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# THERMAL BEHAVIOUR OF LAYERED ORGANIC-INORGANIC NANOCOMPOSITE: BETA-NAPHTOXYACETIC ACID INTERCALATED INTO ZINC-ALUMINIUM LAYERED DOUBLE HYDROXIDE

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## ABSTRACT

An organic-inorganic nanohybrid material of zinc-aluminium-layered double hydroxide containing beta-naphtoxyacetic acid (BNOA) as the interlamella anion was synthesized using co-prepitation method. BNOA ion was successfully intercalated into Zn-Al-layered double hydroxide by expanding the interlayer spacing from 8.93 Å to 19.46 Å based on the PXRD diffractogram of the nanocomposite. Thermal composition (calcination) of the nanocomposite (Zn-Al-BNOA) was studied by heating the samples at 100 – 800 °C under atmospheric condition. The layered structure of the nanocomposite collapsed when the sample was heated at 350 °C and the formation of ZnO phase was observed at 400 °C and higher. Further characterization for the FTIR and organic-inorganic composition and SEM, were also carried out.

*Keywords: Zn-Al-BNOA; nanocomposite; microstructure;*

## INTRODUCTION

Nanoscale materials are one of the most dynamic and fastest growing areas of research in the field of science, engineering and medicine. Layered double hydroxides (LDHs) are one of the nanostructured materials. LDH structure consists of brucite-like $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{m-}{}_{x/m}].nH_2O$ sheets where charge is compensated by anions present within interlayer galleries. One of the most important properties of LDHs is that it has flexibility to incorporate various anions into the interlayer. This unique property of LDH has attracted considerable attention in line to create new compound, which is called nanocomposite through intercalation process. It is useful in a wide range of applications such as in catalysis [1, 2], anion exchange [3], antacid activities [4] and herbicides [5].

The physical and chemical properties of the LDHs depend on the nature of $M^{2+}$ and $M^{3+}$, interlayer anion and the values of x of (responsible for the charge in the layers) [6]. These materials can interact with anions both by interlayer space and external surface. Nevertheless, LDHs have been used to prepare nanoscale organic/inorganic hybrid materials to develop new functional materials such as biological, environmental, agricultural and so on. The main advantage of layered double hydroxide is that its particle size and aspect ratio can be controlled by changing the reaction condition [7]. Because of their highly tunable properties, LDHs are consider as new emerging class of the most favorable layered crystals for the preparation of multifunctional nanocomposites.

Thermal treatment of a nonocomposite was found useful for the orientation of anions in LDH lamella [8]. For example, $SO_3$-β-CD(6)/LDH has been obtained by the intercalation of hexasulfated β-cyclodextrin into magnesium layered double hydroxide at 65 °C. However, as the calcined temperature increased higher than 350 °C, resulted in the collapsed of the lamella due to thermal decomposition of the anion [9]. Other example is thermal transformation of dye-interleaved zinc-aluminium-layered double hydroxide which the basal spacing of the nanocomposite decreased and completely collapsed at 350 °C and also the formation of ZnO phase was observed at 400 °C [10]. In our previous study, β-naphtoxyacetic acid (BNOA) anion has been successdully intercalated into the layered Zn-Al-LDH by spontaneous self-assembly of the organic and inorganic molecules from aqueous solution. Here we report our work on the thermal behaviour of Zn-Al-BNOA nanocomposite (ZAB) and its property transformation on heat treatment. This is important to establish the maximum temperature at which layered material can retain its structure and after which the nanolayered structure collapsed.

## EXPERIMENTAL DETAILS

The synthesis of the intercalated compound, ZAB was done by spontaneous self-assembly method. Mother liquor containing $Zn^{2+}$ and $Al^{3+}$ cations with Zn/Al ratio 2:1 and BNOA anion was prepared and the pH was adjusted to about pH 7. The concentration of BNOA anion used was 0.08 M and the reaction was carried out with stirring under nitrogen atmosphere. The solution was aged for 18 hours in an oil-bath shaker at 70 °C. The resulting precipitate was centrifuged, thoroughly washed and dried in an oven at 70 °C for 3 days and kept in a sample for further use and characterizations.

