International Journal of Technology (2013) 1: 73-80
ISSN 2086-9614 © IJTech 2013

INTERCALATION OF ANTHRANILATE ION INTO ZINC-ALUMINIUM-LAYERED DOUBLE HYDROXIDE

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(Received: December 2012/ Revised: January 2013/ Accepted: January 2013)

ABSTRACT

Nanocomposites of zinc-aluminium-anthranilate (ZAAN) have been synthesized at different concentrations of anthranilic acid by co-precipitation method. These materials have been examined in detail by powder X-ray powder diffraction (PXRD) which showed the expansion of the basal spacing from 0.89 to ca. 1.33 nm and the shifting of the 003 peak towards the lower 2θ angle. This indicates that the anthranilate anion was successfully intercalated into the interlayer gallery. However, FTIR analysis showed nitrate anion was also co-intercalated in the interlayer. The resulting nanocomposites show Type IV adsorption-desorption isotherms indicated the mesoporous structure of the material. BET surface area was found to be slightly different compared to zinc-aluminium-nitrate-layered double hydroxide (ZANO) after the intercalation process took place. Both ZANO and ZAAN have similar surface morphology, namely a flaky-like structure, but they are of different sizes.

Keywords: Anthranilic Acid; Intercalation; Layered Double Hydroxide; Nanocomposites,

1. INTRODUCTION

Layered double hydroxide (LDH), also known as hydrotalcite-like material or as anionic clay, can be represented by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{b+} [A^{n-}_{b/n}].mH_2O$ where M^{2+} is the divalent cation, M^{3+} is trivalent cation and A^{n-} is the interlayer anion (Miyata, 1980). The structures of LDH are very similar to that of brucite, $Mg(OH)_2$ which consist of Mg^{2+} ions coordinated octahedrally by six oxygen atoms belonging to hydroxyl groups. The octahedral units stacked on each other through edges sharing to form infinite sheets (Jones et al., 1998) When a partial replacement of divalent cations by trivalent cations occurred in the layered brucite structure, the positive charge will be introduced in the layer and balanced by anions such as carbonate, nitrate, etc. The schematic diagram of LDH structure with nitrate as the interlayer is shown in Figure 1.

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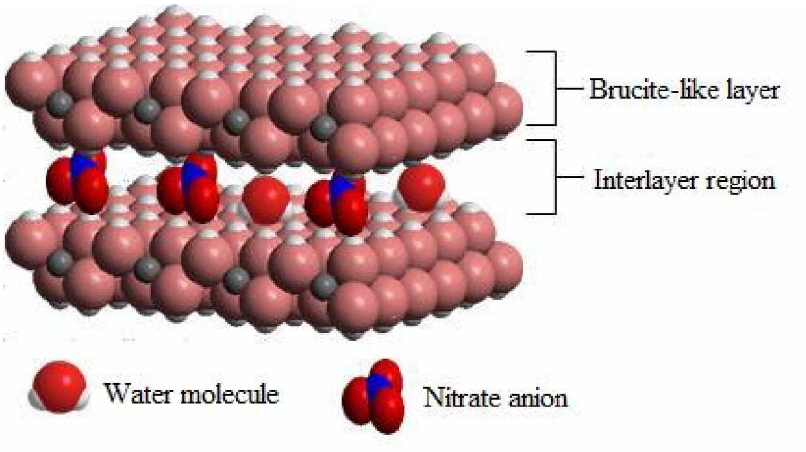

