text{OH})_3$.

3.2. Powder X-Ray Diffraction Characterization

The influence of Mg/Al molar ratio on the phase composition of synthesized product has been investigated by X-ray diffraction. The XRD pattern of prepared hydrotalcite with different Mg/Al molar ratio was showed in Figure. 1.

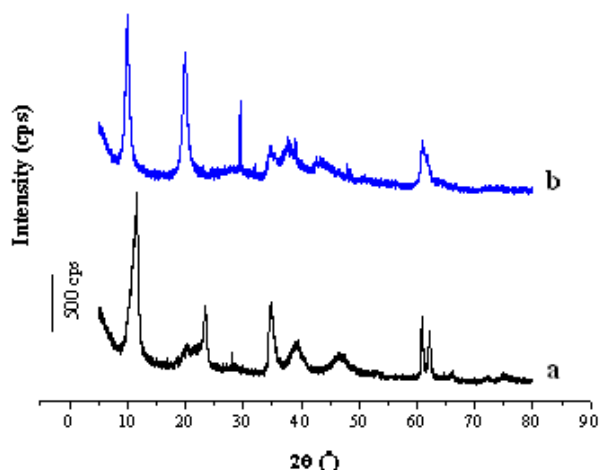


Fig. 1. The XRD pattern of hydrotalcite with molar ratio (a) 2:1 (b) 3:1

The XRD pattern showed typical peaks of layered structure consist of symmetric and sharp peaks with high intensity at low 2θ angle, whereas asymmetric and broad peaks at high 2θ angle. These diffraction patterns indicating good crystallinity of prepared hydrotalcite. Three intense reflections at 2θ values of 11.70° , 23.34° , 34.93° and 9.95° , 19.94° and 29.50° , respectively for molar ratio of Mg/Al 2:1 and 3:1. Based on diffractogram, there are slight shifts particularly on characteristic basal plane d_{003} related to existing anions in the interlayer regions. The difference of anions occurred during synthesis process due to the competition of both anions occupied in the interlayer region. It has also been proven from the diffraction peaks around 60° which correspond that the interlayer of prepared hydrotalcite respectively were carbonate anion and nitrate anion. This result was confirmed by the study of Halcom-Yanberry (2002)⁷. On prepared hydrotalcite HT1, carbonate as a balancing anions because their high affinity in the hydroxide layer over nitrate anions. Meanwhile on HT2, ratio of nitrate salt is much higher as reactant and bigger molecular size than carbonate made nitrate anions occupied in the interlayer region. The diffraction pattern of prepared hydrotalcite HT1 and HT2 has similarity results as reported by Klopogge et al. (2002)⁸, Zhao et al. (2003)⁶, Sharma et al. (2007)⁹ and Mokhtar et al. (2012)¹⁰.

3.3. Infrared Characterization of Hydrotalcite

The infrared spectra of prepared Mg/Al hydrotalcite were shown in Figure. 2 and Table 1 showed comparison of functional group hydrotalcite like material. As seen from Figure. 2, the spectra illustrated characteristic peaks of hydrotalcite like material. The broad and strong absorption band in the range of $3600\text{--}3200\text{ cm}^{-1}$ that is centered at 3400 cm^{-1} due to O-H stretching vibration of the surface and interlayer water molecules. The observed band around $1600\text{--}1700\text{ cm}^{-1}$ is O-H bending vibration of the interlayer water molecules. The resulted infrared spectra confirmed as previous research reported by Cochechi et al. (2010)¹¹, Setshedi et al. (2012) and Mokhtar et al. (2012)¹⁰.