Heat-treated samples of ZAB (ZABCs) were prepared by heating ZAB at various temperatures as shown in Table 1. Heating was done in a furnace at atmospheric pressure for 5 hours. As the heat treatment completed, the sample was left to cool to room temperature and kept in a sample bottle for further use.

Powder x-ray diffraction (PXRD) patterns of the samples were obtained by a Shimadzu Diffractometer XRD-6000, using filtered $CuK_\alpha$ radiation. FTIR spectra were recorded by a Perkin-Elmer 1750 Spectrophotometer. KBr pellet containing 1 % sample was used to obtain the FTIR spectra. The surface morphology of the samples was observed by a scanning electron microscope (SEM), using JOEL JSM-6400. CHNS analyzer, model EA 1108 of Finons Instruments was used for CHNS analyses.

## RESULTS AND DISCUSSION

### *Powder X-ray Diffraction (PXRD)*

Figure 1 shows the PXRD patterns for ZAB and ZABCs prepared by heating at 100-800 °C. As shown in the figure, the basal spacing for ZAB is 19.5 Å compared to around 8.9 Å for Zn-Al-LDH, indicating the expansion of the intergallery layers, as a result of the intercalation of organic species, BNOA anion into the inorganic, Zn-Al interlayer.

The basal spacing shrinked slightly to 19.0 Å and 18.8 Å when ZAB was heated at 100 °C and 200 °C, respectively. Below 300 °C, the principal change is loss of interparticle and intragallery water [11]. Further heating at 300 and 350 °C gave broad peak with basal spacing of around 24.3 Å which indicated the crystallinity of the resulting materials has changed due to the decomposition of BNOA ion in the layered Zn-Al-hydroxide. Further treatment at > 350 °C resulted in the collapsed of the Zn-Al inorganic layered structure. At the same time a new ZnO phase emerged and shows a notable increase in crystallinity with the heating temperature.

### *Fourier Transform-Infrared (FTIR)*

Figure 2 shows the FTIR spectra for ZABs prepared at various temperatures from 100-800 °C. As shown in the figure, in general, ZAB exhibits FTIR bands characteristics for both BNOA ion and Zn-Al-LDH. A band at 3353 $cm^{-1}$ is attributed to OH stretching due to the presence of hydroxyl group of ZAB and/or physically absorbed water. The lower values of $\nu_{O\text{-}H\ sym}$ in these nanocomposites compared to that of free OH groups (>3650 $cm^{-1}$) indicates that all the OH groups are involved in hydrogen bonding with BNOA ion and Zn/Al double metal hydroxide interlayer. The bands at 1583 $cm^{-1}$ is attributed to the carbonyl, C=O stretching vibration and the other sharp intense band at 1417 $cm^{-1}$ is due to $CH_2$ scissoring mode. Band at 1338 $cm^{-1}$ and 1220 $cm^{-1}$ is due to the stretching modes of –COO and C-O-C, respectively [12]. Another two bands at 409 and 577 $cm^{-1}$ can be attributed to the lattice vibration of Zn-O and Zn-OH [13].

No major changes in the FTIR spectrum are observed when sample was calcined below 350 °C, only a decrease in the intensities of the bands belonging to BNOA ion between 1300-1600 $cm^{-1}$, due to the decomposition of BNOA ion at this temperature. This resulted in collapsed of the Zn-Al layered structure as shown by PXRD diffractogram (figure 1). In addition, a new phase, ZnO was formed. An intense band centered at 3400 $cm^{-1}$ due to hydroxyl and water O-H stretch is common to all spectra of ZAB and ZABCs from the untreated to 800 °C treated samples. Heating at 400 °C or higher temperature until 800 °C gave a series of bands at 650 and 550 $cm^{-1}$, which can be associated with the presence of the products of the oxidation of organic component of the material, via a partial combustion process.