Figure 1 Schematic diagram of LDH structure with nitrate as the interlayer

The LDH is worthy of great attention due to its unique layered structure, intercalation, catalyst, and anion-exchange capability (Tang et al., 2008; Rey et al., 1999; Rives & Ulibarri, 1999). LDH is also promising for fabricating organic-inorganic nanocomposite materials through the intercalation of organic compounds in a formed anionic. In this work, we apply anthranilic acid (AA, 2-aminobenzoic acid) into LDH to form nanocomposites. AA is a small organic molecule with amphoteric property and it exhibits an amethyst-like fluorescence solution in alcohols or ether solvents. In a previous study, the AA molecule was inserted into the interlayer region of layered zinc hydroxide nitrate and they reported that the AA is a good candidate as UV absorbents for skin protection (Cursino et al., 2010). AA molecule also is used in cases of pharmaceutical invention such as an anti-endotoxic effect which can induce fever (Fang et al., 2005). We expect that the LDH can be used as a drug carrier in the form of nanocomposites. The release of the encapsulated drug can be controlled thus is hoped that this material will give other pharmaceutical benefits. In the present study, we report the intercalation of AA in the form of the anthranilate ion (Figure 2) into the Zn/Al-NO_3-LDH (ZANO) through the co-precipitation method. The physico-chemical properties of ZANO and ZAAN were investigated by powder X-ray diffraction (PXRD), spectroscopic, elemental analysis, SEM, and an accelerated surface area and porosity analyzer (ASAP).

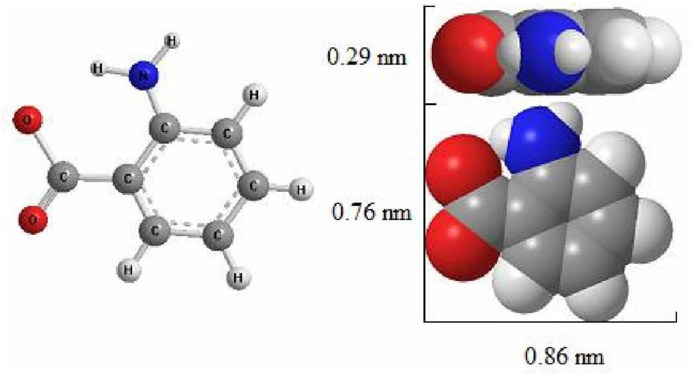

Figure 2 Molecular structure and dimension of anthranilate anion.

2. EXPERIMENTAL

2.1 Materials

$Zn(NO_3)_2.6H_2O$ and NaOH were purchased from Fluka (Buchs, Switzerland). $Al(NO_3)_3.9H_2O$ was purchased from BDH (Poole, England). Anthranilic acid ($C_6H_4(NH_2)CO_2H$) was purchased from Acros (New Jersey, USA). All chemicals and solvents were of analytical grade and were used without further purification. Reversed osmosis water was used throughout in this study.

2.2 Characterizations

Powder X-ray diffraction (PXRD) patterns of the samples were obtained from an automated Shimadzu XRD-6000 X-ray diffractometer with CuKα as the radiation source at a scan speed of 2°/min and wavelength at 0.1540562 nm. The elemental analyses were determined by a CHNS analyzer model CHNS-932 and Perkin Elmer ICP–AES spectrophotometer model Optima 2000DV. IR spectra were recorded on a Perkin-Elmer model 1725X FTIR spectrophotometer in the region of 4000 - 400 cm^{-1} using the conventional KBr pellet method. The surface texture characterization of the materials was carried out by adsorption-desorption of nitrogen gas at liquid nitrogen temperature, 77 K using a Micromeritics ASAP 2000. Specific total surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The microstructures of the samples were performed using a variable pressure SEM (VPSEM LEO 1455VP).

2.3 Synthesis of Zn/Al-NO_3-LDH (ZANO)

The Zn/Al molar ratio was fixed at 3. A mixed aqueous solution or mother liquor of $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ were prepared at pH 7.50 ± 0.05 by drop-wise addition of an aqueous NaOH solution (2.0 M) with vigorous stirring. The titration of NaOH was performed under a constant flow of nitrogen gas in order to avoid or at least minimize the contamination by atmospheric CO_2. The precipitate was aged at 70ºC for 18h, washed and dried in an oven at 70ºC, and ground into fine powder and kept in a sample bottle for further use and characterization.

