Dyes and Pigments 91 (2011) 120–125

Contents lists available at ScienceDirect

Dyes and Pigments

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

Fabrication and properties of Acid Yellow 49 dye-intercalated layered double hydroxides film on an alumina-coated aluminum substrate

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ARTICLE INFO

Article history:
Received 18 December 2010
Received in revised form
5 March 2011
Accepted 7 March 2011
Available online 16 March 2011

Keywords:
Film
Intercalation
Anion-exchange
Layered double hydroxides
Thermal stability
Light fastness

ABSTRACT

The Acid Yellow 49(4-[2-(5-amino-3-methyl-1-phenyl-1H-pyrazol-4-yl)diazenyl]-2,5-dichloro benzenesulfonic acid) (denoted as PPDB) anion intercalated layered double hydroxides (LDH) film was fabricated through an ion-exchange method using a ZnAl–NO_3–LDH/alumina/aluminum film as precursor. The prepared film was investigated by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Thermogravimetric–differential thermal analysis (TG–DTA), UV–visible spectroscopy and the CIE 1976 L*a*b* color difference method. XRD patterns and FT-IR spectra confirm the successful incorporation of PPDB anions into the interlayer galleries of ZnAl–LDH with an expansion of d-spacing from 0.88 nm to 2.51 nm and the disappearance of characteristic absorption band of NO_3^- anions at 1384 cm^{-1}. The SEM morphologies show that the LDH films are mainly oriented with *c* axis of the platelet crystallites parallel to the substrate surface. Additionally, the obtained results suggest that the intercalation of PPDB into ZnAl–LDH host markedly improve the thermal stability and light fastness of PPDB.

1. Introduction

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds, are a class of anionic layered clays with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$ [$0.2 < x < 0.33$, typically abbreviated as $M^{2+}_{(1-x/x)}/M^{3+} - A - LDH$], where M^{2+} and M^{3+} individually stand for various di- and trivalent metal cations in the brucite-like host layers, and A^{n-} represents the interlayer guest anions in the hydrated interlayer galleries [1,2]. Based on their anion-exchange capability and compositional flexibility, LDH materials have received a great deal of attention due to their widespread applications as flame retardants [3], catalysts or catalyst precursors [4,5], adsorbents [6], anion-exchangers [7], drug delivery [8], polymer additives [9] and hybrid pigments [10,11].

Recently, LDH films have attracted considerable interest due to their novel properties and performances compared with their powdered forms, which will lead to an expansion in the applications of LDHs [12]. Usually, the LDH films are prepared by two methods: the physical deposition and the in situ growth or substrate-induced growth. In the former method, the substrate serves as a support for pre-synthesized LDH nanosheets or platelets. Two physical deposition methods are often used to fabricate such LDH films: the solvent evaporation method [13] and the layer-by-layer assembly method [14,15]; in the latter method, the substrate supplies the growing sites for the LDH film, and sometimes also acts as the source of metal cations needed for formation of LDHs. Substrates such as metal sheets [16,17], metal alloys [18,19], porous anodic alumina/aluminum [20], glass [21], sulfonated polystyrene [22], boehmite-coated materials [23] and Al_2O_3-coated materials [24] have been utilized to prepare LDH films by this method, which have the good mechanical strength and high adhesion to the substrate. The LDH films have been employed as heterogeneous catalysts [25], anti-corrosion coatings for metals [18], adsorbents [23], modified electrodes [26], components in optical or magnetic devices [27,28], and sensors [29]. However, there still remains a need for new functional LDH films.

Our previous studies have shown that the incorporation of some organic chromophore anions into the galleries of LDHs effectively enhances the thermal stability and light fastness [30,31]. Therefore colored functional films with excellent thermal stability and light fastness may be synthesized by intercalating dye anions into the interlayer galleries of films of LDHs. Such films can serve as paints which impart color and also provide protection for the substrate.

In this work, incorporation of Acid Yellow 49 (4-[2-(5-amino-3-methyl-1-phenyl-1H-pyrazol-4-yl)diazenyl]-2,5-dichlorobenzene sulfonic acid, abbreviated as PPDB) anions into a LDH film was

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0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.03.012

carried out by an ion-exchange method using a ZnAl–NO_3–LDH film on alumina/aluminum substrate as a precursor, and the thermal stability and light fastness of the film were investigated. The PPDB is a bright yellow dye and widely used in textile dyeing, see its structural formula in Fig. 1. Although the thermal stability of the dye is quite good, its light fastness is poor which severely limits its range of applications. If the PPDB anions can be intercalated into the galleries of films of LDHs, its thermal stability and light fastness may be improved, allowing yellow coating films with excellent thermal stability and light fastness to be fabricated.

