

# Microwave Synthesis of Hydrotalcite by Urea Hydrolysis<sup>†</sup>

Zhiqiang Yang, Kwang-Min Choi, Nanzhe Jiang, and Sang-Eon Park\*

Laboratory of Nano-Green Catalysis and Nano Center for Fine Chemicals Fusion Technology, Department of Chemistry, Inha University, Incheon 402-751, Korea. \*E-mail: separk@inha.ac.kr

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Hydrotalcite, layered double hydroxides (LDH), with hexagonal morphology has been rapidly synthesized by microwave reaction within 1 hour by urea hydrolysis from homogeneous solution. Different synthesis parameters, Mg/Al molar ratio, microwave reaction temperature and microwave power were systematically investigated. Pure hydrotalcite phase was obtained for Mg/Al ratios of 2:1 and 3:1, and higher reaction temperature gave higher crystallinity. The hydrotalcite synthesized at 600W power shows the highest crystallinity and more homogeneous crystal size distribution. The hydrotalcite samples were characterized by powder X-ray diffraction (XRD), simultaneous thermogravimetric/differential thermal analysis (TG/DTA), Fourier Transform Infrared (FT-IR) and Scanning electron micrograph (SEM).

**Key Words :** Hydrotalcite, Urea hydrolysis, Microwave

## Introduction

Recently, a great deal of attention has been paid for the preparation of hydrotalcites and hydrotalcite-like materials, because of their potential applications in the adsorption and separation process, as anion exchangers, as catalysts or catalyst precursors, acid residue scavengers, flame retardants and stabilizers for polymers, as well as for applications in the medical field as antacids, antipeptides and stabilizers.<sup>1</sup> In general, hydrotalcites are also known as anionic clays or layered double hydroxides (LDH). These compounds are often denoted as  $[M(II)_{1-x}M(III)_x(OH)_2](A_{x/n}^{n-}) \cdot mH_2O$ . Wherein, M(II) represents the divalent cations such as  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$  or  $Cd^{2+}$ , M(III) denotes the trivalent cations like  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Ga^{3+}$  or  $Fe^{3+}$ ,  $A^{n-}$  is the compensating anions ( $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$ , organic anions), and m is the content of co-intercalated water.<sup>2</sup> The value of x is normally between 0.17 and 0.33 but there is no limitation. However, pure phases only exist for  $0.2 \leq x \leq 0.33$ . For x values not in this range compounds with different structures are obtained. The structure of LDH can be explained by considering structure of brucite  $Mg(OH)_2$ , which consists of  $Mg^{2+}$  ions coordinated octahedrally by hydroxyl groups. In an LDH, isomorphous replacement of a fraction of the  $Mg^{2+}$  ions with a trivalent cation such as  $Al^{3+}$  results a positive charge on the layers, which necessitates the presence of interlayer charge balancing anions. These  $M^{2+}/M^{3+}(OH)_6$  octahedral form two-dimensional sheets via edge sharing and may stack together by hydrogen bonding between the hydroxyl groups of adjacent sheets.<sup>3</sup>

In all the applications of hydrotalcite, surface and porosity properties of the materials are of great importance for technological performances.<sup>4</sup> Several solution synthetic methods have been developed for the synthesis of LDH, to tune their structural and textural properties, such as copre-

cipitation by alkaline solution at various or constant pH either in water or in water/organic solvent mixtures,<sup>5-7</sup> sol-gel route starting from metal alkoxides or acetylacetonate precursors in ethanol,<sup>8,9</sup> and coprecipitation by thermal hydrolysis of urea as a retardant precipitating agent.<sup>10,11</sup> This urea hydrolysis method allows the separation of nucleation and crystal growth steps during the formation of particles and favors materials with a higher crystallinity degree. Crystallite size and secondary particle morphology may then be tailored by slight modifications of the synthesis conditions, such as the precipitation rate or the nature of the reaction medium.<sup>1</sup>