2.4 Synthesis of Zn/Al-An-Nanocomposite (ZAAN)

ZAAN was synthesized by co-precipitation method similar to the method for ZANO except mother liquor was titrated with an aqueous NaOH solution (2.0 M) and an anthranilic acid solution alternately with vigorous stirring, until the pH of the solution reached a reading of 7.50 ± 0.05.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction study

The PXRD patterns of ZANO and ZAAN at different concentrations of AA are presented in Figure 3. Also shown is the PXRD pattern for pure AA, for comparative purposes. A sharp and symmetrical peak shows that the ZANO and ZAAN have a typical, well order layered structures with a high degree of crystallinity. In ZANO, the (003), (006), (009) diffraction peaks which correspond to the basal and higher reflections appear at 9.8°, 19.77° and 29.96°, respectively. The basal spacing $d_{(003)}$ is 0.89 nm, which is similar to the literature value (Fang et al., 2005). After antranilate (An^-) anions were intercalated into the interlayer galleries of ZANO, the (003) diffraction peak move to 6.7°. The basal spacing of (003) peak for ZANO increased up to 1.32-1.34 nm after the AA was introduced into the materials as evidence of successful intercalation process. Although the intercalation had occurred, the peak for ZANO located at $2\theta = 9.8$ º (marked with ♦) can be still observed for the concentration of AA in the range of 0.0125-0.1 M. This indicates that competition between the anthranilate (An^-) and the nitrate ions for the interlayer spaces occurred. However, as the concentration of AA increased, the (003) peak's intensity for the nanocomposite, ZAAN that appears at lower 2θ angle (ca. 6.7 º) increased (maximum at 0.1 M AA). ZANO phase begins to disappear at 0.2 M of AA, suggesting that the intercalation exchange reaction was completed (El-Toni et al., 2006) thus the pure phase of ZAAN was produced. Sharp and intense peaks were observed and these features reflect a well-crystallised and well-ordered layered structure.

