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Pamoate intercalated Zn-Al layered double hydroxide for the formation of layered organic-inorganic intercalate

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A layered organic-inorganic intercalate was prepared by the self-assembly technique using pamoate (PA) as an organic guest in the Zn-Al layered double hydroxide inorganic host (ZAPAN). Various concentrations of PA, ranging from 0.01 to 0.04 M, were used to prepare the intercalated compound with a constant 4:1 ratio of Zn:Al in the mother liquor. The concentration of PA of 0.02 M at pH 7 was found to give a well-ordered nanolayered organic-inorganic hybrid structure. As a result of successful intercalation of PA anion into the Zn-Al inorganic layered double hydroxide (LDH), the expansion of interlayer spacing to 18 Å was observed in the PXRD diffractogram of the intercalated compound, compared to 9 Å for the Zn-Al LDH with nitrate as the counter anion (ZANIL). FTIR study shows that the intercalated compound resembled the spectra of PA and ZANIL, thus indicating the presence of both functional groups in ZAPAN. It was also found that the BET surface area increased from 6 m^2/g to 90 m^2/g for ZANIL and ZAPAN, respectively. The pore texture of the resulting materials was also changed as the result of the intercalation and the expansion of the basal spacing together with pore formation between the crystallite during the formation of the resulting layered intercalated compound.

Key words: *organic-inorganic intercalate; pamoic acid; layered double hydroxide; hydrotalcite*

1. Introduction

Intercalated compounds of organic-inorganic hybrid type have been extensively studied for some time and it was shown that the resulting properties can be tailored to a specific requirement needed to serve specific purposes. This type or materials can be synthesised by employing a variety of interactions found within the organic and inorganic chemistry, to create a composite with some enhanced property relative to

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that achievable by its counterpart alone, or to combine useful properties of the two within a single material [1].

In the syntheses of organic-inorganic materials of hybrid intercalate type, layered double hydroxides (LDHs) can be chosen as one of the inorganic hosts. LDHs has a general formula $[[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, x is the $M^{3+}/(M^{2+}+M^{3+})$ ratio and A^{n-} is an interlayer anion. Such A^{n-} anions may be polymers [2, 3], organic dyes [4], surfactants [5, 6] or organic acids [7].

Previous work on the intercalation of various organic molecules into the hydroxide layers have been carried out for various purposes and applications. For example, the replacement of inorganic anions in LDHs with organic species such as long-chain surfactants resulted in a modified organo-LDHs with surfaces of hydrophobic properties. Anionic surfactants such as octylsulfate, sodium dodecylsulfate, sodium 4-octylbenzenesulfonate and sodium dodecylbenzenesulfonate were used. The resulting organo-LDHs were studied by evaluating their abilities to adsorptively remove 1,2,4-trichlorobenzene and 1,1,1-trichloroetane from aqueous solutions [5]. Another example is the intercalation of ibuprofen, α-methyl-4-(2-methylpropyl)benzene-acetic acid which is an anti-inflammatory drug into Zn-Al LDH, in order to study the controlled release property of the former from the controlled release formulation [8]. This is particularly useful for medical and agricultural purposes [7].

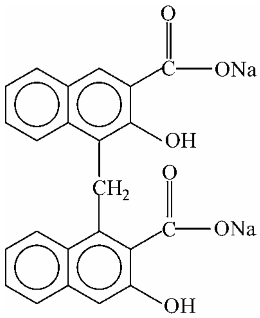

Fig. 1. The molecular formula of pamoate salt

Layered organic-inorganic intercalates can be prepared by propping the LDH inorganic layers apart followed by insertion of the organic moiety. This can be done directly or indirectly. In the direct method or the so-called spontaneous self-assembly method, formation of the resulting material can be accomplished by co-precipitation of cations in a basic aqueous solution in the presence of the anions to be intercalated in the interlayer, followed by ageing processes. In the indirect method, the preparing of the host is followed by its modification or further treatment and finally embedding of anions into the layers [6, 9]. For both methods, physicochemical and structural, properties of the resulting materials depend on the precipitation pH, temperature, ageing time, washing and drying conditions.

