Journal of Solid State Chemistry 183 (2010) 1114–1119

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Synthesis and selective IR absorption properties of iminodiacetic-acid intercalated MgAl-layered double hydroxide

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ARTICLE INFO

Article history:
Received 9 November 2009
Received in revised form
6 March 2010
Accepted 14 March 2010
Available online 18 March 2010

Keywords:
Layered double hydroxide
Intercalation
Iminodiacetic acid
Selective IR adsorption
Polyethylene film

ABSTRACT

An MgAl-NO_3-layered double hydroxide (LDH) precursor has been prepared by a method involving separate nucleation and aging steps (SNAS). Reaction with iminodiacetic acid (IDA) under weakly acidic conditions led to the replacement of the interlayer nitrate anions by iminodiacetic acid anions. The product was characterized by XRD, FT-IR, TG-DTA, ICP, elemental analysis and SEM. The results show that the original interlayer nitrate anions of LDHs precursor were replaced by iminodiacetic acid anions and that the resulting intercalation product MgAl-IDA-LDH has an ordered crystalline structure. MgAl-IDA-LDH was mixed with low density polyethylene (LDPE) using a masterbatch method. LDPE films filled with MgAl-IDA-LDH showed a higher mid to far infrared absorption than films filled with MgAl-CO_3-LDH in the 7–25 μm range, particularly in the key 9–11 μm range required for application in agricultural plastic films.

1. Introduction

The growth of crops requires solar energy. The sun supplies the crops with solar energy during the day but the heat generated by the sunlight will be rapidly lost at night. The wavelengths of heat radiation energy emitted from the earth's surface to the atmosphere at night range from 7 to 25 μm (1428–400 cm^{-1}), with the peak being in the range 9–11 μm (1111–909 cm^{-1}) in the mid infrared region. Polymers such as low density polyethylene (LDPE) are widely used in agricultural plastic films in greenhouses, and the worldwide demand for plastic agricultural films reached 3.6 million tones in 2008. The heat retention properties of LDPE film may be enhanced by incorporating an inorganic material such as talc or china clay as an infrared absorbent [1–3]. However, these substances often contain impurities which promote degradation of the film. Their variable particle size also has an adverse effect on the stability of the film and has the additional disadvantage of reducing transmission of visible light and thermal short wavelength infrared radiation during the day. There is therefore a need to develop synthetic materials with high purity and controllable particle size as alternative inorganic fillers for use in agricultural plastic films.

Layered double hydroxides (LDHs) are a class of anionic clays whose general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdots mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent cations, respectively [4–6]. The interlayer anion (A^{n-}) may be varied over a wide range and the value of the stoichiometric coefficient (x) should generally be between 0.2 and 0.33 in order to obtain pure LDH phases. The laminar structure of LDHs and high charge density of their sheets are responsible for their anionic exchange and intercalation abilities which give them extremely varied potential technological applications in fields such as catalysis, electrochemistry, separation technology and medicine [7–10]. We have developed a new method for the synthesis of LDHs involving separate nucleation and aging steps [11,12], which has the advantage of giving materials with a much narrower range of particle size than can be obtained by conventional coprecipitation. As a result, when the material is incorporated in an LDPE film, the transmission of visible light and thermal short wavelength infrared radiation is higher than in films containing fillers with a wide range of particle size. MgAl-CO_3-LDHs strongly absorb infrared radiation in the range 7–8 μm (1428–1250 cm^{-1}), associated with the ν_3 vibrational mode of the carbonate anion, and is therefore used as an infrared absorbing filler in LDPE films [13–15]. It is far from ideal, however, because it is transparent at the wavelengths where the amount of radiant heat is a maximum.

In order to increase the efficiency of LDHs as a filler, it should be possible to take advantage of their anionic exchange ability to incorporate anions which have strong infrared absorption in the required range. Iminodiacetic acid (IDA) is a white crystalline substance used as an intermediate in the manufacture of chelating agents, surface-active agents, and complex salts, and is cheap and readily available. The chemical structural formula of IDA is shown in Fig. 1.

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0022-4596/$ - see front matter
doi:10.1016/j.jssc.2010.03.022

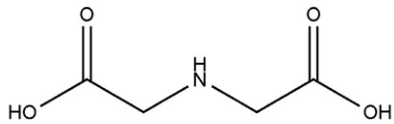

Fig. 1. The chemical structural formula of IDA.

IDA ($C_4H_7NO_4$) shows strong and broad infrared absorption in the range 1800–900 cm^{-1} by virtue of the presence of the C–N, N–H and COOH groups. So we decided to investigate the performance of LDHs containing iminodiacetic acid (IDA) anions as selective IR absorbing agents.

In this work, we use MgAl-NO_3-LDHs prepared by the method of separate nucleation and aging steps [11,12] as a precursor, in order to take advantage of the much narrower range of particle size of the material prepared using this method. Reaction of an MgAl-NO_3-LDH precursor with IDA anions was carried out under mildly acidic conditions. The resulting MgAl-IDA-LDH product was dispersed in LDPE and fabricated into MgAl-IDA-LDH/LDPE films. The infrared absorbing ability of the film was compared with LDPE film containing MgAl-CO_3-LDH.