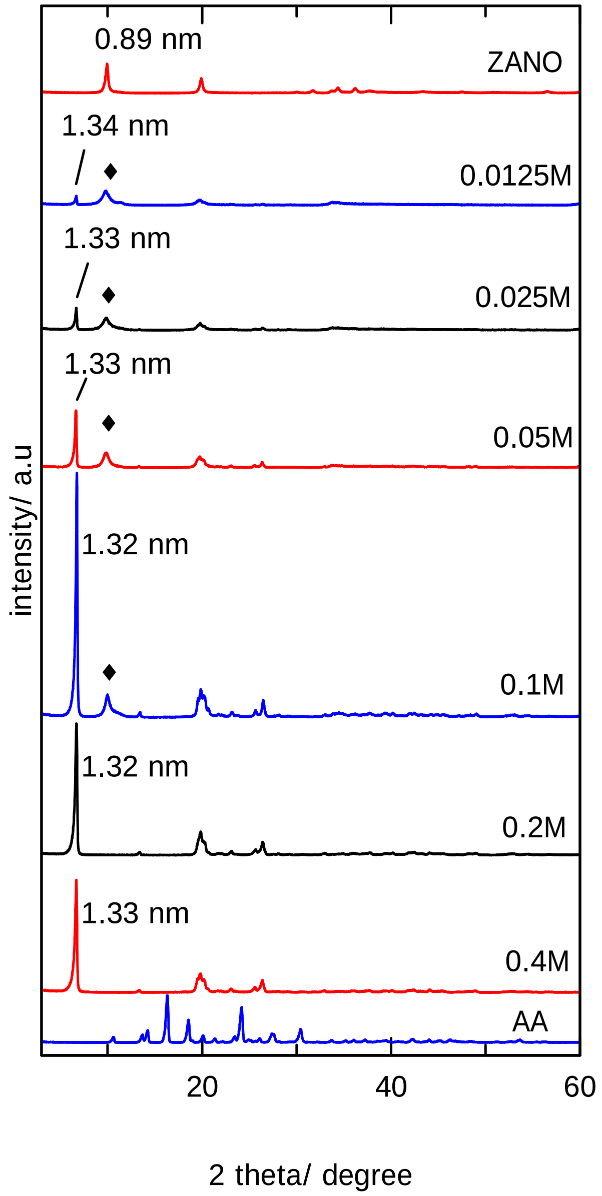

Figure 3 XRD patterns for ZANO and ZAAN at different concentrations of AA

ZAANs have the basal spacing of 1.32-1.34 nm, thus subtracting the thickness of the LDH layers (0.48 nm) (Feng et al., 2006), the calculated gallery height values of ZAAN is in the range of 0.84-0.86 nm and this value is approximately similar to the length of the An$^-$ anion (Figure 2). Thus the orientation of the An$^-$ is most likely in a perpendicular arrangement in the interlayer regions. The nitrate anion co-existed with the An$^-$ anion in the interlamellae as evidenced by the FTIR spectra. Since the basal spacing value is not altered, the arrangement of the nitrate ion is predicted adjacent to the An$^-$ anion as shown in the figure 4. It is noted that the An$^-$ anion started to intercalate into the interlayer and the pure phase of ZAAN was obtained with concentration of AA at 0.2 M. Thus, this ZAAN material was chosen for further characterizations.

3.2 FTIR spectroscopy

FTIR spectra for ZANO and ZAAN are shown in Figure 4. As shown in the figure, ZANO has a broad absorption band at 3428 cm^{-1} that attributed to the OH stretching due to the presence of the hydroxyl groups of the layers and also in both adsorbed and interlayer water molecules. The band at 1622 cm^{-1} is due to the deformation vibration ($\delta_{H\text{-}O\text{-}H}$) of H_2O thus confirming the presence of water molecules in the interlayer region of ZANO (Ferreira et al., 2006). A strong absorption band at 1384 cm^{-1} can be attributed to the presence of the nitrate group, the intergallery anion in ZANO. The bands in the low frequency region, 400–800 cm^{-1} correspond to the lattice vibration modes of M–O and O–M–O (M = Zn, Al) (Ding & Qu, 2005) such as the translation vibrations of Zn-OH at 616 cm^{-1} and Al-OH at around 558 cm^{-1} and deformation vibration of HO-Zn-Al-OH at 426 cm^{-1} (Li et al., 2004) which are typical of this class of materials (Feng et al., 2006).

The two bands at 3324 and 3240 cm^{-1} in AA were attributed to $–NH_2$ stretching vibration and few bands in a range, 760-800 cm^{-1} were attributed to C-H aromatic, out of plane vibration. The strong band at 1584 cm^{-1} is attributed to C=O stretching vibration. As AA has an aromatic ring, C=C stretching absorption at 1460 cm^{-1} and a strong peak at 758 cm^{-1} attributed to =C-H out-of-plane (oop) bending are evidence of *ortho*-disubstituted ring (Pavia et al., 2001).

The FTIR spectrum of ZAAN shows a mixture of each spectrum of ZANO and AA indicating both functional groups are simultaneously present in the resulting nanocomposite. The presence of a band at 1384 cm^{-1} which is attributed to nitrate group in the nanocomposite which is marked with (♦) reveals that the An^- anion was co-existed with the nitrate anion in the interlamellae of the resulting materials.

3.3 Elemental analysis

Table 1 shows the elemental content of the as obtained materials. As shown in the table , the molar ratio of the material is around 3.0, similar to the mother liquor initial ratio. The weight percentage of C, H and N is also shown in the table 1. There was no C content in ZANO (as expected) but after the intercalation process, the content of C can be observed in ZAAN due to the encapsulated of An^- anion in the interlayer. Percentage of the H and N content were increased after the intercalation due to the presence of the An^- anion, which contains H and amino group in the molecule. However, not the entire N due to the amino groups, this is because FTIR spectra revealed that, An^- anion and nitrate group are co-intercalated in the interlayer gallery. The ideal formula for ZAAN, based on the elemental content and Zn/Al ratio is $[Zn_{0.77}Al_{0.23}(OH)_2][An^-]_{0.22}\,[NO_3]_{0.01}.mH_2O$.

