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Synthesis of a Novel Organic-Inorganic Cloprop-Zinc-Aluminium-Layered Double Hydroxide Nanohybrid

Sintesis Satu Bahan Novel Nano-Hibrid Organik-Bukan Organik daripada Dua Lapisan Hidroksida Cloprop-Zink-Alumunium

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Abstract

Phenoxyherbicides, namely 2(3-chlorophenoxy) propionic acid (cloprop) was intercalated into the interlamellae of Zn/Al-layered double hydroxide (LDH) by direct co-precipitation method. Powder x-ray diffraction patterns of the resulting materials show that the interlayer spacing expanded from 8.9 Å in the Zn/Al-LDH to 20.5 Å in the nanohybrid. This together with FTIR and compositional studies show that cloprop was successfully intercalated into the Zn/Al-layered double hydroxides interlayer for the formation of organic-inorganic nanohybrid. TGA/DTG thermal analysis shows that hybridization of cloprop into the interlayers of Zn/Al-LDH host enhanced the thermal stability of cloprop.

Keywords Zn/Al-layered double hydroxide; 2(3-chlorophenoxy)propionic acid; nanohybrid; direct co-precipitation.

Abstrak

Fenoksiherbisida, 2(3-klorofenoksi) propionik asid (cloprop) telah diinterkalasikan ke dalam ruang antara lapisan hiroksida berlapis ganda Zn/Al (Zn/Al-LDH) dengan menggunakan kaedah pemendakan terus. Corak pembelauan sinar-x serbuk bagi bahan yang terhasil menunjukkan pembesaran ruang antara lapisan daripada 8.9 Å bagi Zn/Al-LDH kepada 20.5 Å bagi bahan nanohibrid. Keputusan FTIR dan kajian komposisi menunjukkan bahawa cloprop telah berjaya diinterkelasikan ke dalam ruang antara lapisan hidroksida berlapis ganda Zn/Al-LDH. Analisis terma TGA/DTG menunjukkan bahawa penghibridan cloprop ke dalam ruang antara lapisan perumah Zn/Al-LDH dapat menambahkan kestabilan terma bagi cloprop.

Kata kunci hiroksida berlapis ganda Zn/Al; 2(3-klorofenoksi)propionik asid; nanohibrid; kaedah pemendakan terus.

Introduction

Layered inorganic materials, especially layered double hydroxides (LDHs) have attracted the interest of researchers in this area, not only as a subject for fundamental studies but also for various industrial applications. This is because of their attractive properties which can be tailor-made for specific purposes. LDHs have been studied for their potential use in a wide range of important areas such as catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical sciences and environmental applications (Cavani *et al,*. 1991; Newman *et al*., 1998; Rives, 2001; Duan, 2005; Evan *et al*., 2006].

The structure of LDH consists of brucite-like sheets in which divalent cations are partially replaced by trivalent cations. Consequently, the layers are positively charged and interlayered anions, A^{n-}, neutralize these charges and can be replaced by other anions via anion exchange process (Cavani *et al.*, 1991). The LDH general formula is: $(M^{2+}_{1-x} M^{3+}_{x} (OH)_2)_x(A^{n-})_{x/n}.mH_2O$, where M^{2+} = Mg, Zn, Ni, Cu, Mn; and M^{3+} = Al, Cr, Fe; x=0.2–0.4. A is an anion, such as $Cl^{-,}$ CO_3^{2-}, SO_4^{2-}, NO_3 and ClO_4^- (Newman *et al*., 1999). The intercalation process can be approached by two routes: direct co-precipitation and indirect ion exchange process. In the direct route, the guest anions can be intercalated by spontaneous self-assembly technique (Messersmith *et al.*, 1995), in which the LDH and the guest anions are included in the mother liquor. On the other hand, in the indirect route, intercalation of the guest anions can be done by first preparing the LDH followed by modification and finally intercalation of the guest molecules into the interlayer (Bonnet *et al.*, 1996).

In the present work, 2(3-chlorophenoxy) propionic acid, known as cloprop (Figure 1) has been intercalated into Zn/Al-layered double hydroxide (Zn/Al-LDH) by direct co-precipitation method. Cloprop is one of the derivative of phenoxyalkane carboxylic acid that acts as a plant growth regulator as well as herbicides, which is commonly used for control of weeds in wheat, rice, maize and aquaculture (Walker, 2001).

