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FORMATION OF ZINC ALUMINIUM LAYERED DOUBLE HYDROXIDES -4(2,4-DICHLOROPHENOXY)BUTYRATE NANOCOMPISITES BY DIRECT AND INDIRECT METHODS

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Abstract

4-(2,4-dichlorophenoxy)butyric acid (DPBA) was intercalated between the interlamellae of Zn/Al layered double hydroxides (LDHs). Two methods of intercalation were adopted, (a) direct synthesis by co-precipitation of metal nitrates and DPBA and (b) ion exchange of LDH nitrate with the organic anion. The resulting materials were characterized by x-ray diffraction and infrared spectroscopy. Both methods afford well ordered nanocomposite materials at the same pH and ratio but at different concentrations. The x-ray diffraction patterns showed that the interlayer spacing distances increased from 8.9 Å to 28.7 Å and 29.4 Å for DPBA-LDH synthesized by ion exchange method and by direct method, respectively. The optimum condition were obtained at DPBA concentration of 0.2 M by direct co-precipitation method compared to 0.025 M by ion exchange method.

Abstrak

Asid 4-(2,4-diklorofenosil)butirik (DPBA) telah diinterkelasikan di antara ruang antara hidroksida berlapis ganda Zn/Al (LDHs). Penginterkelasian telah dilakukan dengan menggunakan dua kaedah iaitu (a) sintesis secara langsung dengan ko-pemendakan logam nitrat dan DPBA dan (b) pertukaran ion nitrat daripada LDH dengan anion organik. Produk telah dicirikan dengan menggunakan pembelauan sinar-x dan spektroskopi infra merah. Kedua kaedah tersebut telah menghasilkan sebatian nanokomposit yang tersusun pada pH dan nisbah yang sama tetapi pada kepekatan yang berbeza. Pola belauan sinar-x menunjukkan peningkatan ruang diantara dua lapisan daripada 8.9 Å kepada 28.7 Å dan 29.4 Å bagi DPBA-LDH yang masing-masing telah disintesis dengan menggunakan kaedah pertukaran ion dan secara langsung. Keadaan optimum bagi kepekatan DPBA yang disintesis menggunakan kaedah ko-pemendakan secara langsung adalah 0.2 M manakala 0.025 M bagi kaedah pertukaran ion.

Introduction

Hydrotalcite-like compounds, also called anionic clays or layered double hydroxide (LDHs) constitute a unique class of layered solids comprised of positively charged, brucite-like layers separated by charge balancing anions. The general formula that represents this class of material are $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+} (A^{m-})_{x/m}.nH_2O$, where M^{2+} is a divalent cation (Ca^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}), M^{3+} is a trivalent cation (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Mn^{3+}), A^{m-} is an interlayer anion (Cl^{-}, NO^{3-}, CIO^{4-}, CO^{3-}, SO_4^{2-} and many other inorganic anions).The x value i.e. the charge density is equal to the molar ratio, $M^{3+}/(M^{2+}+M^{3+})$. One of the most important properties of the hydrotalcite-like compounds is their high anionic exchange capacity, related to their lamellar structure, that allows the exchange of their original anions with those present in an aqueous solution [1, 2, 3]. Owing to rich intercalation chemistry of LDHs, these materials have extensive applications as catalysts, urea biosensors and supports, absorbents, optical and electric functional materials, flame retardants and polymer stabilizers [4, 5, 6, 7]. Recently, particular attention has been focused on LDHs based controlled release systems [8].

Synthesis, characterization and application of organo/LDHs nanocomposites prepared by the intercalation of organic substances into LDHs have been reviewed [9]. The intercalation of organic substances into LDHs has generally been accomplished by various methods, namely anion exchange, reconstruction, direct co-precipitation and hydrothermal methods [10, 11, 12, 13]. The co-precipitation and anion exchange method has often been used for the formation of organo LDH nanocomposites. A set of different methods of preparation

have been performed to insert [2-(2,6-dichlorophenylamino)-phenyl]acetic acid (DPAPAc) into a Mg/Al (2:1) LDHs and it was been shown that different methods give a different expansion of the interlayer spacing [14].
In this study, the intercalation DPBA into the interlayer of Zn/Al-LDH (R=3 and pH=7.5) by two different methods namely direct co-precipitation and anion exchange method were investigated. 4-(2,4-dichlorophenoxy)butyric acid (DPBA) (Figure 1) is one derivative of phenoxyalkane carboxylic acid that acts as a plant growth regulator as well as herbicides are commonly used for control of weeds in wheat, rice, maize and aquaculture. These compounds account for most herbicide production worldwide.

