Journal of Industrial and Engineering Chemistry 22 (2015) 63–69

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

The effect of the divalent metal on the intercalation capacity of stearate anions into layered double hydroxide nanolayers

Mahboobeh Eili [a,*], Kamyar Shameli [b,**], Nor Azowa Ibrahim [b], Mansor Bin Ahmad [b], Wan Md Zin Wan Yunus [c]

[a] Faculty of Basic Sciences and Advanced Technologies, University of Science and Culture, Park Avenue, Ashrafi Esfahani Boulevard, Tehran IR14536-33143, Iran
[b] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang, Selangor 43400, Malaysia
[c] Department of Chemistry, Centre for Defence Foundation Studies, National Defence University of Malaysia, Kuala Lumpur 57000, Malaysia

ARTICLE INFO

Article history:
Received 21 February 2014
Accepted 16 June 2014
Available online 24 June 2014

Keywords:
Layered double hydroxide
Comparison
Intercalation capacity
Elemental analysis
Thermogravimetric analysis

ABSTRACT

A comparison has been made of the intercalation capacity of the stearate anions into the two different anionic clays: magnesium aluminum layered double hydroxide (Mg_3Al LDH) and zinc aluminum layered double hydroxide (Zn_3Al LDH). The anionic clays Mg_3Al LDH and Zn_3Al LDH were firstly prepared by co-precipitation method from nitrate salts solution and then modified by stearate anions through an ion exchange reaction. The properties, morphologies and ion exchange ability of these two clays have been studied by XRD, TGA, SEM, TEM and CHNS that show the ability of Zn_3Al LDH to capture stearate anions is greater than Mg_3Al LDH.

Introduction

Layered structure solids are very useful materials because of their wide potential applications in different fields such as catalysts [1], ion exchangers [2], sorbents [3], and electrochemistry [4]. They can divided into different groups, taking into account the charge excess within the layers, include negatively charged layers solids like montmorillonite, positively charged layers solids like layered double hydroxide (LDH) and neutrally charged layers such as mica and graphite [5]. Among these materials both phyllosilicate clays and LDHs have attracted an increasing amount of attention due to the presence of electrical charges within the layers and therefore their capability to ion-exchange that is an important property for different applications.

However, LDHs present certain specific advantages, which are lacking in layered silicates type nanoclays such as their relative ease and low cost of synthesis, thermal and chemical stability, surface properties, nontoxicity, adjustability of their particle size and aspect ratio by changing the reaction conditions and the wide range of choice for surfactants like fatty acid salts, sulfonates, sulfates, phosphates, etc., that can intercalated between the layers for extensive applications in different fields [6–8].

Layered double hydroxides (LDHs) are anionic clays which can be represented as $[M(II)_{1-X}M(III)_X(OH)_2]^{X+}[A^{n-}_{X/n} \cdot mH_2O]^{X-}$ where M(II) and M(III) are divalent and trivalent cations, respectively, and A^{n-} is an exchangeable anion [9,10]. LDHs are composed of octahedral $M^{2+}(OH)_6$ brucite-like layers which are positively charged by the partial substitution of M^{3+} for M^{2+}. Thus, anions are intercalated into the interlayers in order to compensate the positive layer charges [11,12]. Every M(II) and M(III) ions which have similar ionic radius to accommodate in the holes of the close packed configuration of OH groups in the brucite-like layers can form LDH but depend on the nature of cations, the obtained LDH can have different physical characteristics such as surface basicity and ion exchange capacity [13,14]. LDHs with different cations, such as Mg, Mn, Fe, Co, Ni, Cu, and Zn for divalent cations and Al, Mn, Fe, Co, Ni, Cr, and Ga for trivalent cations have been studied, however, the most reported have been focused on using MgAl LDH and ZnAl LDH, since zinc, magnesium and aluminum yield more environmentally friendly materials [8,15–17].

Inorganic–organic nanocomposite materials with functional organic compounds immobilized into a layered inorganic matrix have potential to offer scientific and technological advantages, since the organized two-dimensional arrays of organic species between the interlayers can result in novel functions that are different to the typical functions of the individual organic species [18–23].

* Corresponding author.
** Corresponding author. Tel.: +60 3 8946 6775; fax: +60 3 8943 5380.
E-mail addresses: m_eili@yahoo.com (M. Eili), kamyarshameli@gmail.com (K. Shameli).

http://dx.doi.org/10.1016/j.jiec.2014.06.025
1226-086X/

The intercalation of organic anions such as carboxylate groups is an important aspect of layered double hydroxide (LDH) for further research into the development of interesting properties and potential application in the fields such as polymer/LDH nanocomposites [24–27] and drug delivery [28,29].

The intercalation of some short length chain fatty acids into different kinds of LDHs has been investigated [30]. However, apparently there is no report of comparison the intercalation capacity of the stearate anions into the Mg_3Al LDH and Zn_3Al LDH. In this study Mg_3Al LDH and Zn_3Al LDH matrices have been used for the intercalation of stearate anions to study the effect of divalent metal on the properties of pristine and modified LDHs.

Materials and methods

Materials

Magnesium nitrate hexahydrate and aluminum nitrate nonahydrate were supplied by HmbG, Germany. Zinc nitrate hexahydrate was purchased from Bendosen Laboratory Chemicals, Malaysia. Sodium hydroxide pellets was obtained from Merck, Germany. Sodium stearate was purchased from R & M chemicals, U.K. Chloroform was purchased from Merck, Germany and polylactide resin 4042D was supplied by Nature Works LLC, U.S.A. All the above commercial chemicals were used as received.