In this paper, we report on the intercalation of the anions of 1,1′-methylene-bis -[2-hydroxy-3-naphthoic acid] (pamoic acid, pamoate) into the Zn-Al LDH to form a new organic-inorganic hybrid intercalated material. The molecular structure of the pamoate salt ($C_{23}H_{14}O_6Na_2$) is shown in Fig. 1. It is the salt of an aromatic dicarboxylic acid, used as a means of masking unpleasant tastes or prolonged therapeutic action by forming slightly soluble salts with certain basic drugs [10]. A derivative of pamoic acid, pyrantel pamoate, is used for the treatment of infestation of gastrointestinal parasite [11].

2. Experimental

All chemicals used in this synthesis were obtained from various chemical suppliers and used without any further purification. All solutions were prepared using deionized water.

The synthesis of the intercalated compound, ZAPAN, was done by the spontaneous self-assembly method. A mother liquor containing Zn^{2+} and Al^{3+} cations with Zn/Al initial ratio $R_i = 4$ and PA was prepared. pH was adjusted to about 7. The concentration of PA was from 0.01 M to 0.04 M and the reaction was carried out under nitrogen atmosphere. The solution was aged for 18 h 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 bottle for further use and characterizations. A similar method was adopted for the preparation of Zn-Al LDH with nitrate as the intergallery anion (ZANIL) by omitting the addition of PA solution in the mother liquor.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained with a Shimadzu Diffractometer XRD-6000, using filtered CuK_α radiation. FTIR spectra were recorded by a Perkin-Elmer 1750 Spectrophotometer. KBr pellet containing a 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. A CHNS analyser, model EA 1108 of Finons Instruments, was used for CHNS analyses. The percentage of PA in ZAPAN was established by means of a UV-visible technique using a Perkin-Elmer UV-visible Spectrophotometer model Lambda 20. The Zn/Al ratio of the resulting ZAPAN was determined by an inductively coupled plasma emission spectrometry (ICP-ES) with a Labtest Equipment Model 710 Plasmascan sequential emission spectrometer.

Surface characterization of the materials was carried out by the nitrogen gas adsorption-desorption technique at 77 K using a Micromeritics ASAP 2000. Samples were degassed in an evacuated-heated chamber at 120 °C, overnight.

3. Results and discussion

3.1. Powder X-ray diffraction

Figures 2a–f show PXRD patterns of the LDH, ZANIL and its intercalated compound, ZAPAN, prepared using various concentrations of PA from 0.01 M to 0.04 M. As shown in Fig. 2a, the basal spacing for ZANIL with nitrate as the interlamella anion is 9 Å which is similar to the value reported previously [12].

The PXRD pattern for ZAPAN is shown in Fig. 2c with basal spacing of 18 Å. The expansion of basal spacing from ZANIL to ZAPAN is due to the inclusion of PA into the LDH lamella with an orientation that warrants the expansion of the LDH lamella. This can only be achieved if suitable concentration of PA is available in the mother liquor, under the experimental conditions stated earlier. Noteworthy also that for ZAPAN prepared by using 0.03 M and 0.04 M PA, a number of peaks which are characteristic of PA phase were detected. This might be due to the unintercalated PA, which was adsorbed onto the surface of ZAPAN due to a high concentration of PA being used in the synthesis.