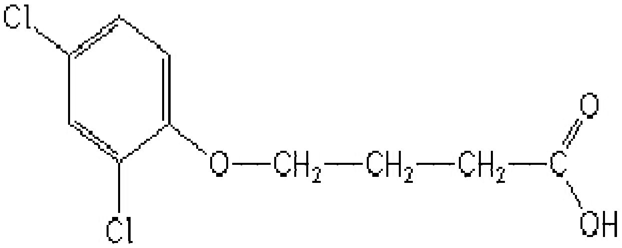


Figure 1: Structure of DPBA (4-(2,4-dichlorophenoxy)butyric acid)

Experimental

Characterization

Powder X-ray diffraction patterns were recorded from a range of 2-60° on an ITAL 2000 diffractometer using Cu K_a radiation at 40 kV and 30 mA. FTIR spectras of the materials were recorded over the range 400-4000 cm^{-1} on a Perkin-Elmer 1752X Spectrophotometer using the KBr disc method. A CHNS analyzer, model CHNS-932 of LECO Instruments, was used for CHNS analyses. The Zn to Al molar ratio of the resulting Zn/Al-LDH-nanocomposites was determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Perkin-Elmer spectrophotometer model Optima 2000DV under standard condition. Surface characterization of the materials was carried out by the nitrogen gas adsorption-desorption technique at 77 K using a Micromeritics ASAP 2000. Sample was degassed in an evacuated-heated chamber at 120 °C, overnight.

Synthesis

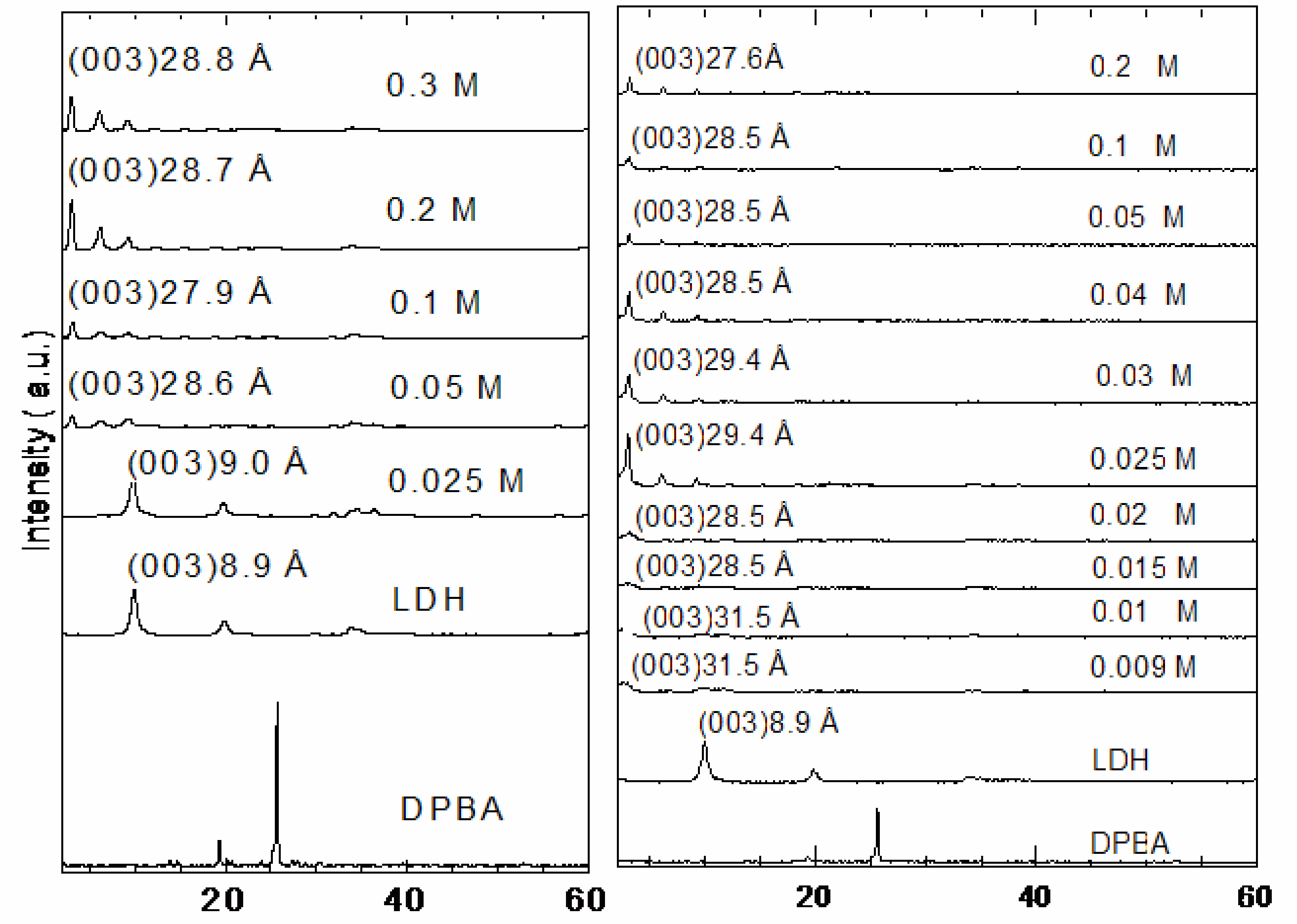
The preparative methods adopted in this study were direct co-precipitation and anion exchange. In the direct co-precipitation method, a mother liquor containing Zn^{2+} and Al^{3+} cations with Zn to Al initial molar ratio R_i = 3.0 and DPBA was prepared. The resulting solution was adjusted to pH 7.50 ± 0.02 by dropwise addition of aqueous NaOH (2.0 M). The concentrations of DPBA used were from 0.025 to 0.3 M and the reaction was carried out under nitrogen atmosphere. The precipitate was aged at 70 ^oC in an oil bath shaker for 18 hours. The synthesized material was then centrifuged, thoroughly washed with deionized water and dried in an oven at 70 ^oC. The resulting nanocomposite was then grinded into fine powder and stored in sample bottle for further use and characterizations.