Synthesis of Mg_3Al LDH

The pristine Mg_3Al LDH with NO_3^- as interlayer anion was prepared by first adding dropwise an aqueous solution of NaOH (1 M) into a 250 ml solution containing exactly weighted of 19.22 g $Mg(NO_3)_2{\cdot}6H_2O$ and 9.38 g $Al(NO_3)_3{\cdot}9H_2O$ (with the mol ratio of 3–1 respectively) until pH 9 was obtained. During the co-precipitation process, nitrogen gas was bubbled throughout the reaction system to minimize the presence of CO_3^{2-} in the solution. The resulting suspension was then shaken at 100 rpm and 70 °C for 16 h. The slurry was filtered, washed thoroughly with deionized water and then dried at 60 °C to obtain the Mg_3Al LDH. The final product was ground and sieved using sieve to particles of less than 100 μm.

Synthesis of Zn_3Al LDH

The original Zn_3Al LDH with NO_3^- as interlayer anion was prepared by the same process of the synthesis of Mg_3Al LDH. The details were as followed: 22.30 g $Zn(NO_3)_2{\cdot}6H_2O$ and 9.38 g $Al(NO_3)_3{\cdot}9H_2O$ were dissolved into 250 ml deionized water. The pH of the solution was adjusted by dropwise addition of 1 M aqueous solution of NaOH under the nitrogen environment until pH 7.0 was obtained. After shaking of the resulting suspension at 100 rpm at 70 °C for 16 h, the precipitate formed was collected and washed with deionized water and then dried at 60 °C to obtain the original Zn_3Al LDH. The final product was ground and sieved using sieve with pore size of 100 μm.

Preparation of stearate-Mg_3Al LDH and stearate-Zn_3Al LDH

The stearate-modified LDHs were prepared by replacing the nitrate ions existing in the interlayers of the LDHs with stearate ions via ion exchange reaction using the following procedure. Exactly weighted of the dry Mg_3Al LDH or Zn_3Al LDH (1.00 g) was first transferred into 750 ml of a 0.003 M solution of sodium stearate and stirred for 24 h at room temperature for Mg_3Al LDH, while for Zn_3Al LDH the temperature was adjusted to 70 °C. The white solid obtained was then filtered, washed with deionized water three times and dried in a vacuum desiccator at room temperature.

Characterization techniques

X-ray diffraction (XRD) patterns of the LDHs and composites were recorded using a Shidmadzu XRD 6000 Diffractometer at 30 kV and 30 mA with Cu-K_α radiation of the wavelength of 1.5405 nm in 2θ range from 2 to 50°. Fourier transform infrared (FTIR) spectra of the materials were recorded on a Perkin Elmer, FTI 1650 Spectrum BX, England Spectrometer. Spectra were recorded from 400 to 4000 cm^{-1} using a KBr disk method. Scanning electron microscopy (SEM) images were obtained using a Philips XL30 environmental scanning electron microscope. The clean and dry samples were first coated with gold using a Bal-Tec SCD 005 sputter coater. The transmission electron microscopy (TEM) images were obtained by employing a transmission electron microscope Hitachi, H7100 with an accelerating voltage of 200 kV. The samples were dispersed in chloroform and diluted to the right concentration. The suspension was then dropped on to the TEM sample grid and allowed it to dry. The very thin layer on the grid was observed on the microscope. The percentage of carbon (C), hydrogen (H) and nitrogen (N) in the pristine and modified LDHs was determined by a LECO Corporation CHNS-932 Elemental Analyzer. The thermogravimetric analysis (TGA) of the samples was carried out by a Perkin Elmer Thermobalance TGA7. The samples were studied under a nitrogen gas atmosphere with a flow of 20 cm^3 min^{-1} using a scan rate of 10 °C min^{-1}.

Results and discussion

Characterization of Mg_3Al LDH, Zn_3Al LDH, stearate-Mg_3Al LDH and stearate-Zn_3Al LDH

The XRD patterns in the range of 2θ from 2 to 50° for the pristine and modified LDHs are shown in Figs. 1 and 2. It is apparent that both LDH and stearate-Mg_3Al LDH are crystalline in nature with well-defined layered structure. The basal spacing (d) of the LDHs or stearate-LDHs is calculated from the first diffraction peak using Bragg's equation, $n\lambda = 2d \sin\theta$, where n is equal to 1 for the ⟨0 0 3⟩ peak, λ is the wave length of Cu-K_α radiation, and θ is the half of the scattering angle. The intercalation of the stearate anions is clearly seen in each case by the significant increase in basal spacing (Table 1) compared with that in the nitrate precursor [31].

From the comparison of the basal spacing of stearate-Mg_3Al LDH and stearate-Zn_3Al LDH, it is apparent that the increment of the basal spacing in stearate-Zn_3Al LDH is clearly more than that of

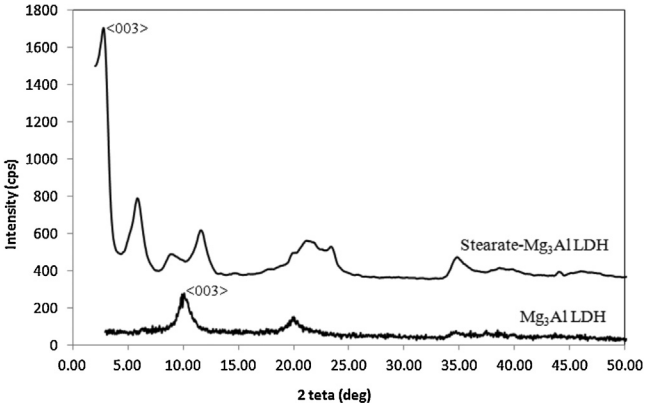

Fig. 1. XRD pattern of (a) pristine Mg_3Al LDH and (b) stearate-Mg_3Al LDH.