2. Experimental section

2.1. Chemicals

$Mg(NO_3)_2 \cdots 6H_2O$, $Al(NO_3)_3 \cdots 9H_2O$, NaOH and Na_2CO_3 were all of A.R. grade. Iminodiacetic acid ($C_4H_7NO_4$) was C.P. grade purchased from Sinopharm Chemical Reagent Co. Ltd. Low density polyethylene (LDPE) resin 1I2A was purchased from China Sinopec Yanshan Chemical Corporation. Deionized water was used in all experiments and it had a conductivity of less than 10^{-6} S cm^{-1}.

2.2. Preparation of MgAL-NO_3-LDH precursor

An aqueous mixed salt solution containing Mg^{2+} and Al^{3+} was prepared with Mg/Al molar ratio of 2.0 in which the concentration of Mg^{2+} was 0.8 mol L^{-1}. An aqueous mixed base solution containing NaOH was prepared with $n(\mathrm{NaOH})/[n(\mathrm{Mg}^{2+})+n(\mathrm{Al}^{3+})]=2.0$. The mixed salt solution was mixed with the base solution in a modified colloid mill reactor following the procedure developed in our laboratory [11,12,16]. The resulting slurry was aged at reflux temperature for 6 h. The precipitate was then filtered, and washed until the washings reached pH$\sim$7. Some wet filter cake was set aside for the preparation of MgAl-IDA-LDH and the remainder was dried in a desiccator to afford MgAl-NO_3-LDH powder. This process allowed the amount of solid in the wet cake to be estimated.

2.3. Preparation of MgAl-IDA-LDH

IDA (5.3 g, 0.04 mol) was dissolved in deionized water, from which the CO_2 had been removed by boiling and then cooling under nitrogen. The pH value of the solution was adjusted to around 4.2 by the addition of NaOH. The wet cake of MgAl-NO_3-LDH (35.2 g, calc. 0.02 mol of NO_3^-) was dispersed in deionized water and added dropwise into the reactor, with the pH being maintained at 4.5 during the whole reaction. The resulting slurry was aged at reflux temperature for 6 h. The reaction was carried out under a stream of N_2. The precipitate was then filtered, washed and dried in a desiccator to obtain the MgAl-IDA-LDH powder.

2.4. Preparation of MgAl-CO_3-LDH

In order to compare the infrared absorption ability of MgAl-IDA-LDH with that of MgAl-CO_3-LDH, MgAl-CO_3-LDH was prepared. An aqueous mixed salt solution containing Mg^{2+} and Al^{3+} was prepared with Mg/Al molar ratio of 2.0 in which the concentration of Mg^{2+} was 0.8 mol L^{-1}. An aqueous mixed base solution containing NaOH and Na_2CO_3 was prepared with $n(\mathrm{CO_3^{2-}})/n(\mathrm{Al}^{3+})=2$ and $n(\mathrm{NaOH})/[n(\mathrm{Mg}^{2+})+n(\mathrm{Al}^{3+})]=1.6$. The mixed salt solution was mixed with the base solution in a modified colloid mill reactor following the procedure developed in our laboratory [11,12,16]. The resulting slurry was aged at reflux temperature for 6 h. The precipitate was then filtered, washed and dried in a desiccator to obtain the MgAl-CO_3-LDH powder.

2.5. Preparation of LDH/LDPE films

MgAl-IDA-LDH and MgAl-CO_3-LDH were mixed with LDPE in a double-roller mixer, with the final content of LDHs fixed at 4 wt.%. In order to disperse LDHs in LDPE uniformly, masterbatch technology was used: 4 g of LDPE granules and 3 g of LDHs were blended in double-roller mixer for 15 min at 130 °C to give a masterbatch. 1.4 g of the masterbatch was then blended with 13.6 g of LDPE for 5 min at 130 °C. The resulting composites were then moulded at 160 °C into films with a thickness of 100 μm.

2.6. Analysis and characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 powder X-ray diffractometer (Cu Kα radiation, $\lambda=0.15406$ nm) between 3° and 70° with a scan speed of 5° min^{-1}. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer using the KBr pellet technique (sample/KBr = 1/100 weight ratio) in the range 4000–400 cm^{-1} at a resolution of 2 cm^{-1}. The compositions of Mg and Al in samples were determined with a Shimadzu ICPS-7500 inductively coupled plasma (ICP) emission spectrometer using solutions prepared by dissolving the samples in dilute HNO_3 and the content of carbon and nitrogen was determined using a Elementar Vario EI elemental analyzer. Thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained on an HCT-2 instrument in the temperature range 60–650 °C with a heating rate at 10 °C min^{-1} in air. The morphology of the LDH particles was examined by scanning electron microscopy (SEM) using a Hitachi S-4700 microscope. A Hitachi H-800 transmission electron microscope (TEM) was used to observe the dispersion of LDH fillers in LDPE. The LDH/LDPE composite was microtomed as very thin slices using a cryo-microtome in liquid nitrogen and then imaged by TEM.

2.7. Infrared absorbance and visible light transmittance tests

The infrared absorbance was recorded on a Bruker Vector 22 instrument. The average transmittance over different wavelength ranges was calculated by the integration method. The visible light transmittance was recorded using a Shimadzu UV-2501PC instrument in the wavelength range 380–780 nm using air as reference. The average transmittance was calculated by the integration method.