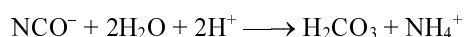
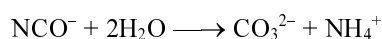
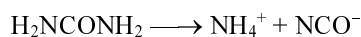
Microwave irradiation has been applied for the rapid synthesis of inorganic solids and organic synthetic reactions.<sup>12</sup> Application of a microwave technique to the conventional hydrothermal process is gaining importance, especially, in the synthesis of nanoporous materials.<sup>13</sup> Our group has used microwave method for the synthesis of nanoporous materials such as ZSM-5, TS-1, AlPO, MCM-41, SBA-15 and SBA-16.<sup>14-16</sup> It offers many advantages over the conventional hydrothermal synthesis, such as rapid and homogeneous heating throughout the reaction vessel, the possibility of selective heating of desired materials, homogeneous nucleation, and short crystallization time.<sup>17,18</sup> We also have found that this technique can provide an efficient way to control particle size distribution and macroscopic morphology of nanostructured materials.<sup>19</sup> More specifically, in the case of Mg/Al LDHs, Fetter *et al.*<sup>20,21</sup> have found that microwave irradiation of the coprecipitated gel allows well-crystallized and pure hydrotalcite-like phases to be obtained, and the ageing time can be reduced from 18-24 h to 2-10 min. Moreover, these authors have found that hydrotalcites obtained by this method present smaller crystallite sizes and higher specific surface areas than conventional samples, synthesized aging of the gels at 423 K for 24 h. However, the hydrotalcite samples prepared via this method showed poor morphology.

<sup>†</sup>This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

In this study, we combined the urea hydrolysis and microwave irradiations to rapid synthesize the well-crystallized hydrotalcite with good hexagonal morphology. To the best of our known, there has been no report on the microwave synthesis of hydrotalcite materials by urea hydrolysis. However, to control this synthesis procedure, the effect of the various parameters, which determine the synthesis, have to be studied. The understanding of those parameters should provide a control on the structural and morphological characteristics of these materials. Different synthesis parameters were investigated such as Mg/Al mole ratio, microwave power and reaction temperature.

### Experimental

**Hydrotalcite samples synthesis.** Mg/Al hydrotalcites with different Mg/Al molar ratios of 1.0, 2.0, 3.0 and 4.0 were prepared by microwave synthesis from homogeneous solutions of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and urea. The samples were designated as Mg1Al, Mg2Al, Mg3Al and Mg4Al, respectively. The numbers indicate the Mg/Al molar ratio. All the chemicals were from Aldrich with Analar grade and used as received. The required amounts of reactants *viz.*  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and urea were dissolved in 60 mL of deionized water and the solution was transferred to microwave autoclave (MARS, microwave accelerated reaction system). The concentration of ( $\text{Mg}^{2+} + \text{Al}^{3+}$ ) was kept at 0.1 mol/l and the molar ratio of urea/( $\text{Mg}^{2+} + \text{Al}^{3+}$ ) is 2. The solution was treated at 120 °C for 1 hour by microwave irradiation and the power was 300 W. At 120 °C urea will hydrolysis to provide the alkaline condition and release carbonate anion. Urea hydrolysis procedure is listed as follows:



After synthesis, the precipitate was filtered and washed with deionized water to get neutral pH. The white filtered solid was dried overnight in oven at 100 °C. The sample Mg/Al = 2 was microwave treated at 120 °C with powers of 300, 600 and 1200 W for 1 h to investigate the microwave power effect. It was also treated at different temperatures (100 °C, 120 °C, 140 °C, and 160 °C) to investigate the effect of temperature.

**Characterization.** Powder X-ray diffraction (XRD) patterns of the samples were obtained using Rigaku Mini Flex diffractometer having Cu K $\alpha$  radiation (40 kV, 30 mA). The samples were scanned for  $2\theta$  values ranging from 5 to 70°. TG-DTA thermograms were recorded on Perkin-Elmer TGA 7 thermal analysers in the temperature range from 30 to 800 °C at a heating rate of 10 °C/min in nitrogen atmosphere. Scanning electron micrograph (SEM) images were obtained using Hitachi Scanning Electron Microscope (Model S-4200).

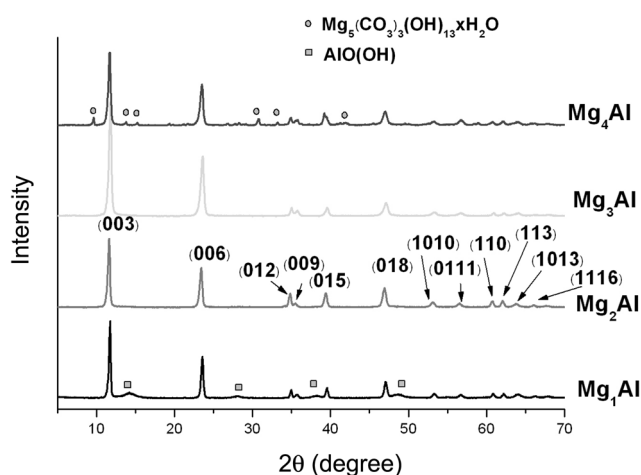
FT-IR spectra were recorded on Bio-RAD FTS 135 C

spectrometer in the wavelength range of 400-4000  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution.