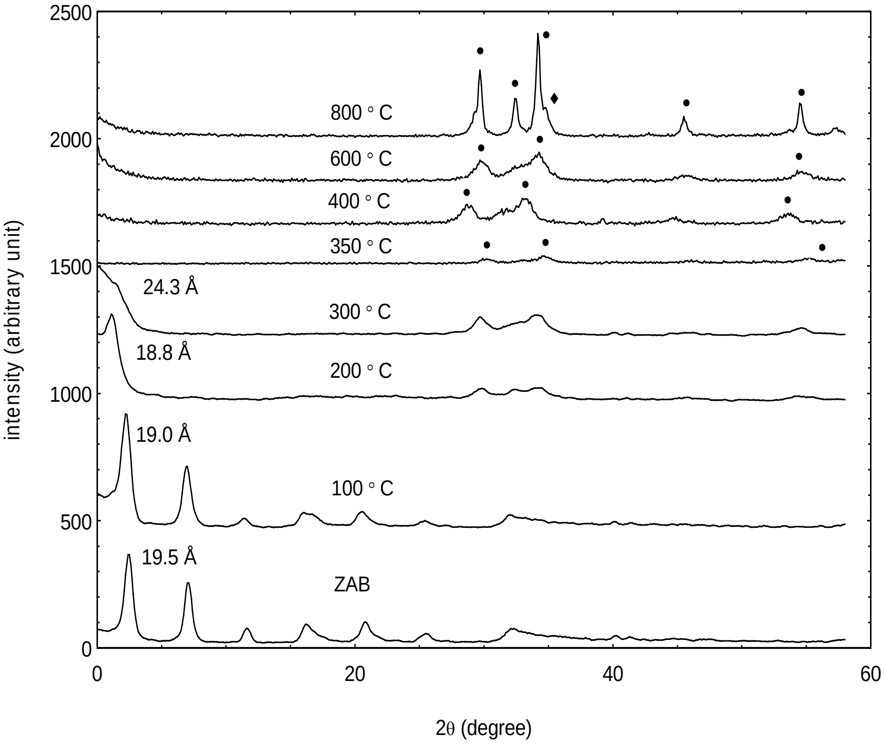

Figure 1: PXRD patterns for ZAB and ZABCs prepared at various temperatures 100-800 °C. (•) ZnO