In the anion exchange method, layered double hydroxides of Zn/Al with nitrate as the interlayer gallery anion was exchanged with DPBA (as guest anion) to form Zn/Al-DPBA nanocomposite. About 2.00 g Zn/Al-LDH was put in contact with 100 ml aqueous solution of DPBA and aged for 18 hours at 70 ^oC, at various concentrations (0.009 - 0.2 M) of guest anions solution. The solution was aged for another 18 hours at 70 ^oC. The slurry was centrifuged, washed with deionized water and then dried in an oven at 70 ^oC, ground and kept in sample bottle for further use and characterizations.

Results and Discussion

Figure 2 shows PXRD patterns of LDH and its intercalated compound, DPBA-LDH nanocomposites prepared using various concentrations of DPBA from 0.05 to 0.3 M by the direct co-precipitation method. As shown in Figure 2 the basal spacings, 27.9 – 28.8 Å were obtained for the nanocomposites synthesized at 0.05 – 0.3 M. No intercalation was observed at 0.025 M of DPBA. Comparatively, sample synthesized through the anion exchange method yielded basal spacing of 27.6 – 31.5 Å when 0.009 – 0.2 M DPBA were used. As shown in Figure 2 the basal spacing of LDH with nitrate as the interlamella anion was 8.9 Å similar to the value reported previously [15].

The expansion of basal spacing from LDH to DPBADI (Zn/Al-DPBA nanocomposite synthesis by direct method) and DPBAEX (Zn/Al-DPBA nanocomposite synthesis by anion exchange method) was due to the inclusion of DPBA into the LDH interlamella with orientations that warrant the expansion of the LDH lamella. DPBADI prepared using 0.2 M in direct co-precipitation and 0.025 M in anion exchange method produced sharp, symmetrical and intensive peaks, especially for the (003) peak. Relatively pure intercalated compound were obtained at the concentration indicated. All of the main diffraction characteristics of the intercalated sample prepared by both methods was similar and is a result of successful intercalation of DPBADI and DPBA EX prepared from 0.2 M and 0.025 M was subsequently used for further characterization.