### Results and Discussion

**Mg/Al molar ratio.** Figure 1 shows the XRD patterns of microwave synthesized hydrotalcite samples with different Mg/Al molar ratio. The sharp peak (003) indicates the formation of highly crystalline materials. Indexing of the diffraction peaks was done using standard JCPDS file. The reflections were indexed in a hexagonal lattice with an R3m rhombohedral symmetry. The parameter  $a$  of LDH corresponding to the cation-cation distance within the brucite-like layer and can be calculated by  $a = 2 \times d_{110}$ . On the other hand, the  $c$  parameter is related to the thickness of the brucite-like layer and the interlayer distance and can be obtained from  $c = 3 \times d_{003}$ . The results are shown in table 1. For Mg/Al ratio of 1:1, the Mg-Al Hydrotalcite(HT) formed a mixture of HT-like phase and boehmite ( $\text{AlOOH}$ ). Pure hydrotalcite phase was obtained for Mg/Al ratios of 2:1 and 3:1 while a mixture of a HT-like phase and  $\text{Mg}_5(\text{CO}_3)_3(\text{OH})_{13} \cdot x\text{H}_2\text{O}$  (determined by JCPDS file) was obtained for Mg/Al ratio of 4:1. Excess Al and Mg present in the experimental solution may undergo side reactions in presence of excess urea, leading to the formation of impurities other than the hydrotalcites.

**Microwave power effect.** To study the microwave power effect the samples with a ratio of Mg/Al = 2 were chosen.

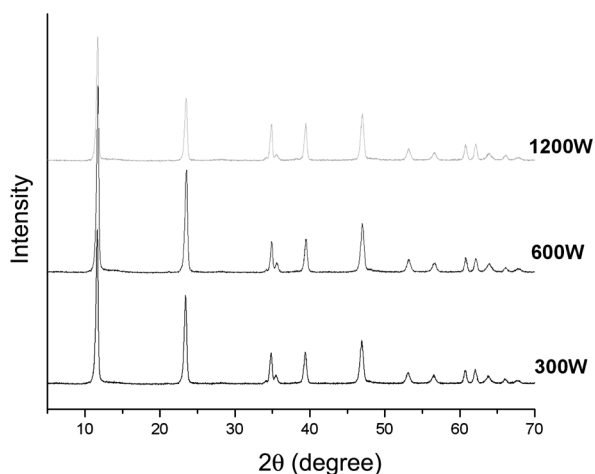


**Figure 1.** Powder XRD patterns of microwave synthesized hydrotalcites with different Mg/Al molar ratio.

**Table 1.** Lattice parameters and crystallite phase of microwave synthesized hydrotalcite samples by urea hydrolysis

Sample	x	c (Å)	a (Å)	Crystallite phase
Mg <sub>1</sub> Al	0.50	22.557	3.044	LDH, AlOOH
Mg <sub>2</sub> Al	0.33	22.788	3.052	LDH
Mg <sub>3</sub> Al	0.25	22.482	3.048	LDH
Mg <sub>4</sub> Al	0.20	22.635	3.046	LDH, Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>3</sub> (OH) <sub>13</sub> ·xH <sub>2</sub> O

$x$  is the molar ratio of  $\text{Al}/[\text{Al}+\text{Mg}]$ ,  $c$  parameter is related to the thickness of the brucite-like layer and the interlayer distance,  $a$  parameter is corresponding to the cation-cation distance within the brucite-like layer.

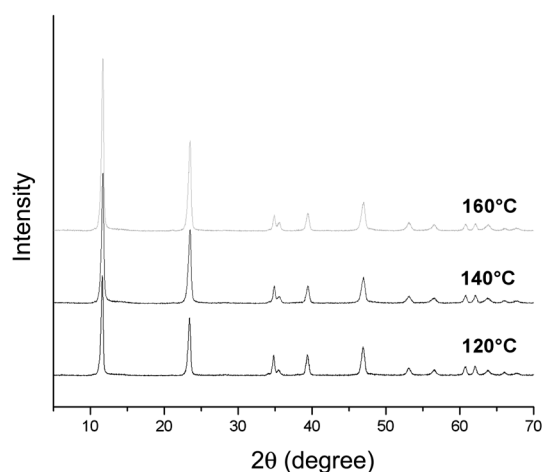


**Figure 2.** Powder XRD patterns of microwave synthesized hydrotalcites under different power.

The hydrotalcite samples were synthesized at 120 °C with microwave powers of 300, 600 and 1200 W for 1 h. Powder X-ray diffraction patterns presented in Figure 2 show that well crystallized hydrotalcite-like compounds are obtained, no other compounds are identified. As the interplanar distance 003 is *ca.* 7.596 Å, the intercalated anions are expected to be carbonate. Because for the nitrate intercalated hydrotalcite, the interplanar distance 003 is supposed to be 9.03 Å. So from XRD result we can know that the intercalated anion is not nitrate but carbonate. The hydrotalcite synthesized at 600 W power shows the highest crystallinity. The particle morphology obtained by SEM is compared in Figure 3. All samples show the good hexagonal morphologies. As the microwave irradiation power increase the particle size increase. In the 1200 W irradiation sample, large crystal size ( $> 3 \mu\text{m}$ ) is present. If the power is 600 W, the crystal size distribution and the shape become more homogeneous.