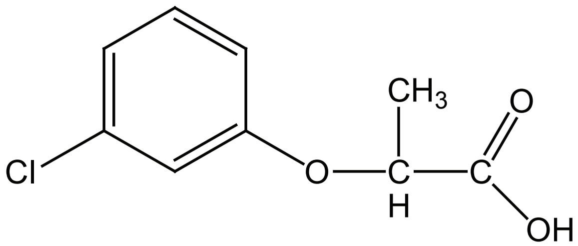

Figure 1 Structure of 2(3-chlorophenoxy) propionic acid (cloprop)

Materials and Method

All chemicals used in this synthesis were obtained from various chemical suppliers and used without further purification. All solutions were prepared using deionized water. All the reactions were carried out in an inert atmosphere of nitrogen.

The preparation of the nanohybrid was carried out by using the direct co-precipitation method. A mother liquor containing Zn^{2+} and Al^{3+} cations with Zn to Al initial molar ratio, R = 3.0 and 0.025 - 0.3 M cloprop were prepared. The resulting solution was adjusted to pH 7.50 ± 0.02 by dropwise addition of an aqueous NaOH (2.0 M). The resulting precipitate was aged at 70 °C in an oil bath shaker for 18 hours. The synthesized material was then centrifuged, thoroughly washed with deionized water and then dried in an oven at 70 °C. The resulting nanohybrid was then powdered and stored in a sample bottle for further use and characterizations.

Powder X-ray diffraction (PXRD) patterns were recorded from 2° - 60° on an ITAL 2000 diffractometer using Cu K_{α} radiation at 40 kV and 30 mA. FTIR spectra of the materials were recorded over the range 400 - 4000 cm^{-1} on a Perkin-Elmer 1752X Spectrophotometer using KBr disc method. The elemental composition of the samples and the Zn/Al molar ratio of the resulting nanohybrid and Zn/Al-LDH were determined by using inductively couple plasma-atomic emission spectrometry (ICP-AES) using a Perkin Elmer Spectrophotometer model Optima 2000DV under standard conditions and CHNS analyzer model CHNS-932 (LECO). Thermogravimetric and differential thermogravimetric analyses (TGA/DTG) were carried out using a Mettler Toledo TGA/DTA 851 thermogravimetric analyzer with heating rate of 10 °C min^{-1} between 35-1000 °C, under nitrogen flow rate of about 50 μl min^{-1}.

Results and Discussion

In Figure 2, PXRD patterns of Zn/Al-LDH and its intercalated compound, cloprop-Zn/Al-LDH nanohybrid prepared using various concentrations of cloprop from 0.025 M to 0.3 M by the direct co-precipitations method. As shown in Figure 2 the basal spacing of Zn/Al-LDH with nitrate as the interlamella anion is 8.9 Å similar to the value reported previously compared to the synthesized nanohybrids, 20.1 Å - 20.5 Å (Miyata, 1980). The expansion of the interlayer spacing of Zn/Al-LDH with nitrate as the counter anion compared to the nanohybrid, i.e. when cloprop was exchanged with the nitrate indicating the successful intercalation of the phenoxyherbicides anion into the interlamellae region. Based on the PXRD patterns given in Figure 2, intercalation of cloprop prepared at 0.3 M was considered as the high crystallinity phase pure, well ordered nanohybrid in which up to 5 harmonics can be observed. This material was then subsequently used for further characterization and labeled as CPPADI.

Figure 3 shows FTIR spectra of the Zn/Al-LDH, cloprop and CPPADI. Zn/Al-LDH spectrum shows a broad absorption peak in the region 2800–3800 cm^{-1} centered at 3454 cm^{-1} and is assigned as O–H stretching mode and deformation vibration of the LDH layer or interlayer water molecules. A band observed at 1637 cm^{-1} is assigned to the bending vibration of interlayer water molecules and NO^{-}_{3} gives a very strong absorption peak at 1378 cm^{-1}, and this peak was disappeared after the intercalation process, supporting that NO^{-}_{3} was completely replaced by the cloprop. A band in the lower frequency region corresponds to the lattice vibration mode such as the translation vibrations of Zn-OH can be observed at 611 cm^{-1} and deformation vibration of OH-Zn-Al-OH at 441 cm^{-1} (Fogg *et al*., 1998; Choy *et al*., 2000).

