UNIVERSITI PUTRA MALAYSIA

MICROWAVE-ASSISTED SYNTHESIS OF LAYERED DOUBLE HYDROXIDES AND THEIR NANOCOMPOSITES

OW WEE SHING TAT

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By

OW WEE SHING TAT

Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Science and Environmental Studies Universiti Putra Malaysia

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LIST OF ABBREVIATIONS

AQ26	Anthraquinone-2,6-disulfonate anion
ASAP	Analysis Surface Area and Porosity
BET	Brenauer, Emmett and Teller
BJH	Barrett, Johner and Halenda
CHNS	Carbon, Hydrogen, Nitrogen Analysis
D	Brucite-like layer thickness
DCIE	Different Colour Index Evaluation
D^{P}_{avg}	Average pore diameter
FTIR	Fourier Transform Infra-red
HT	Hydrotalcite
ICP-AES	Inductived Couple Plasma – Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
LDH	Layered Double Hydroxide
M(II)	Divalent metal ions, Mg^{2+} or Zn^{2+}
P_r	Relative pressure
PXRD	Powder X-ray Diffraction
R_{dis}	Ratio of Mg^{2+} to Al^{3+} discharged, R = Mg/Al
R_{form}	Ratio of Mg^{2+} to Al^{3+} formed
r^c	Core radius
r^p	Pore radius
SEM	Scanning Electron Microscopy / Micrograph
t	Adsorbate layer thickness
TGA	Termogravimetric Analysis
a	Superlattice cell parameter for hexagonal
x	Fraction of Al^{3+} in brucite-like layer, $x = Al/(Al+Mg)$
α	Slant angle
β	True half-maximum breadth
θ	X-ray diffraction angle
δA^p	Incremental surface area
δv^p	Incremental pore volume
η	Crystal strain

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree Master of Science

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By

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August 1999

Chairman: **Associate Professor Mohd. Zobir Hussein, Ph.D.**

Faculty: **Science and Environmental Studies**

A series of hydrotalcite (HT) compounds of the type $[Mg_{1-x}Al_x(OH)_2][CO_3]_{x/2}\cdot mH_2O$ had been synthesised using conventional co-precipitation method with R_{dis} = Mg/Al = 1 to 10 in order to establish the relationship between composition and the basic properties. It was found that pure HT compounds were obtained in the range of R_{dis} = 2 to 4. The materials were also synthesised by microwave-assisted method using a home cooking microwave oven at various ageing times, from 0.5 to 10.0 minutes. The discharged ratio of R_{dis} = 3, 4, and 6 were chosen in this study. The resulting synthetic materials afford well-crystallised hydrotalcite even at a very short microwave exposure time of about 6.0 minutes as compared with the conventional method that took about 18hrs. However, the conventional method gave good crystallinity. On the other hand, the microwave-assisted method gave better pore size distribution as compared to the conventional method. Better crystallinity was observed as the exposure time increased for all R_{dis}. Structural characterisations were done by powder X-ray diffraction (PXRD). The grain sizes and crystal strain of the materials using PXRD were calculated.

Modification of hydrotalcite had also been done by replacing its anions with anthraquinone-2,6-disulfanate ions (AQ26), which were present in the interlayer of brucite-like ($[Mg_{1-x}Al_x(OH)_2]^{x+}$ and $[Zn_{1-x}Al_x(OH)_2]^{x+}$). Layered nanocomposite materials were prepared by using direct synthesis method which involved adding NaOH(aq) into a mixed of

$M(II)(NO_3)_2$, $Al_2(NO_3)_3$ and $Na_2(AQ26)$ aqueous solutions at pH7.50 ± 0.05 with different M(II):Al:AQ26 ratios of 4:1:0.00, 4:1:0.10, 4:1:0.25, 4:1:0.50 and 4:1:1.00. The expansion of the galleries height from 8.9 Å to 19.1 Å had been observed in X-ray diffraction data that indicating that the intercalation of the AQ26 anion replacing the nitrate anion in the interlayer of the layered double hydroxide had occurred. This conclusion has been supported by the FTIR spectrum that shows the co-existence of NO_3^- anion that gave sharp absorption band at 1380 cm^{-1} (ν[N–O]) and broad peak at 1200 cm^{-1} for asym ν[S–O] for AQ26. Only M(II):Al:AQ26 ratio of 4:1:0.25 and above gave pure AQ26 intercalated LDH with no presence of NO_3^- anion in the interlayer. These ratios showed that AQ26 anion was perpendicular to the metal hydroxide layer (α = 90°). Three types of AQ26 species (i.e. $AQ26^{2-}$, $AQ26^-$ and neutral) had been suspected to exist in the interlayer.