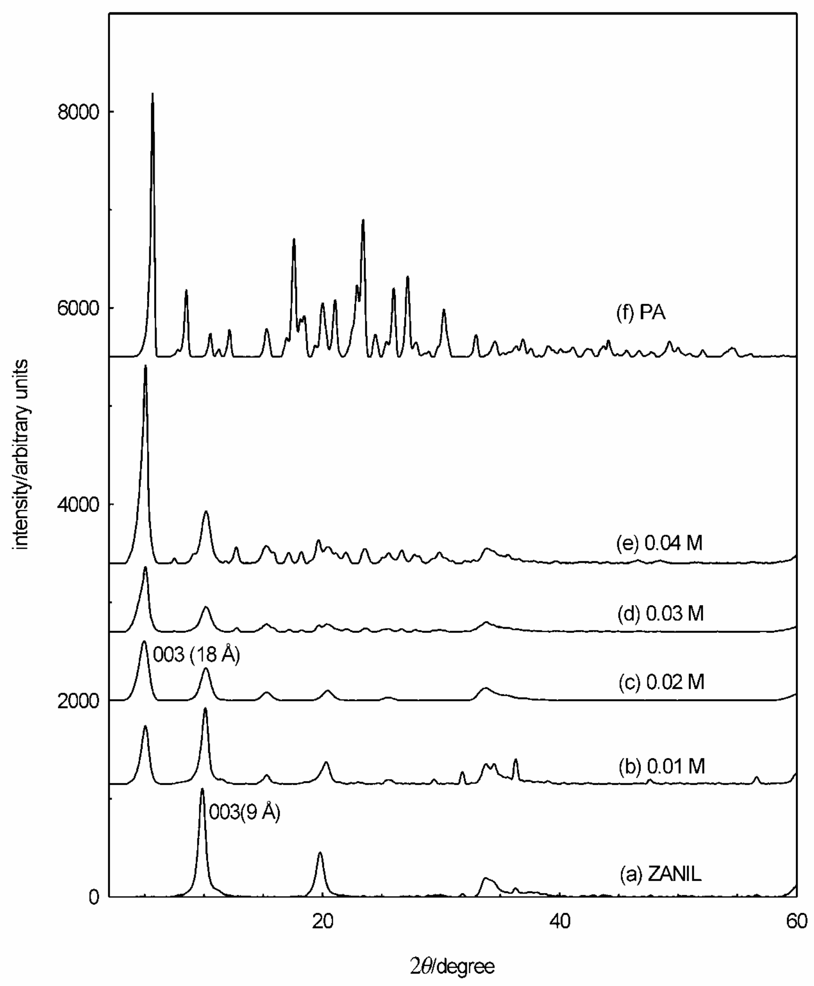

Fig. 2. PXRD pattern for ZANIL and its intercalated compound with PA (ZAPAN) prepared at various concentrations of PA

For ZAPAN prepared using 0.01 M PA, ZnO phase was also detected. ZAPAN prepared by using 0.02 M PA produced sharp, symmetrical and intense peaks, especially for the (003) peak, and relatively pure intercalated compound was obtained at this concentration. As a result of successful intercalation of PA, ZAPAN prepared from 0.02 M PA was subsequently used for further characterizations.

3.2. FTIR spectroscopy

In figure 3, the FTIR spectra for PA, ZANIL and ZAPAN are shown. The FTIR spectrum for ZANIL (Fig. 3a) shows a broad absorption band centred at around 3438 cm^{-1} which is due to the presence of OH stretching modes of the hydroxyl group of LDH and/or physically adsorbed water molecules. The band at 1629 cm^{-1} is due to $\nu_{H\text{–}O\text{–}H}$ bending vibrations. A sharp and very intense band located at approximately