(a) (b)

2q/degrees

Figure 2: PXRD patterns of DPBA-nanocomposites synthesized by (a) direct method and (b) ion exchange methods

The presence of the intercalation species in the Zn/Al LDH was also supported by FTIR results. The FTIR spectra of Zn/Al-LDH, DPBA-LDH and DPBA molecules in the region between 400-4000 cm^{-1} are illustrated in Figure 3.

The FTIR spectra for Zn/Al-LDH shows a broad and strong band in the range 3200-3600 cm^{-1} centered at 3419 cm^{-1} which is due to O-H stretching vibration of the surface and interlayer water molecules [1]. A band observed at 1638 cm^{-1} is assigned to the bending vibration of interlayer water molecules and a strong band at 1383 cm^{-1} is due to stretching vibration of NO_3^-. Bands in the lower frequency region correspond to lattice vibration modes such as the translation vibrations of Zn-OH at 622 cm^{-1} and deformation vibration of OH-Zn-Al-OH at 411 cm^{-1} [16,17].

The FTIR spectra of the pure DPBA is illustrated in Figure 3 and shows a broad band at 3419 cm^{-1} which can be attributed to the O-H stretching vibration. A sharp band at 1717 cm^{-1} is due to the stretching of C=O. Bands at 1472 cm^{-1} and 1402 cm^{-1} are attributed to stretching vibrations of aromatic ring C=C and strong bands at 1278 cm^{-1} and 1209 cm^{-1} are due to the symmetric and asymmetric stretching modes of C-O-C. A sharp band at 745cm^{-1} is attributed to C-Cl stretching [18].

The FTIR spectra of Zn/Al-DPBA nanocomposites synthesized with both methods, in Figure 3 show both the characteristic bands of pure DPBA and the typical LDH bands. This indicates that the DPBA anions have been intercalated into the interlayer galleries of the LDH. Some of the bands are slightly shifted in position, presumably because of the intercalation between DPBA anion and host layer. The bands at 1578, 1559, 1392 and 1390 cm^{-1} of the DPBADI and DPBAEX spectra are attributed to the stretching mode of the carbonate anion in a symmetric environment. The absence of the peak at 1383 cm^{-1} corresponding to nitrate anions in particular, confirms that all the interlayer nitrate anions have been fully replaced by DPBA.