The FTIR spectrum of the pure cloprop is illustrated in Figure 3 and shows a broad band at 3459 cm^{-1} which can be attributed to the O-H stretching vibration. A sharp band at 1713 cm^{-1} is due to the stretching of C=O. Bands at 1469 cm^{-1} and 1400 cm^{-1} are attributed to stretching vibrations of aromatic ring, C=C and strong bands at 1288 cm^{-1} and 1217 cm^{-1} are due to the symmetric and asymmetric stretching modes of C-O-C. A sharp band at 854 cm^{-1} is attributed to C-Cl stretching (Choy *et al.*, 2000).

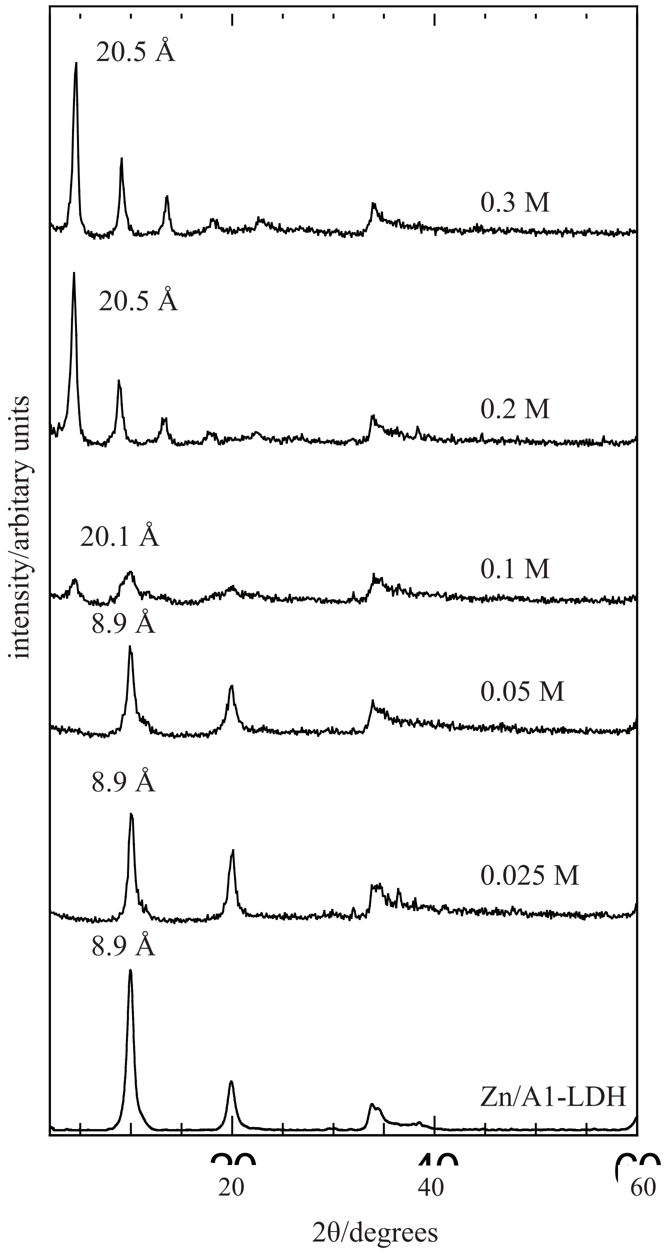

Figure 2 PXRD patterns of Zn/Al-LDH and its nanohybrids prepared at various concentrations of cloprop, 0.025-0.3 mol/L