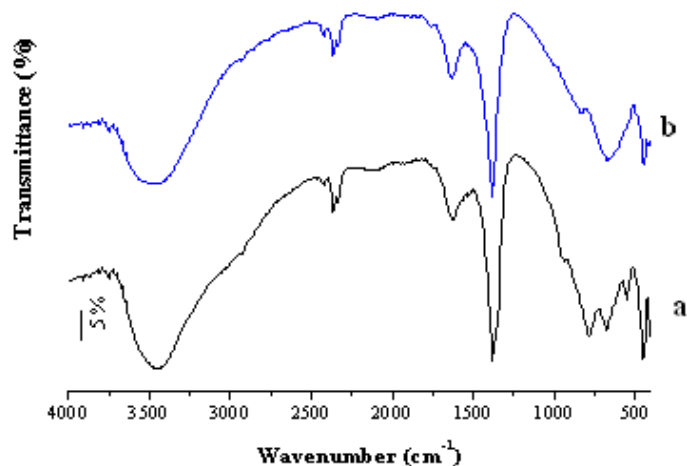


Fig. 2. Infrared Spectra of hydrotalcite with molar ratio (a) 2:1 (b) 3:1

Data in Table 1, showed that the influence of Mg/Al molar ratio exhibit shift of bands to the higher frequency ($3456\text{-}3464\text{ cm}^{-1}$) due to the Mg-OH stretching and also O-H bending ($1627\text{-}1635\text{ cm}^{-1}$) as reported by Sharma et al. (2007)⁹. Strong and sharp band of nitrate anion observed at 1381 cm^{-1} and weak band around 830 cm^{-1} .

Table 1. Comparison of Mg/Al functional group with different molar ratio

Characteristic band	Wave number (cm^{-1})	
	Mg/Al 2:1	Mg/Al 3:1
O-H stretching vibration	3456	3464
O-H bending vibration	1627	1635
$\text{CO}_3^{2-}/\text{NO}_3^-$ vibration	1381	1381
NO_3^- vibration	-	833
Al-OH translation	786	-
$\text{CO}_3^{2-}/\text{NO}_3^-$ vibration	671	678
Mg-O-Al vibration	455	447

3.4. Scanning Electron Microscopy Analysis

The SEM images of prepared hydrotalcite were recorded to observe the effect of molar ratio on the morphology of material. The micrographs at different Mg/Al molar ratio were shown in Figure 3.

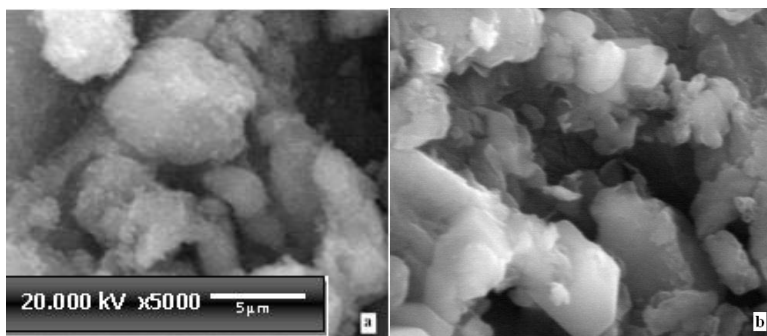


Fig. 3. SEM images of hydrotalcite with molar ratio (a) 2:1 (b) 3:1

The image demonstrates the crystal are very thin. The crystallinity of prepared hydrotalcite were well and also in line with characteristic reflections appeared from XRD pattern. The morphology of prepared hydrotalcite were formed as an accumulation of nano particles aggregates. The molar ratio composition of metal cations exhibit slight difference in morphology of prepared hydrotalcite. The final prepared hydrotalcite product is γ -AlOOH+Mg_xAl_{1-x}-NO₃/Mg_xAl_{1-x}-HCO₃ similar as previous reported by Wang et al. (2012)¹³.

3.5. Surface Elemental Analysis

The composition of the observed particles on the surface material was determined by EDX. The result of elemental analysis of prepared hydrotalcite at different Mg/Al molar ratio is listed in Table 2.

Table 2. Result of elemental analysis by using EDX

Element (% Wt)	Mg/Al 2:1	Mg/Al 3:1
O	54.89	51.42
Mg	24.87	15.53
Al	16.64	8.38
Na	-	11.50
C	-	4.26
N	-	8.91

It is noted that ratio of magnesium and aluminum content for both prepared hydrotalcite were still lower of the theoretical value. It is due to the pH during synthesis of hydrotalcite under optimum condition. The hydrotalcite samples were synthesized at pH 8.5, resulted the molar ratios respectively were 1.49 and 1.85 indicating that only small fraction of prepared hydrotalcite were formed. According to Wang et al. (2012)¹³, the molar ratio of prepared hydrotalcite with the synthesis pH 8-9 is around 1.5-2.3. It is also confirmed by FTIR that anions in the interlayer region around these pH synthesis are NO₃⁻, HCO₃⁻, and CO₃²⁻.

Conclusion

It was confirmed that Mg/Al hydrotalcite were successfully prepared using co-precipitation method. The chemical properties of prepared hydrotalcite was affected by molar composition and showed by diffraction pattern, infrared spectra, morphology structure, and elemental analysis as well.

Acknowledgements

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