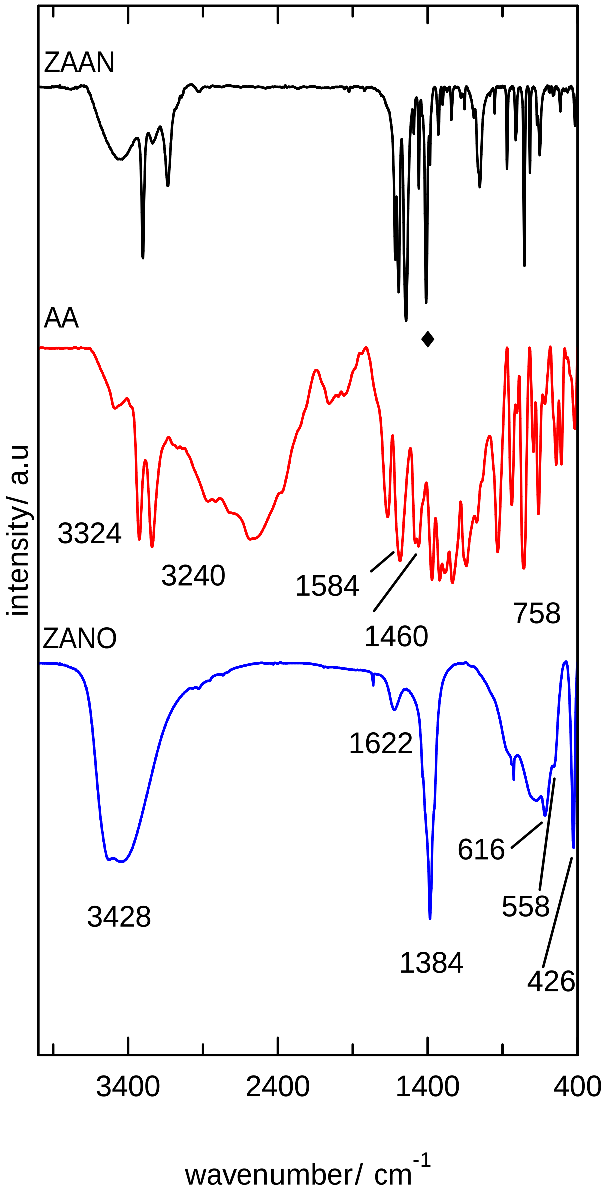

Figure 4 FTIR spectra of ZANO, AA and ZAAN

Table 1 Elemental analysis, BET and BJH of materials

Material	Ratio of Zn/Al	Basal spacing (nm)	Weight percentage (%)			BET surface area (m^{2}g^{-1})	BJH desorption average pore (nm)
			C	H	N		
ZANO	3.3	0.89	0.00	2.40	4.02	10.4	23.9
ZAAN	3.3	1.32	47.33	3.40	7.86	12.3	10.0
AA	-	-	64.78	4.99	0.49	-	-
AA*	-	-	61.31	5.11	10.22	-	-

* calculated from formula of AA

3.4 Surface properties and morphology

Figure 5 (a) shows that the shapes of the curves are typically of Type IV adsorption isotherms, which indicate that the adsorbents are of a mesopores structure. The characteristic feature of

Type IV isotherm is the hysteresis loop of the materials. Both ZANO and ZAAN show Type H3 hysteresis loop that the steep region of the desorption branch leading to a lower closure point occurs at a relative pressure which is almost dependent mainly on the nature of the adsorption. This indicates that the materials having aggregates of plate-like particles are giving rise to slit-shaped pores (Choy et al., 2004). Both materials show a mesoporous property (Figure 5 (b)), as the pore size distribution is large and spread over the mesopore region (2-50 nm). The difference in the pore size distribution profile of nanocomposites is attributed to the modification of the pore by An^- anion after the intercalation process. The surface area for ZAAN slightly increased, but the BJH average pore diameter decreased after the intercalation process (Table 1). SEM micrographs of the synthesized materials illustrated in Figure 6 shows that both ZANO and ZAAN have similar structures, which is flake-like, but with different sizes of the flake structure.