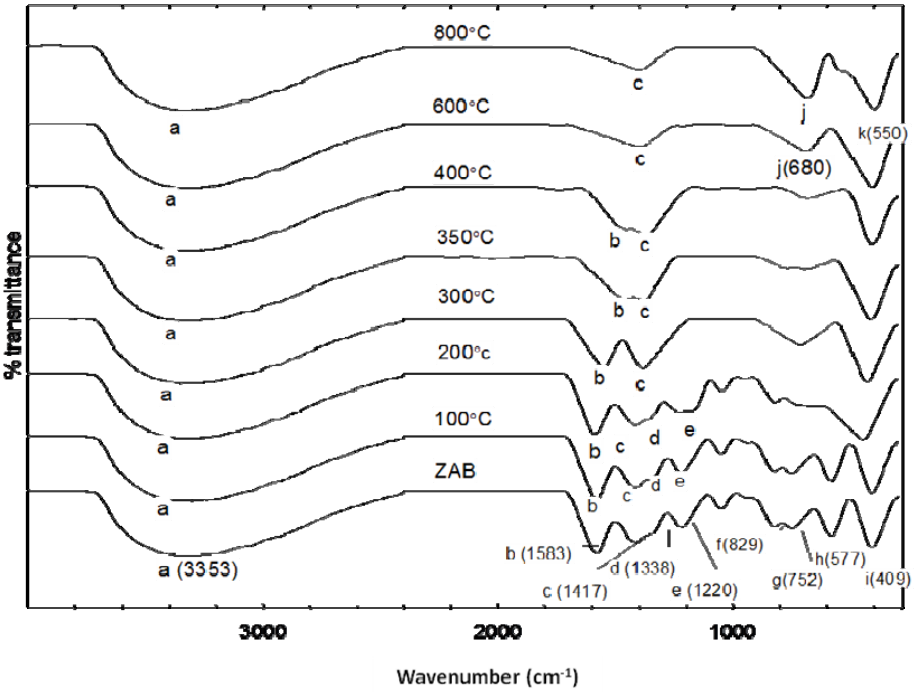

Figure 2: FTIR spectra for ZAB and ZABCs prepared at various temperatures, 100-800°C

### *Organic-Inorganic Composition*

The CHNS analysis shows that ZAB contained 26.2 % of carbon which indicated that BNOA ion was successfully intercalated in the interlayer lamella of ZAB as shown in Table 1. As the calcination temperature increased to 300 °C, the carbon content in the nanocomposite increased slightly to 32.2 %. This is due to the loss of the other loosely held components from the nanocomposite, thus leading to the apparent increase in the carbon content. The carbon content in ZABCs decreased drastically to 18.4 % as the calcination temperature was increased to 400 °C. This indicated that the BNOA anion had partially decomposed and the structure of the layered Zn-Al hydroxide collapsed as shown in the PXRD diffractogram. Only a trace of BNOA moiety was still present in the Zn-Al interlayer at 600 °C and higher temperature.

Table 1: Physio-chemical properties of ZAB and ZABCs prepared at various temperature

| Calcination temperature (°C) | Basal spacing (Å) | Phase detected | % C | % BNOA loading (w/w) |
|---|---|---|---|---|
| ZAB | 19.5 | Nanocomposite | 26.2 | 36.5 |
| 100 | 19.0 | Nanocomposite | 29.3 | 40.6 |
| 200 | 18.8 | Nanocomposite | 32.2 | 45.1 |
| 300 | 24.3 | Nanocomposite | 18.4 | 26.0 |
| 350 | Collapsed | ZnO | 2.00 | 2.86 |
| 400 | Collapsed | ZnO | 1.23 | 1.56 |
| 600 | Collapsed | ZnO | 0.46 | 0.50 |
| 800 | Collapsed | ZnO | 0.50 | 0.50 |

Table 1 also shows that the percentage of BNOA loading of ZABCs increased from 36.5 % (w/w %) to 45.1 % 9w/w %) as the calcined temperature increased to 200 ° C. The layered structure collapsed at 350 °C and the percentage of BNOA loading is decreased to 2.86 % (w/w %). As the calcination temperature increased further to 600 and 800 °C, the percentage of BNOA loading is decreased to 0.5 % (w/w %) for each other.

### *Surface morphology*

Figure 3 shows the surface morphology of ZAB obtained by SEM, showing a typical morphology of a nonocomposite with agglomerates of compact and non-porous structure. It is also similar to the morphology of other nanocomposite, such as Zn-Al-Alizarin red S [10], Zn-Al-poly(styrene sulfonate) [3] and Zn-Al-glutamate [14]. The morphology of the structure transformed to a porous amorphous-like structure as the calcined temperature increase. There was no strong evidence that a distinctive structure for ZnO crystallites was observed although its formation was shown in the x-ray diffractogram.