In the microwave-assisted method, the ratio of 4:1:0.25 for Mg–Al–AQ26 system and 4:1:1.00 for Zn–Al–AQ26 system had been studied because of their good crystallinity. However microwave-assisted method, the Zn–Al–AQ26 system gave negative effect with the formation of ZnO. The formation of ZnO would increase with increasing exposure time. The Mg–Al–AQ26 system of other hand, gave poor crystal formation. The BET surface area increased from 92.8 to 112.4 m^2/g, showing an increase of 21% by using microwave-assisted method for Mg–Al–AQ26 system. The ratio of mother solution changed from 4:1:0.25 to 4:2.90:2.35 (conventional method) and 4:3.41:1.50 (microwave-assisted method) for Mg–Al–AQ26 system while changes from 4:1:1.00 to 4:1.02:1.67 and 4:0.97:1.63 for conventional and microwave-assisted methods respectively were observed for Zn–Al–AQ26 system.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS SEBATIAN HYDROKSIDA BERLAPIS GANDA DAN NANOKOMPOSITNYA DENGAN BANTUAN GELOMBANG MIKRO

Oleh

OW WEE SHING TAT

Ogos 1999

Pengerusi: **Profesor Madya Mohd. Zobir Hussein, Ph.D.**

Fakulti: **Sains dan Pengajian Alam Sekitar**

Satu siri R_{dis} = 1 hingga 10 hydrotalsit (HT) jenis $[Mg_{1-x}Al_x(OH)_2][CO_3]_{x/2}.mH_2O$ telah disintesiskan dengan menggunakan kaedah konvensyenal ko-pemendakan untuk mendapatkan perkaitan antara komposisi dan sifat-sifat umum. Didapati pada julat R_{dis} = 2 hingga 4 fasa hidrotalsit tulen telah dihasilkan. Kaedah sintesis bantuan gelombang mikro dengan mengunakan ketuhar gelombang mikro biasa pada masa pendedahan dari 0 5 ke 10 0 minit dengan R_{dis} = 3, 4 dan 6 dipilih untuk kajian ini. Keputusan menunjukkan pembentukan hablur yang baik berlaku pada masa yang singkat lebih kurang 6.0 minit dengan mengunakan kaedah bantuan gelombang mikro berbanding dengan kaedah konvensyenal yang mengambil masa lebih kurang 18jam. Akan tetapi kaedah konvensyenal masih memberikan pembentukan hablur terbaik. Walaubagaimana pun, kaedah bantuan gelombang mikro memberikan taburan saiz liang yang lebih sekata jika dibanding dengan kaedah konvensyenal. Ia menberikan pembentukan hablur yang baik pada masa pendedahan yang lama untuk semua R_{dis} Kajian sifat struktur sebatian mengunakan kaedah pembelauan sinar-X dalam keadaan serbuk dijalankan. Saiz dan ketegangan hablur dikirakan daripada data pembelauan sinaran-X.

Modifikasi pada hidrotalsit dilakukan dengan mengantikan amon inter-lapisan seakan brusit ($[Mg_{1-x}Al_x(OH)_2]$ dan $[Zn_{1-x}Al_x(OH)_2]$) dengan ion antrakuinon-2,6-disulfonik Sebatian nanokomposit berlapis disintesiskan dengan kaedah pemendakan terus di mana