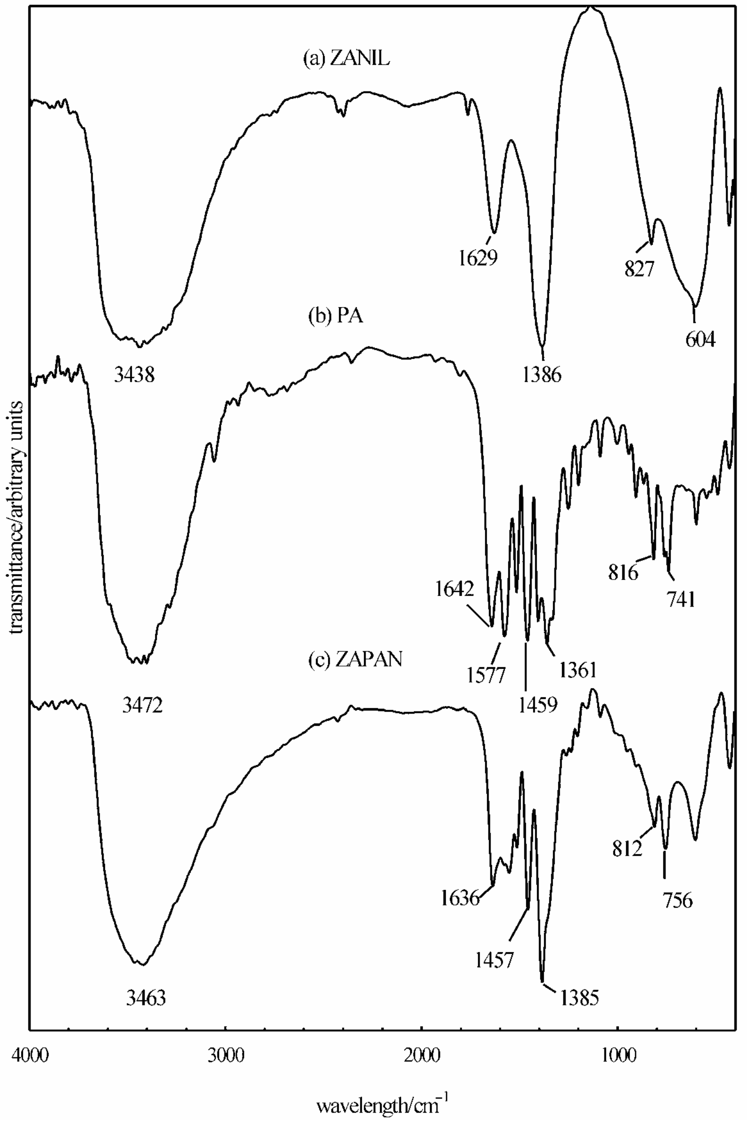

Fig. 3. FTIR spectra for: a) ZANIL, b) PA, c) ZAPAN

1386 cm^{-1} is attributed to the ν_3 (NO_3^-) vibration [13]. Another two bands at 604 cm^{-1} and 432 cm^{-1} can be attributed to the Al–OH and Zn–Al–OH bending vibrations, respectively [6].

Figure 3b shows the FTIR spectrum of PA displaying a broad band at 3472 cm^{-1}, which is attributed to the OH stretching vibration. Strong bands at 1577 and 1361 cm^{-1} are due to the antisymmetric and symmetric stretching modes of –COO, respectively [8]. The bands at 1516 and 1642 cm^{-1} are attributed to the stretching vibrations of aromatic rings, C=C, and the other sharp intense band at 1459 cm^{-1} is due to CH_2 scissoring mode. Strong bands near 741–816 cm^{-1} can be attributed to the presence of phenyl ring substitution [14].

The FTIR spectrum of ZAPAN synthesized by using 0.02 M PA is shown in Fig. 3c. As expected, the spectrum resembles a mixture of both the spectra of PA and ZANIL, indicating that both functional groups of PA and ZANIL are simultaneously present in ZAPAN and confirm the intercalation of PA in the interlamella of ZANIL.

3.3. Organic-inorganic composition

The organic and inorganic composition of ZANIL and ZAPAN is compared in the table. The ratios of Zn/Al (R_f) in ZANIL and ZAPAN are 3.0 and 3.3, respectively. Compared to 4.0 for the initial ratio in the mother liquor, a slightly lower R_f value than R_{initial} indicates that not all Zn^{2+} ions in the mother liquor were used for the formation of positively charged layers of the inorganic double hydroxide during the formation of ZANIL or ZAPAN.

Table. Physicochemical properties of ZANIL and ZAPAN

Salt	^aR_f	*C* wt.%	*PA* wt.%	*N* wt.%	BET surface area ($m^2 \cdot g^{-1}$)	BJH desorption pore volume ($cm^{-3} \cdot g^{-1}$)	BJH average pore diameter (Å)
ZANIL	3.0	–	–	3.8	6	0.028	87
ZAPAN	3.3	24.1	44.2	0.8	90	0.342	115

^aR_f = final ratio.

The CHNS analysis shows that ZAPAN contained 24.1% of carbon which indicated that PA was successfully intercalated in the interlayer lamella of ZAPAN. The CHNS analysis also shows that ZANIL contained 3.8% of nitrogen. This is in agreement with the presence of a strong, sharp band at about 1386 cm^{-1} in the FTIR spectrum of ZANIL in Fig. 3a, which might be due to the presence of nitrate. As shown in the table, the percentage of PA intercalated into the interlayer of ZAPAN is 44.2% measured by an UV-visible spectrophotometer.