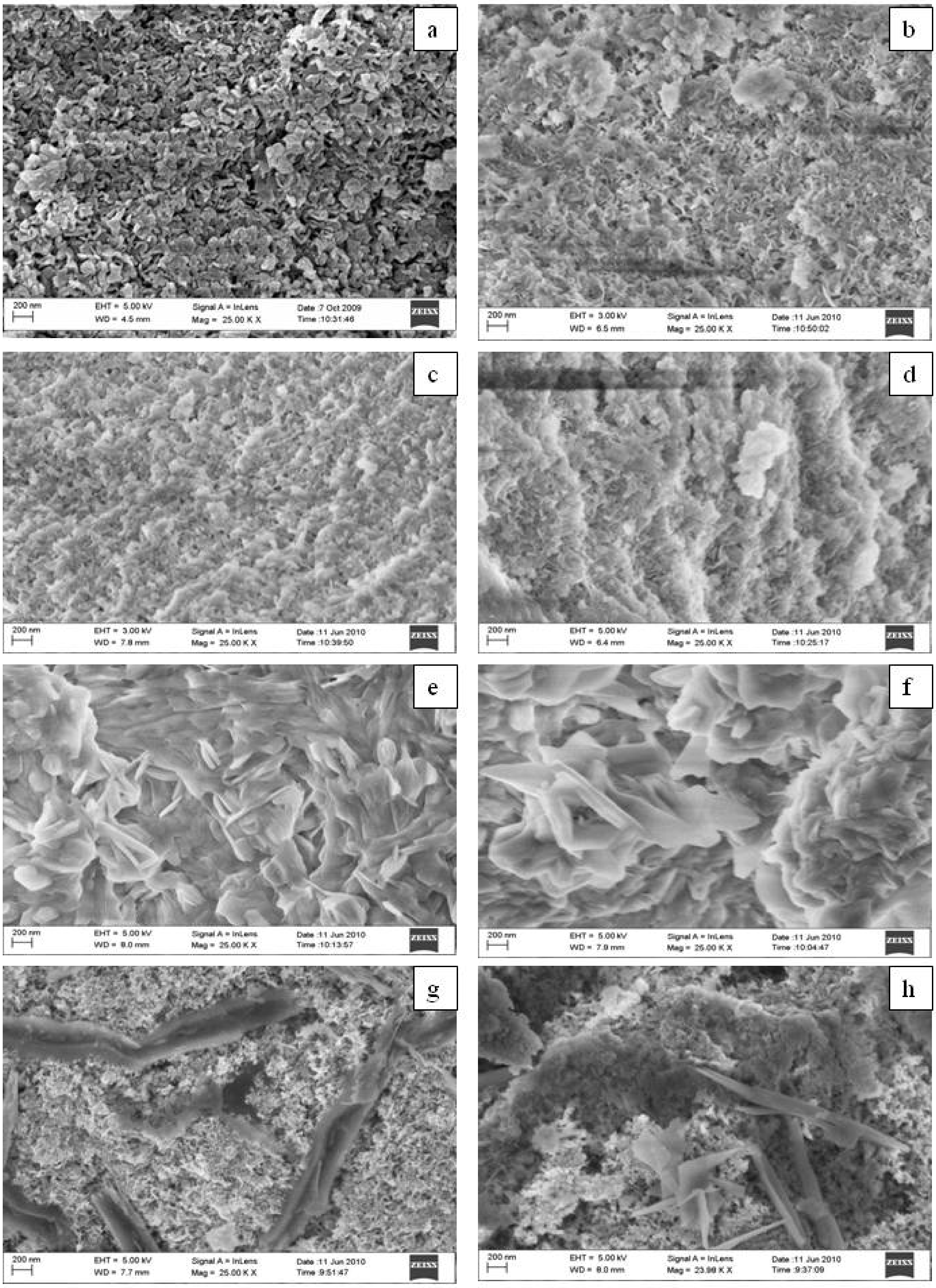

Figure 3: Electron micrographs for a) ZAB and ZABCs prepared at various temperatures b) 100 °C; c) 200 °C; d) 300 °C; e) 350 °C; f) 400°C; g) 600 °C; h) 800 °C

## CONCLUSION

The study showed that the nanolayered structure of the material collapsed at around 350°C due to the composition of the organic moiety. This is supported by CHNS analysis which shows the decrease of the carbon content with increasing temperature. At the same time a new phase of ZnO was formed as the temperature increased to 400-800°C. The morphology of ZAB shows agglomerates of compact and non-porous structure and they become more porous as the temperature increased.

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