larutan NaOH(ak) ditambahkan kedalam larutan campuran garam $M(II)(NO_3)_2$, $Al_2(NO_3)_2$ dan Na_2(AQ26) pada pH7.50 ± 0.05 dengan nisbah M(II):Al:AQ26 pada 4:1.0.00, 4:1:0.10, 4·1:025, 4:1.0.50 dan 4:1:1.00. Pengembangan jarak inter-lapisan daripada 8.9 Å kepada 19.1 Å dalam data pembelauan sinaran-X menunjukkan interkalasi AQ26 menggantikan anion nitrat pada inter-lapisan dalam hidroksida berlapis ganda. Kenyataan ini disokong oleh data Infra-merah yang menunjukkan kewujudan bersekali anion NO_3^- yang memberikan serapan yang tajam pada 1380 cm^{-1} (ν[N–O]) dan serapan lebar pada 1200 cm^{-1} bagi antisym ν[S–O] untuk AQ26. Hanya nisbah 4:1:0.25 atau lebih bagi M(II):Al:AQ26 memberikan interkalasi AQ26 tulen tanpa kewujudan anion NO_3^- pada inter-lapisan. Nisbah ini menujukkan anion AQ26 berkedudukan tegak terhadap lapisan logam hidroksida (α = 90°). Tiga jenis spesis AQ26 (iaitu $AQ26^{2-}$, $AQ26^-$ dan neutral) disyaki wujud dalam inter-lapisan.

Dalam kaedah bantuan gelombang mikro, nisbah 4:1:0.25 bagi sistem Mg–Al–AQ26 dan 4:1:1.00 bagi sistem Zn–Al–AQ26 digunakan dalam kajian kerana pembentukan hablur yang baik. Walaubagaimana pun, kaedah bantuan gelombang mikro bagi sistem Zn–Al–AQ26 menunjukkan kesan negatif dengan pembentukan ZnO. Pembentukan ZnO bertambah bila masa pendedahan bertambah. Disebaliknya, sistem Mg–Al–AQ26 memberi pembentukan hablur yang kurang baik. Luas permukaan BET bertambah sebanyak 21% daripada 92.8 kepada 112 m^2/g dengan menggunakan kaedah bantuan gelombang mikro bagi sistem Mg–Al–AQ26. Nisbah larutan induk berubah daripada 4.1:0.25 kepada 4:2.90:2.35 (kaedah konvensyenal) dan 4:3.99:1.10 (kaedah bantuan gelombang mikro) bagi sistem Mg–Al–AQ26, manakala bagi sistem Zn–Al–AQ26 perubahan dari 4:1:1.00 kepada 4:1.02:1.67 dan 4:0.97:1.63.

CHAPTER I

INTRODUCTION

History of Hydrotalcite

Hydrotalcite was first discovered in Sweden around 1842 as natural mineral clay that can be easily crushed into a white powder. Later, Professor E. Manasse [1] of mineralogy at University of Florence, Italy, found that this mineral is made up of magnesium, aluminium, hydroxides, carbonate and water molecules. Its exact formula is $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. Due to inadequate crystallographic data led to an uncertainty of the hydrotalcite structure at that time. In 1942, Feitknecht [2] proposed that the structure of these clays consists of a double sheet structure as follows:

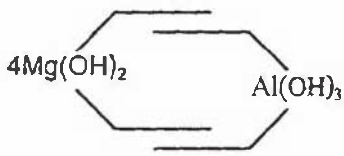


Figure 1.1: Structure of hydrotalcite as suggested by Feitknecht in 1942 [2].

Feitknecht named it "*doppelschichtstrukturen*" which mean "double sheet structure", in which the magnesium hydroxides and aluminium hydroxides are on different sheets. From an X-ray investigation by Aminoff and Broome [3], it was shown that hydrotalcite had two polytypes, namely rombohedral and hexagonal. The actual structure of hydrotalcite has been determined by Allmann in 1968 [4], it was composed of positively charged brucite-like ($Mg(OH)_2$) layers of divalent (Mg^{2+}) and trivalent (Al^{3+}) metal hydroxides ($[Mg_{1-x}Al_x(OH)_2]^{x+}$) located in the same layer. Excess positive charge was compensated or stabilised by carbonate anions that are negatively charged with water molecules presented in the interstitial position. The rombohedral and hexagonal structures are known as *pyroaurite* and *sjögrenite* [5], respectively.