3.4. Thermal analysis

The results of thermogravimetric analyses (TGA) and differential TGA (DTG) of PA, ZANIL and ZAPAN are shown in Fig. 4. ZANIL, which is a hydrotalcite-like

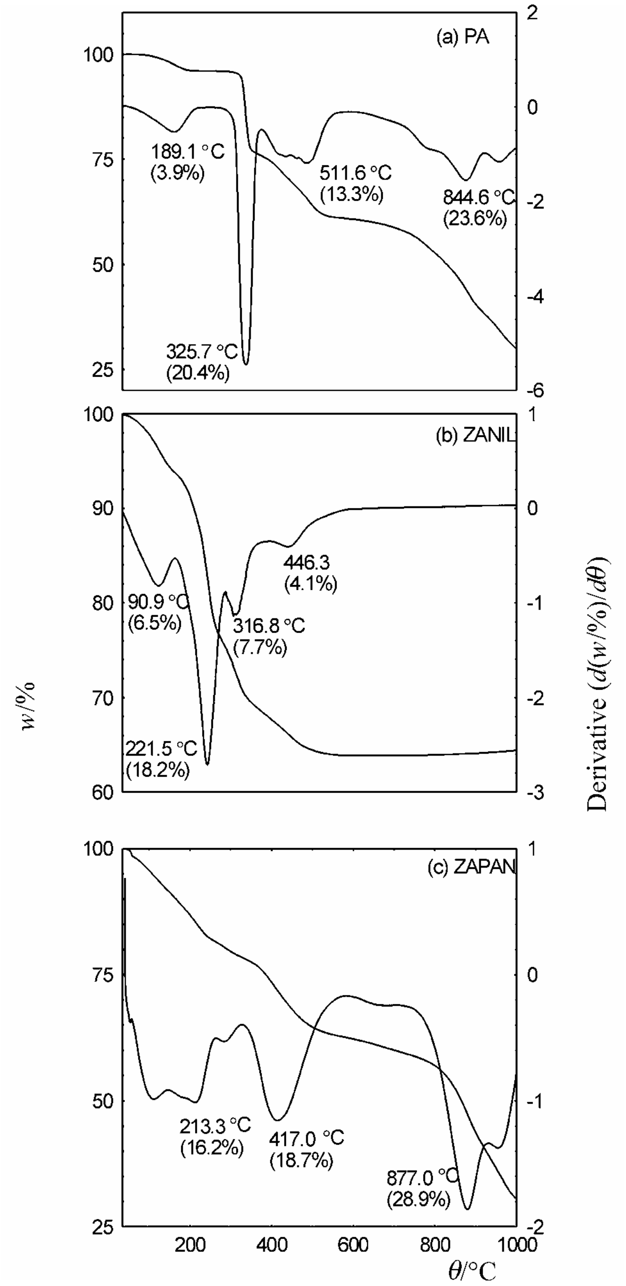

Fig. 4. TGA and DTG thermograms for: a) PA, b) ZANIL, c) ZAPAN

compound, shows four major stages of the weight loss process occurring at the temperature maxima of 90.9, 221.5, 316.8 °C and 446.3 ºC, with weight losses of 6.5, 18.2, 7.7 and 4.1%, respectively. The first weight loss corresponds to the removal of water physisorbed on the external surface of the particles. The second weight loss is attributed to strongly held water molecules [15]. The third and fourth weight losses are almost completed at 450 ºC and correspond to removal of hydroxyl groups from the brucite-like layers and the removal of interlayer anions. The DTG curves for PA exhibit four major stages of weight loss process at the temperature maxima of 189.1 ºC (3.9%), 325.7 ºC (20.4%), 511.6 ºC (13.3%) and 844.6 ºC (23.6%). The TGA shows the first weight loss below 200 ºC which is ascribed generally to the loss of physically adsorbed water. The second weight loss can be attributed to the evolution of carbon dioxide and water by thermal decomposition of the organic molecules. Decomposition at higher temperature (above 400 ºC) is due to a non-vaporizable nature of the organic anions [16]. The DTG curves of ZAPAN show three major stages of weight loss. The first weight loss is due to the removal of water physisorbed on the external surface of the powder particles. The second one should be due to simultaneous loss of carbonate and dehydroxylation of the brucite-like layer and the third weight loss above 800 ºC corresponds to the decomposition of the organic moiety in the interlayer lamella of the nanohybrid material [17]. The percent weight losses are 16.2, 18.7 and 28.9% at 213.3, 417 and 877 ºC, respectively.