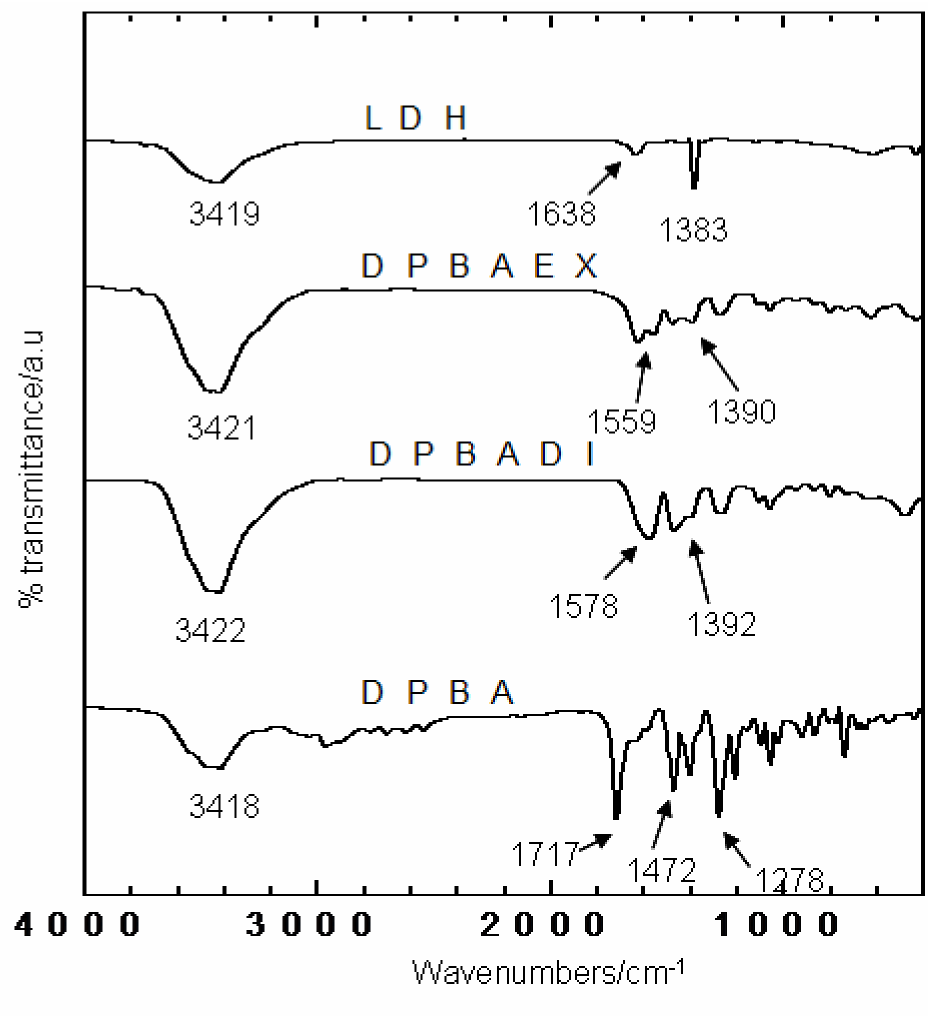


Figure 3: The FTIR spectra of LDH, DPBAEX, DPBADI and DPBA

Table 1 shows the elemental composition of LDH, DPBADI and DPBAEX. The ratio of the resulting Zn/Al (R$_f$) in LDH, DPBADI and DPBAEX are 2.8.3.0 and 2.3, compared to 3.0 in the initial ratio in the mother liquor. This shows that not all Zn^{2+} ions in the mother liquor were used for the formation of positively charged in LDH and DPBAEX nanocomposites.

CHNS analysis showed that LDH contains 3 % of nitrogen, which agrees nicely with the presence of a strong, sharp band at 1383 cm^{-1} in the FTIR spectra of LDH shown in Figure 3 that corresponds to the nitrate group.

The CHNS analysis also shows that both DPBADI and DPBAEX contained around 26 % of carbon that indicated that the same amount DPBA was intercalated into the interlayer lamella of LDH regardless of their method of preparation. As shown in Table 1, the percentage of DPBA intercalated into interlayer of LDH was 53.9-53.7 % with carbon content of about 26.4-26.1 %.

Table 1: Elemental composition of LDH, DPBA, DPBADI and DPBAEX

Compound	R_f	% C	% N	% DPBA (w/w)	BET surface area (m^2/g)	BJH pore diameter (Å)	Total pore volume (cm^{-3}/g)
LDH	2.8	0	3.1	-	1.3	163	0.005
DPBADI	3.0	26.4	0	54.7	4.6	151	0.019
DPBAEX	2.3	26.1	0	53.9	2.3	125	0.009

The percentage of carbon in DPBA is 47.3 compared to theoretical value 48.1.

The nitrogen adsorption-desorption isotherms for LDH, DPBADI and DPBAEX show features which can be ascribed to Type IV in IUPAC classification, indicating mesopore-types of material[19]. The adsorption of LDH and nanocomosites increased slowly at low pressure in the range 0.0-0.8 and followed by rapid adsorption of the absorbent at 0.8 and above relative pressure. The desorption branch of the hysteresis loop for DPBADI is much narrower compared to LDH and DPBAEX, indicating different pore texture of the resulting materials.