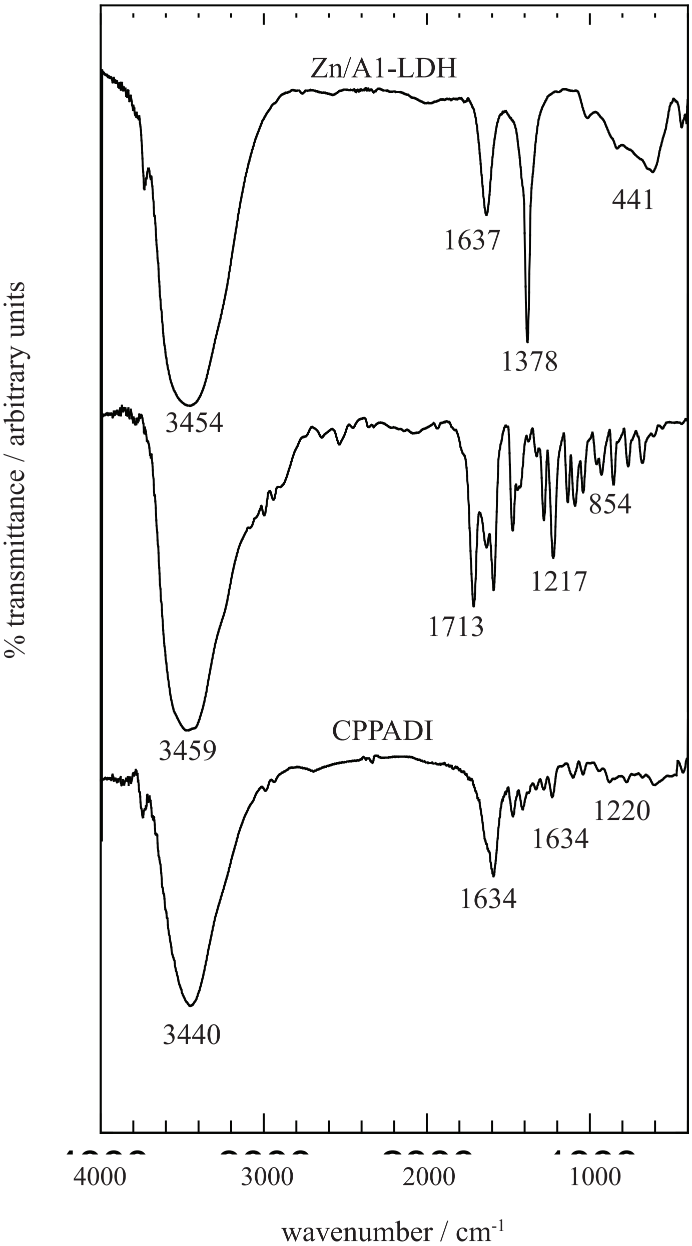

Figure 3 FTIR spectra of Zn/Al-LDH, cloprop and the nanohybrid, CPPADI

The FTIR spectrum of CPPADI in Figure 3 shows that the spectrum resembles a mixture of both the FTIR spectra of cloprop and Zn/Al-LDH, indicating that both functional groups of cloprop and Zn/Al-LDH are simultaneously present. The absence of the peak at 1378 cm^{-1} which is due to nitrate anion confirms that the interlayer nitrate counter anions have been fully negated by cloprop during the synthesis.

Table 1 Basal spacing and chemical composition of the host, Zn/Al-LDH and the nanohybrid, CPPADI

Sample	d Å	Zn/Al molar ratio	molecular fraction (x_{Zn})	N (%)	C (%)	[a]anion (%w/w)
Zn/Al-LDH	8.9	2.8	0.74	3.0	0.0	-
CPPADI	20.5	2.9	0.74	0.0	20.6	38.2

[a] = estimated from CHNS analysis based on pure cloprop.

Table 1 shows the elemental composition of Zn/Al-LDH and CPPADI. The ratio of the resulting Zn/Al (R_f) in Zn/Al-LDH and CPPADI is 2.8 and 2.9, respectively compared to 3.0 for the initial molar ratio in the mother liquor. This shows that the ratio was adjusted accordingly to balance the charge of the anions, either nitrate or cloprop in Zn/Al-LDH and CPPADI nanohybrid, respectively. CHNS analysis shows that Zn/Al-LDH contains 3 % nitrogen, which agrees nicely with the presence of a strong, sharp band at 1383 cm^{-1} in the FTIR spectrum of Zn/Al-LDH as shown in Figure 3, which corresponds to the nitrate group. The CHNS analysis also shows that CPPADI contained around 20.6 % carbon which confirmed that substantial amount of cloprop was actually intercalated into the interlayer lamellae of Zn/Al-LDH (Hussein *et al.*, 2010). The percentage loading of cloprop intercalated into interlayer of Zn/Al-LDH was estimated to be 38.2 %.

The TGA-DTG thermograms of Zn/Al-LDH, cloprop and CPPADI nanohybrid are shown in Figures 4(a, b and c). In the case of pure cloprop, there are two thermal events which can be observed at 204.3 °C and 336.7 °C, attributed to the decomposition and subtle combustion of cloprop with weight loss of 98.3 %. The TGA/DTG profiles of Zn/Al-LDH shows four thermal events of weight loss which occurred at 112.9 °C, 234.8 °C, 304.3 °C and 369.1 °C, with weight loss of 6.8 %, 15.6 %, 5.9 % and 7.5 %, respectively. The first weight loss in Zn/Al-LDH 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. The third and fourth weight losses which are almost complete at 370 °C, correspond to removal of hydroxyl group from brucite-like layers and the removal of interlayer anions, respectively.