**Temperature effect.** The XRD patterns of the samples prepared at different temperatures (120, 140, and 160 °C) for 1 hour under 300 W power are shown in Figure 4. All the samples exhibit well-crystallized hydrotalcites structures with intense and well-defined peaks. With the increase of synthesis temperature the crystallinities of microwave synthesized samples increase obviously.

**TG-DTA analysis.** Figure 5 shows the TG-DTA curves of microwave synthesized hydrotalcites (Mg2Al and Mg3Al).

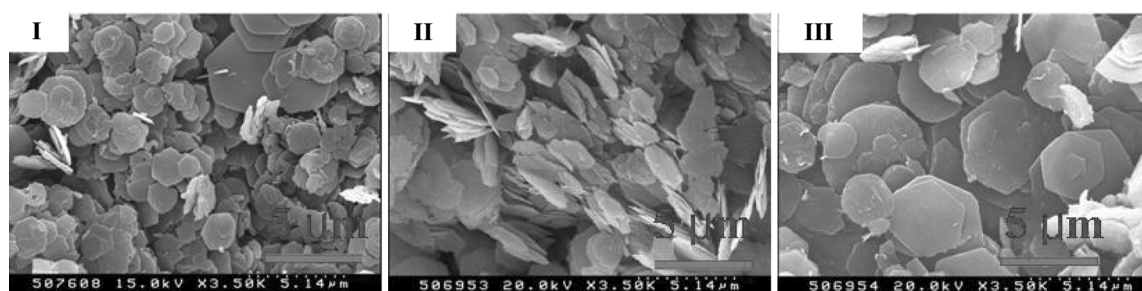


**Figure 4.** Powder XRD patterns of microwave synthesized hydrotalcites under different reaction temperature.

The TG-DTA curves of both samples may be divided into two well-differentiated main regions. In the first one, ranging from 80 to 250 °C there is an endothermic peak related to the dehydration of the sample. The second region, ranging from 260 to 600 °C corresponds to the weight loss due to the dehydroxylation and de-carbonation reactions.<sup>11</sup> From XRD results we can know that there is no nitrate anion in the interlayer space. Only  $\text{CO}_3^{2-}$ -LDH was obtained after microwave synthesis. So there is no de-nitration reactions.

**FT-IR spectra.** Figure 6 displays the infrared spectra of the Mg1Al, Mg2Al, Mg3Al, and Mg4Al hydrotalcites in the region 400-4000  $\text{cm}^{-1}$ . The high frequency region shows a broad peak at about 3450  $\text{cm}^{-1}$  for all samples. This broad peak due to OH stretching of hydrogen-bonded hydroxyl groups and  $\text{H}_2\text{O}$  are skewed on the right-hand side and have a net shoulder at 3060  $\text{cm}^{-1}$  due to hydrogen bonding between  $\text{H}_2\text{O}$  and interlayer carbonate anions.<sup>22</sup>

In the lower frequencies, the peak at 1637  $\text{cm}^{-1}$  in all the samples can be attributed to the bending mode of interlayer water. The main absorption band of the carbonate anions was observed at 1370  $\text{cm}^{-1}$  ( $\nu_3$ ). With decrease in concentration of Al in the hydrotalcites, this peak splits into double bands indicating a lowering of carbonate anion symmetry. This type of double band appearance for carbonate ion is a topic of considerable interest. It was reported that there exists some kind of interactions between the carbonate ions