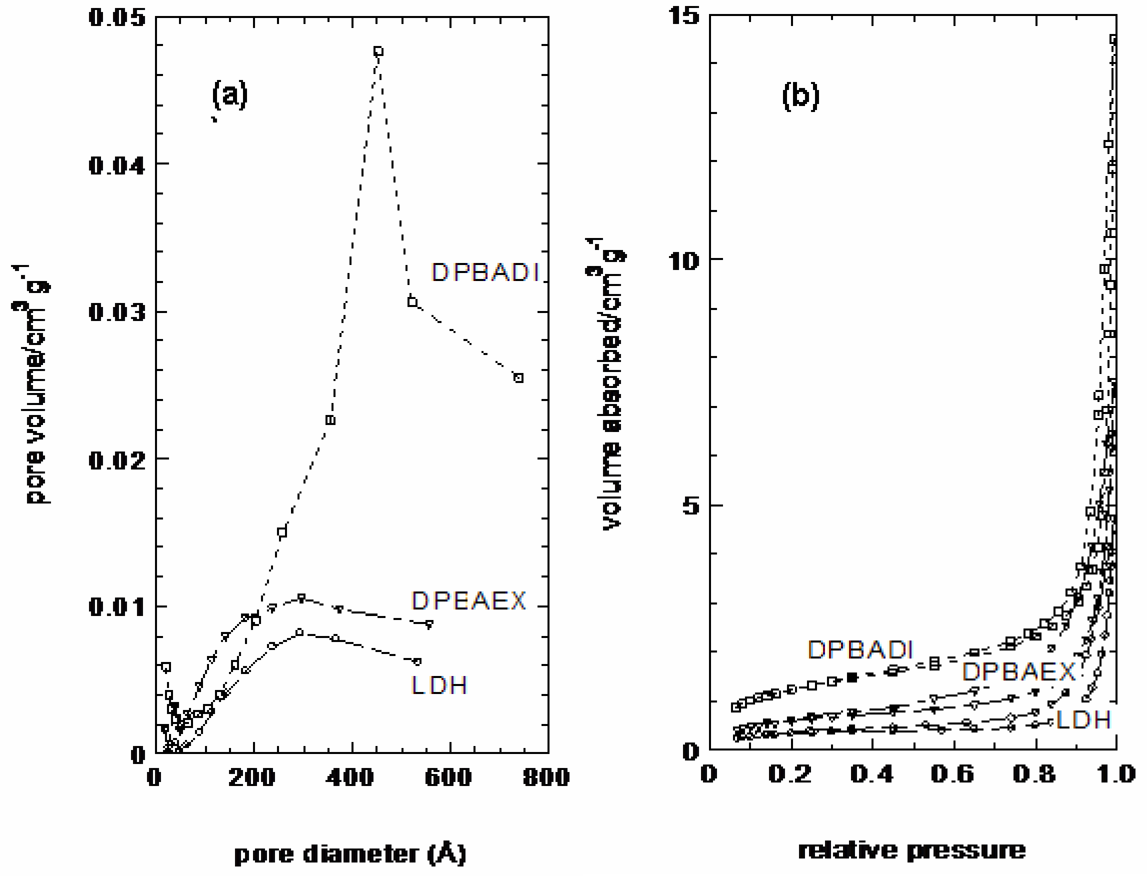


Figure 3: (a) BJH pore size distribution and (b) adsorption-desorption isotherms for LDH, DPBADI and DPBAEX

The values for specific surface areas, determined by BET method are shown in Table 1, and this shows that intercalation has increased the value from 1.3 to 4.6 m^2/g for LDH and DPBAEX, DPBADI nanocomposites, respectively. The BJH pore size distribution for DPBADI and DPBAEX are shown in Figure 3. The results of N_2 adsorption-desorption isotherm, for both nanocomposites show mesoporous property, with BJH pore diameter for DPBADI and DPBAEX lower than that of LDH, amounting to 151 Å, 125 Å and 163 Å. A sharp double-peaked pore size distribution was observed for DPBADI centered at around 400 Å and 500 Å and the intensity of pore volume distribution shows that DPBADI is higher than DPBAEX. Generally, the total pore volume (Table 1) shows the increasing values of LDH to DPBA nanocomposites due to insertion of DPBA into the LDH interlayer.

Conclusion

Nanocomposites of Zn/Al layered double hydroxides-DPBA have been synthesized by using direct and indirect methods. The resulting materials were obtained using 0.2 M DPBA by direct co-precipitation method and 0.025 M by ion exchange method. The obtained materials show basal spacing increase from 8.9 Å to 28.8 Å, which indicated the intercalation of DPBA into interlamella of Zn/Al layered double hydroxides was successfully accomplished. Elemental analysis of the nanocomposites showed that 55 % and 62 % of DPBA were intercalated into the interlayer using the direct and indirect method, respectively. The introduction of DPBA into the interlayer space of LDH is evidenced by FTIR spectra, which showed the existence of absorption bands for nanocomposites resembling a mixture of both the DPBA and LDH absorption characteristics, which again indicates that DPBA was successfully intercalated into the Zn/Al interlayer. DPBAEX showed pore size distribution similar to LDH. Presumably the pore texture was not modified very much by the intercalation process using ion exchange method. However in the case of DPBADI in which the co-precipitation was adopted the pore size distribution showed completely different behaviors.

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