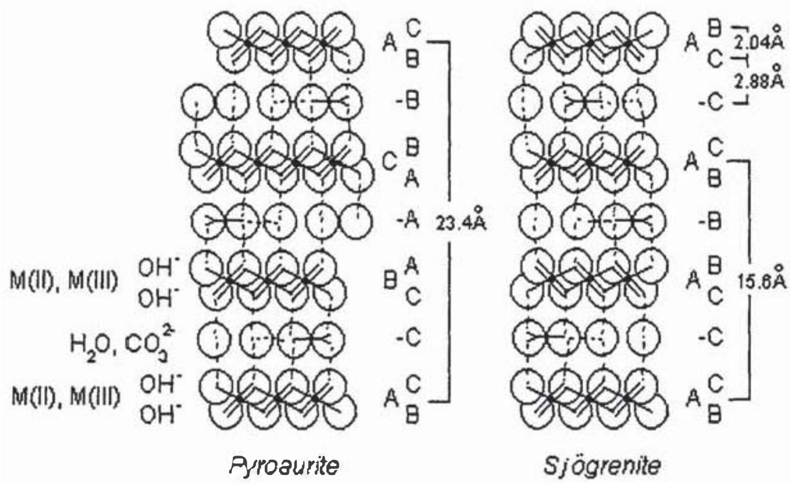


Figure 1.2: Stacking sequences of rombohedral symmetry (*pyroaurite*) and hexagonal symmetry (*sjögrenite*) [5].

Other natural clay minerals that have shown the same structure as hydrotalcite (they so-called hydrotalcite-like compounds) have also been found such as iowaite (Mg^{2+}–Fe^{3+}–Cl^-), meixmente (Mg^{2+}–Al^{3+}–OH^-), carrboydite (Ni^{2+}–Al^{3+}–SO_4^{2-}), motukorecite (Mg^{2+}–Al^{3+}–SO_4^{2-}), honessite (Ni^{2+}–Fe^{3+}–SO_4^{2-}) and woodwardite (Cu^{2+}–Al^{3+}–SO_4^{2-}) [6]. The first paper in open literature referring to hydrotalcite-like compounds appeared in 1971, written by Miyata *et al.* [7] dealing with basic catalysis. Hydrotalcite was synthesised in the laboratory for the first time by Allmann [8] in 1968 by using $MgCl_2$ and $AlCl_3$ mixed solution titrated with NaOH and Na_2CO_3 mixed solution. Later it Powder X-ray Diffraction (PXRD) data patterns were recorded in JCPDS (Joint Committee on Powder Diffraction Standards) pattern number 22-700 (Appendix B).

Brucite Structure

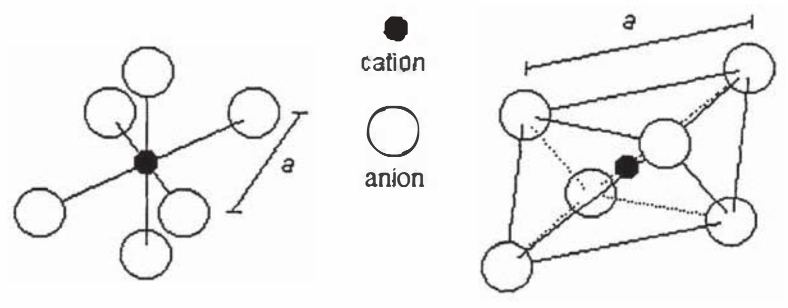
The hydrotalcite structure ($[Mg_{1-x}Al_x(OH)_2]^{x+}[CO_3^{2-}]_{x/2}.mH_2O$) is resembled of that brucite-like structure ($Mg(OH)_2$). The only difference is that hydrotalcite consists of a brucite-like layer structure that has anions and water molecules between the layers. In ionic (ceramic) solid, the packing of the ions is detennined primarily by the following factors:

1. The relative size of the ions in the ionic solid, as shown in the table below:

Table 1.1: Limiting Radius for Different Coordination Numbers [9].

Coordination number	Geometry	Limiting radius ratio
		0.225
4	Tetrahedral	
		0.414
6	Octahedral	
		0.732
8	Cubic	
		1.00

2. The need to balance electrostatic charges to maintain electrical neutrality in the ionic solid.



(a) NaCl (b) $Mg(OH)_2$

Figure 1.3: Octahedron showing octahedral coordination of six anions around a central cation for (a) NaCl and (b) $Mg(OH)_2$ where '*a*' is hexagonal cell parameter.