**Figure 3.** SEM images of microwave synthesized hydrotalcites under different power (I: 300W, II: 600W, III: 1200W)

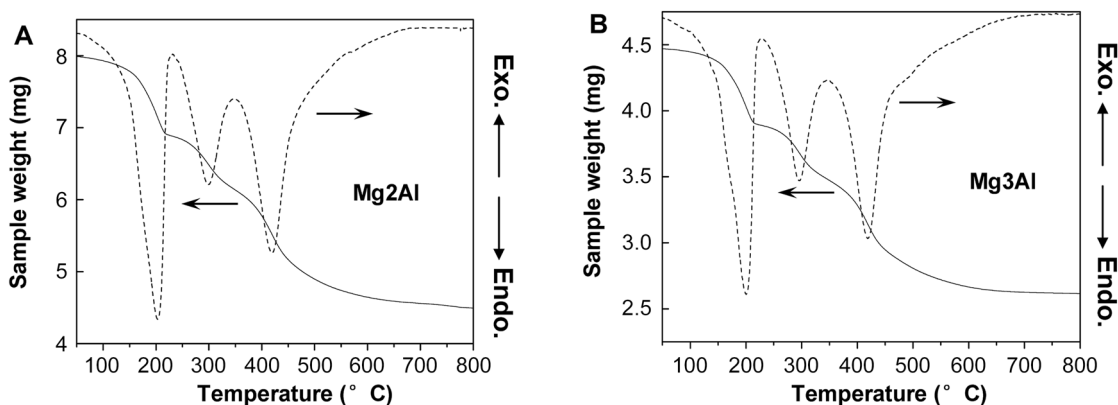


Figure 5. TG-DTA curves of microwave synthesized hydrotalcites (A. Mg<sub>2</sub>Al, B. Mg<sub>3</sub>Al).

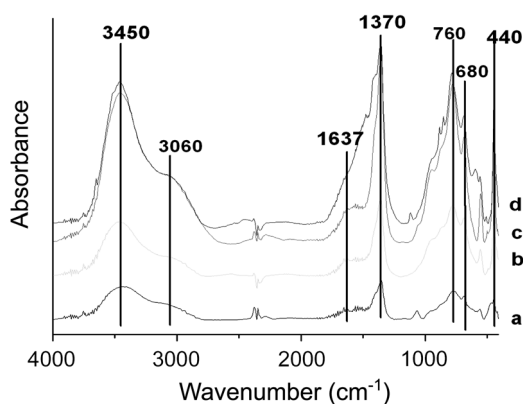


Figure 6. FT-IR spectra of microwave synthesized hydrotalcites under with different Mg/Al molar ratio (a: Mg<sub>1</sub>Al, b: Mg<sub>2</sub>Al, c: Mg<sub>3</sub>Al, d: Mg<sub>4</sub>Al).

and water molecules in the interlayer or cations from the layers causing a decrease in site symmetry.<sup>23</sup> Disorder in the interlayer spacing has also been attributed to this observation. It was also proposed that the site group splitting would result in the activation of the  $\nu_1$  vibrational mode at about  $1050\text{ cm}^{-1}$ .<sup>24</sup> This was found to be true for Mg<sub>1</sub>Al, Mg<sub>4</sub>Al but not for Mg<sub>2</sub>Al and Mg<sub>3</sub>Al. The shift of  $\nu_1$  mode towards higher wave number has been attributed to the decrease of trivalent cation in the brucite layer.<sup>25</sup> The absence of a  $\nu_1$  mode peak for Mg<sub>2</sub>Al and Mg<sub>3</sub>Al shows that the above assumption is justified. At the lower end of IR spectrum, for a typical hydrotalcite one expects two bands around  $680$  and  $880\text{ cm}^{-1}$  characteristic of  $\nu_4$  and  $\nu_2$  modes of the interlayer carbonate group and another set of two bands around  $553$  and  $760\text{ cm}^{-1}$  characteristic of translation modes of the hydroxyl groups influenced by the trivalent aluminium.<sup>23</sup> The divalent metal content in the hydrotalcite structure influences the exact position of these bands. The  $\nu_4$  mode of carbonate ion appears as a shoulder at  $680\text{ cm}^{-1}$  in all the samples whereas the  $\nu_2$  mode appears as a shoulder at  $880\text{ cm}^{-1}$  for all the samples. The peak at  $440\text{ cm}^{-1}$  ( $\delta\text{O-M-O}$ ) characteristic of lattice vibrations of [Mg, Al] octahedral sheets evidences the crystallization of the LDH phase.<sup>1</sup> The observed discrepancies were consistent with our XRD results.

## Conclusion

Hydrotalcite with hexagonal morphology was successfully and rapidly synthesized by microwave reaction from homogeneous system. The structures of the hydrotalcite samples were identified by powder X-ray diffraction and FT-IR spectra. Pure hydrotalcite phase was obtained for Mg/Al molar ratio of 2:1 and 3:1. The hydrotalcite synthesized at 600W power shows the highest crystallinity and more homogeneous crystal size distribution. These samples which were synthesized at different temperatures reveal that as the increase of microwave reaction temperature the crystallinities of hydrotalcites increase.

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