The TGA-DTG curves of CPPADI reveal four distinguishable weight loss steps occurred at 86.3 °C, 191.0 °C, 350.9 °C and 860.8 °C with losses of 9.0 %, 7.5 %, 31.7 % and 20.5 %, respectively. The first step weight loss is due to the removal of surface physisorbed water molecules and the second stage was attributed to the removal of interlayer anion and dehydroxylation of the hydroxyl layer. The third and fourth weight losses above 300 °C correspond to the major decomposition/combustion of the organic moiety in the interlayer of the nanohybrid, leaving only a relatively less volatile metal oxide. For cloprop and the Zn/Al-LDH, thermal studies show that the temperature maxima at 204.3 ^oC and 234.8 ^oC are observed compared to 350.9 ^oC for the CPPADI nanohybrid. This indicates that cloprop

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encapsulated into the inorganic interlamellae is thermally more stable than their counterpart in the sodium salt form.

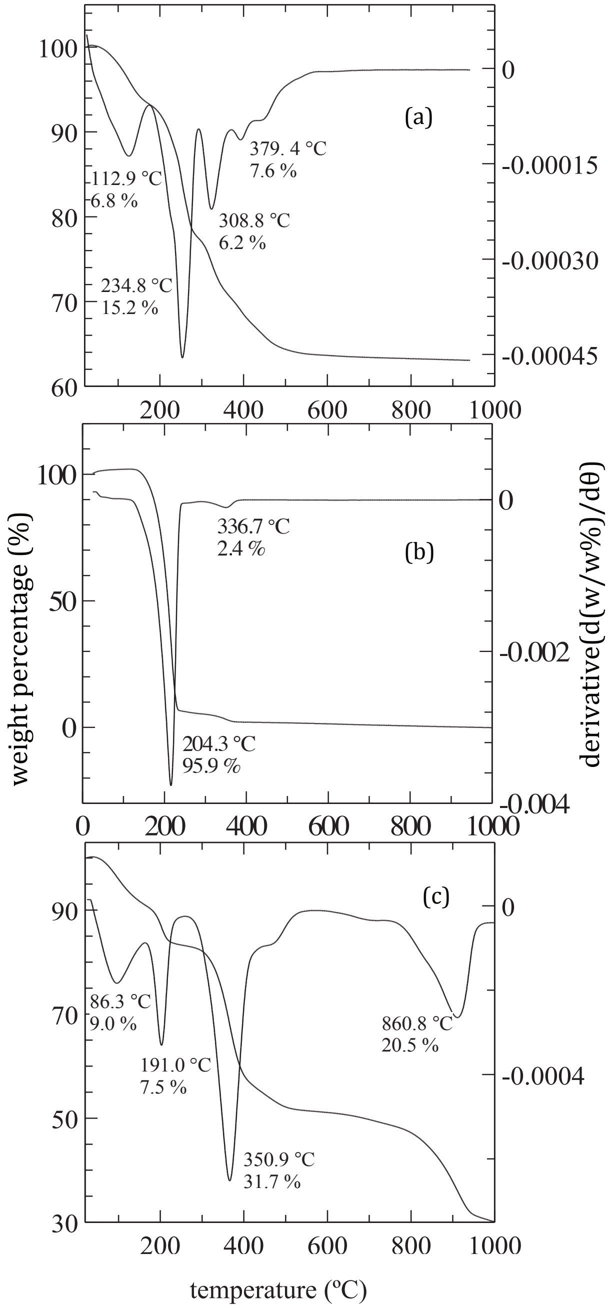

Figure 4 DTA-DTG thermograms of Zn/Al-LDH (a), cloprop (b) and the nanohybrid, CPPADI (c)

Conclusions

Well ordered, pure phase hybrid organic-inorganic layered material, Zn/Al-cloprop nanohybrid (CPPADI) could be synthesized by adopting self assembly method or the so called co-precipitation method with the molar ratio of Zn to Al was set at 3. Powder x-ray diffractograms show that the basal spacing of the Zn/Al-layered double hydroxide expanded from 8.9 Å when nitrate is present as the counter anion, compared to around 20.5 Å when cloprop was intercalated for the formation of a new nanohybrid. Loading percentage of cloprop in the nanohybrid was estimated to be 38.2 %. FTIR study shows the absorption bands of the nanohybrid resembling a mixture of cloprop and Zn/Al-LDH absorption characteristics, which again indicates that cloprop was actually intercalated into the Zn/Al interlayers. Thermal analyses show that cloprop is much more stable in the intercalated form compared to its counterpart in the acid form.

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