Comparison of Figs. 4a and 4c shows that the temperature maximum for the decomposition of the organic moiety is higher in the latter which proves that PA intercalated inside the LDH is thermally more stable than its original form as a sodium salt.

3.5. Surface properties

Isotherm, surface area and pore size distribution. In order to study the effect of surface properties of the resulting material upon successful intercalation of PA inside the Zn-Al LDH for the formation of an intercalated compound, we measured the surface area and pore size distribution using nitrogen gas adsorption-desorption technique at 77 K.

Figure 5 shows the adsorption-desorption isotherms for ZANIL and ZAPAN. As shown in the figure, the adsorption-desorption isotherm for ZAPAN is of type IV, indicating mesopores-type material (20–500 Å) [18], with adsorption increasing fairly rapidly at low relative pressure in the range of 0.0–0.05, followed by a slow uptake of the absorbent at a higher relative pressure of 0.5–0.6. Further increase of the relative pressure to > 0.6 resulted in a rapid adsorption of the adsorbent, reaching an optimum at more than 220 cm^3/g at STP.

A general shape of the isotherm for ZAPAN does not differ very much from that of ZANIL, the type IV isotherm still remains. However, as shown in Fig. 5, the adsorbate uptake is slow in the relative pressure range of 0.0–0.9, after which rapid adsorption can be observed. An optimum uptake was only about 20 cm^3/g at STP, indicating slow uptake of the nitrogen gas. The desorption branch of the hysteresis loop for ZAPAN is much narrower compared to ZANIL, indicating different pore texture of the resulting material.

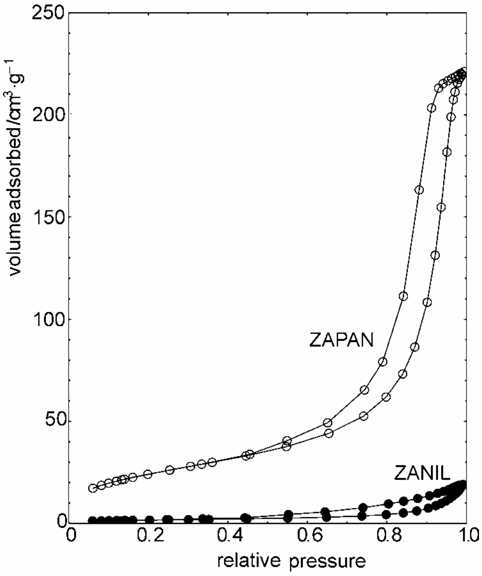

Fig. 5. Adsorption-desorption isotherms for ZANIL and ZAPAN

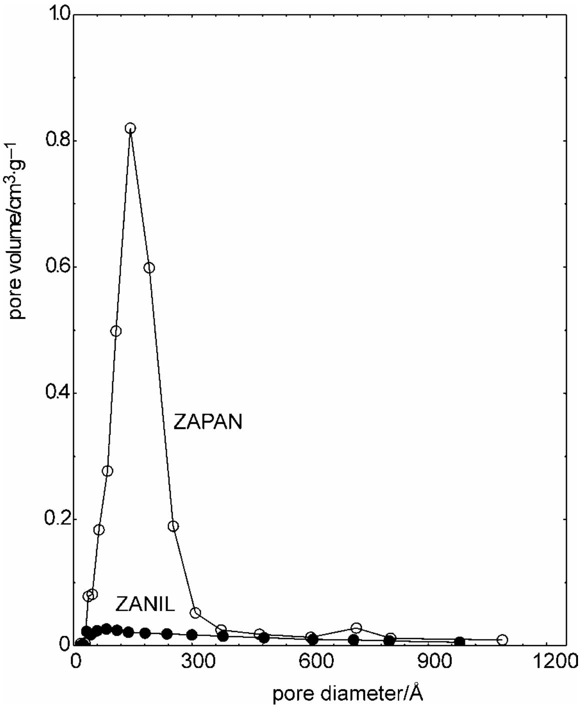

Fig. 6. BJH pore size distribution for ZANIL and ZAPAN

The surface properties of ZANIL and ZAPAN are summarised in the table. The intercalation of PA ion has increased the BET specific surface area from 6 m^2/g for ZANIL to 90 m^2/g for ZAPAN. The table shows that the BET average pore diameter for ZAPAN is lower than that of ZANIL, amounting to 149 Å and 173 Å, respectively. On the other hand, the BJH desorption pore volume of ZAPAN is higher than that of ZANIL (0.342 to 0.028 cm^3/g, respectively).