The relative size for $r_{Mg(+2)}/r_{OH(-1)}$ = 0.86 Å/1.23 Å = 0.70, and at this condition Mg^{2+} is suitable to fill in the octahedral sites where '*a*' was regarded as hexagonal superlattice parameter [10], with a structure similar to NaCl (Figure 1.3) showing octahedral coordination of Cl^- anions around a central Na^+ cation where the $r_{Na(+1)}/r_{Cl(-1)}$ = 1.16 Å /1.67 Å = 0.70, which is greater than 0.414 but less than 0.732.

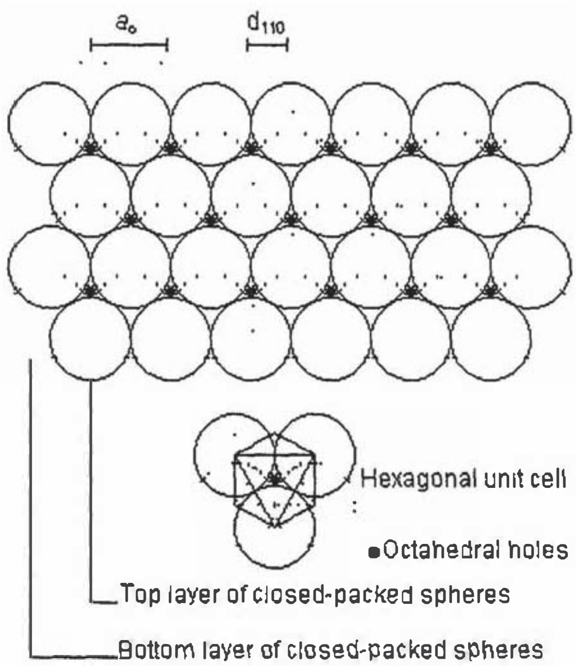


Figure 1.4: Top view for brucite closed-packed structure where one layer of octahedral holes had been fully filled by metal ions (•) and the other layer is empty.

Mg^{2+} ion has two positive charges while OH^- ion has one negative charge. Therefore to stabilise the charge, one Mg^{2+} ion must be accompanied by two OH^- ions. In this case the coordination ratio of cation to anion coordination has to be 1:2. When half of the octahedral holes have been filled by cations, the coordination ratio will be 6:3. Figure 1.4 shows what the close-packed structure looks like.

Here, six oxygen atoms in the form of hydroxides octahedrally surround the magnesium cation, resulting in octahedral shared edges to form an infinite sheet. These sheets are stacked on top of each other and are held together by hydrogen bonds, as shown in Figure 1.5.

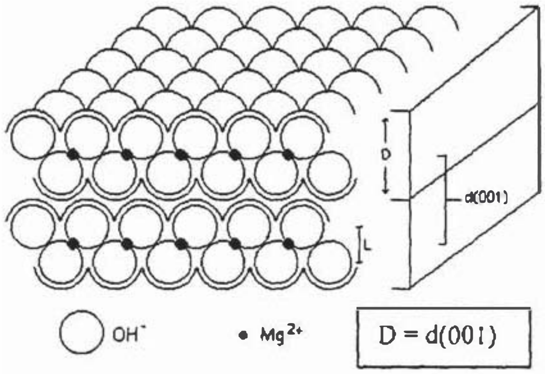


Figure 1.5: Side view for brucite structure where one layer of octahedral holes had been fully filled by metal ions and the other layer is empty.

If 'a' is parameter of the hexagonal unit cell corresponding to the distance between two metal ions in an adjacent octahedral site or hydroxide ions, the thickness of the brucite sheet can be calculated. Where distance between top and bottom hydroxide sheets is 'L'.

$$a = \sqrt{2}\ r_{(M\text{-}OH)} \qquad [1\text{-}1]$$

$$L = (2/\sqrt{3})r_{(M\text{-}OH)} \qquad [1\text{-}2]$$

where $r_{(M\text{-}OH)}$ is the metal ion–hydroxide ion distance,

$$r_{(M\text{-}OH)} = r_{Mg(+2)} + r_{OH(-1)} \qquad [1\text{-}3]$$

Therefore, the layer thickness will be 'D' (Figures 1.7 and 1.8 can be referred to verification of these equations).

$$\begin{aligned} D &= L + 2r_{OH(-1)} \\ &= (2/\sqrt{3})r_{(M\text{-}OH)} + 2r_{OH(-1)} \end{aligned} \qquad [1\text{-}4]$$