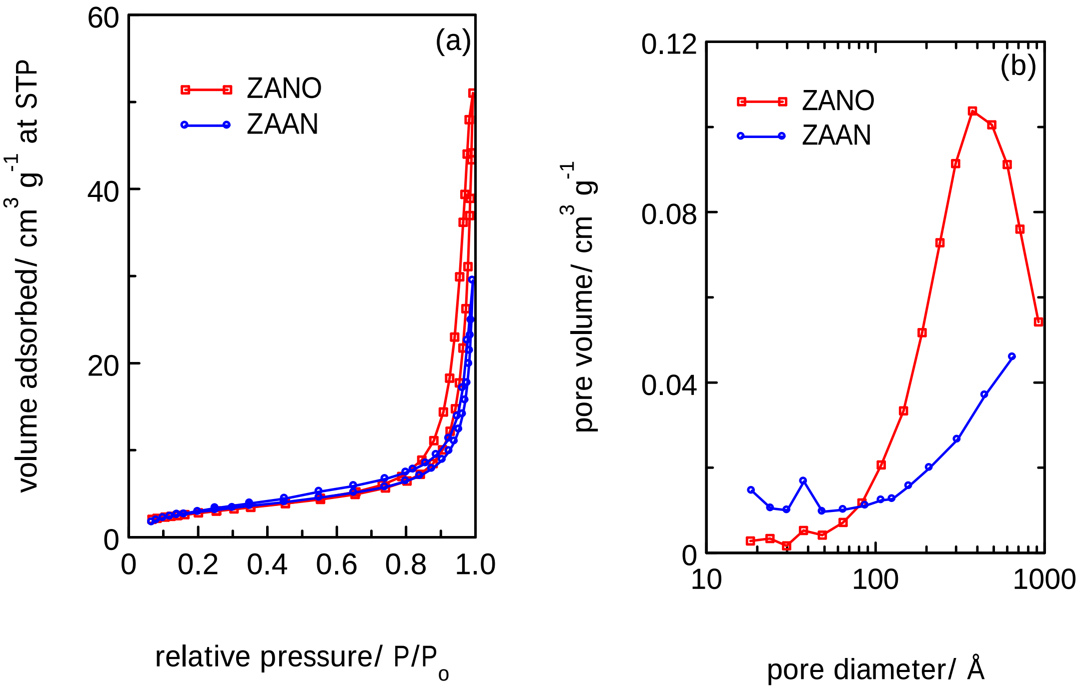

Figure 5 (a) Adsorption-desorption isotherms and (b) BJH pore size distribution for ZANO and ZAAN

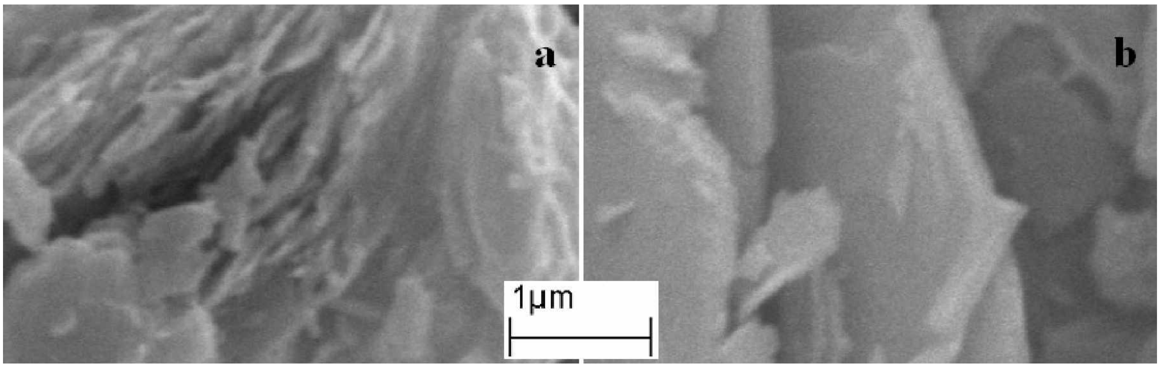

Figure 6 SEM images for (a) ZANO and (b) ZAAN at magnification of 10K

4. CONCLUSION

The ZAAN materials were successfully synthesized by intercalation of An^- anion into the interlayer of ZANO with concentration of AA at 0.2 M. Both ZANO and ZAAN had Type IV adsorption isotherms with Type H3 hysteresis loop indicating that materials have slit-shaped pores.

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