The BJH pore size distribution for ZANIL and ZAPAN are presented in Fig. 6. Both materials show mesopores, in agreement with the adsorption isotherm of type IV. BJH pore size distribution for ZANIL shows a broad peak at around 100 Å while for ZAPAN an intense peak centred at around 145 Å is observed as well as another a very small, weak one at 700 Å, indicating modification of pore texture in agreement with the formation of a new intercalated compound with a basal spacing of 18 Å.

3.6. Surface morphology

Figures 7a and b show the morphology of ZANIL and ZAPAN obtained by an SEM. ZANIL and ZAPAN show typical morphology of LDH and its intercalated compound, which points to the existence of agglomerates of compact and non-porous granule structure.

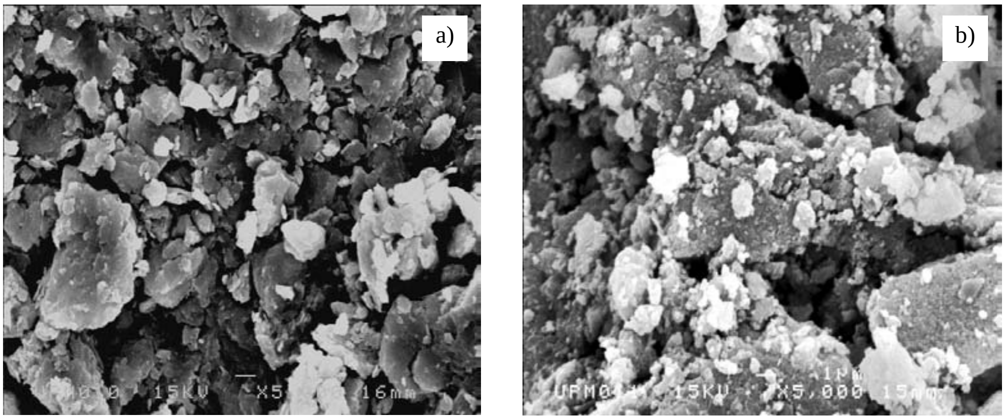

Fig. 7. Surface morphology for: a) ZANIL, b) ZAPAN

As shown in the figures, there is no significant difference in the morphology of the two samples. It is also very similar to the morphology of other intercalated compounds, such as Zn-Al-ibuprofen LDH, Mg-Al-poly(acrylic acid) LDH, Mg-Al -poly(vinylsulfonate) LDH and Mg-Al-poly(styrenesulfonate) LDH [2, 8].

4. Conclusion

Layered organic-inorganic intercalates can be prepared by using PA as a guest in Zn-Al LDH inorganic hosts by a self-assembly technique, with Zn:Al ratio of the mother liquor of 4:1. PXRD shows that the basal spacing of the Zn-Al LDH with nitrates as the intergallery anions expanded from 9 Å to 18 Å to accommodate the PA anions for the formation of the Zn-Al LDH-PA layered inorganic-organic hybrid intercalated compounds. The FTIR study shows that the intercalated compound resembled the spectra of PA and ZANIL, indicating the presence of both functional groups in ZAPAN. It was also found that the BET surface area increases from 6 m^2/g to 90 m^2/g for the host (ZANIL) and the intercalated compound (ZAPAN), respectively, if 0.02 M PA is used for the synthesis of the latter. The pore texture of the resulting materials also changed as a result of the intercalation and the expansion of the basal spacing together with pore formation between the crystallite during the formation of the resulting layered intercalated compound. The morphologies of the LDH and its intercalated compound are quite similar, showing agglomerates and non-porous structures, the intercalation not very much influencing the morphology of the resulting intercalated compound.

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