2. Experimental section

2.1. Materials

Ammonia ($NH_3 \cdot H_2O$), sodium hydroxide (NaOH), ammonium nitrate (NH_4NO_3), ethanol (C_2H_5OH) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) were A.R. grade reagents. Water was deionized and decarbonated, with an electrical conductivity less than 10^{-6} S cm^{-1}. The aluminum substrate (purity: >99.5%; thickness: 0.1 mm) was purchased from Shanghai Jingxi Chemical Technology Co. Acid Yellow 49 was a commercial product with a purity of 94% and recrystallized twice from water before use.

2.2. Preparation of ZnAl–NO_3–LDH/alumina/aluminum precursor film

The aluminum sheet was firstly treated with 0.5% NaOH solution in order to remove the oxidation on the surface according to the literature [16] and then further ultrasonically treated in water and ethanol for 10 min each. The preparation of the ZnAl–NO_3–LDH/alumina/aluminum precursor film was similar to that reported elsewhere [32]. Dilute ammonia (2.5%, 4.5 mL) was added to a solution of $Zn(NO_3)_2$ (0.025 M, 100 mL) and NH_4NO_3 (0.15 M) to make a milky white solution. The resulting solution was transferred to a conical flask and the Al substrate was immersed in the above solution. Then the flask was sealed and the reaction was carried out with magnetic stirring at 80 °C for 12 h. The resulting film was rinsed four times with water and then dried at 80 °C for 24 h.

2.3. Synthesis of ZnAl–PPDB–LDH/alumina/aluminum film

The PPDB anion intercalated film was prepared by the ion-exchange method using the ZnAl–NO_3–LDH/alumina/aluminum film as a precursor. The precursor film was immersed in the solution of PPDB (0.1 M, 100 mL) in a sealed beaker and maintained at 100 °C for 2.5 h. The film was then removed and rinsed five times with hot water and subsequently dried at 100 °C for 12 h.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD–6000 diffractometer with monochromatic Cu K_α radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 30 mA. FT-IR spectra were collected on a Bruker Vector 22 infrared spectrophotometer using the KBr disk method with a weight ratio of sample/KBr of 1:100. Thermogravimetric–differential thermal analysis (TG–DTA) curves were recorded on a PCT–IA instrument in the temperature range of 80–700 °C with a heating rate of 10 °C min^{-1} in flowing air. The morphology of the films was investigated by means of a scanning electron microscope (SEM, Hitachi S–3500N). The accelerating voltage applied was 20 kV. Elemental analyses for metal elements in the LDH powder scraped from film were performed using an ICPS–7500 model inductively coupled plasma emission spectrometer (ICP-ES). Carbon, hydrogen and nitrogen analyses were carried out on Elementar vario EL Analyzer. The color difference (ΔE) of materials aged under UV light was determined in terms of CIE 1976 L*a*b* using a TC-P2A automatic colorimeter. The CIE 1976 L*a*b* is a color scale based on the Opponent-Colors theory, among L*, a* and b* values indicate the level of light–dark, red–green and yellow–blue colors [33,34].

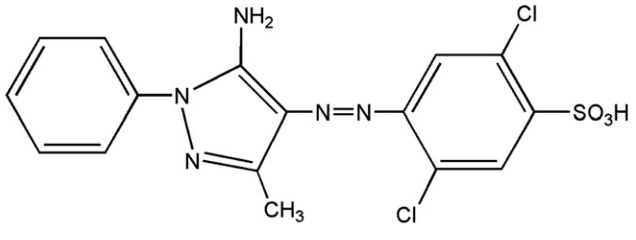

Fig. 1. The structural formula of Acid Yellow 49.

3. Results and discussion

3.1. Structure and morphology of the film

Elemental analysis results (wt%) of the powder scraped from the film: Zn = 43.13, Al = 10.61 for ZnAl–NO_3–LDH precursor; Zn = 21.79, Al = 4.79, C = 22.83, H = 3.26, N = 8.00 for ZnAl–PPDB–LDH. A little alumina in the powder scraped is detected as there is an alumina layer between the LDH crystallite and the aluminum substrate [16]. Based on Zn and C content, our evaluated results show that each molar ZnAl–PPDB–LDH with a formula of $Zn_{0.738}Al_{0.262}(OH)_2(PPDB^-)_{0.262} \cdot 0.71H_2O$ is mixed with ca. 0.064 M Al_2O_3 in the scraped powder.

Fig. 2 shows the XRD patterns of the aluminum substrate, ZnAl–NO_3–LDH film precursor, PPDB, ZnAl–PPDB–LDH film and ZnAl–PPDB–LDH powder scraped from the film. The XRD pattern of the ZnAl–NO_3–LDH film precursor displays both the characteristic peaks of the aluminum substrate and ZnAl–NO_3–LDH. The [003] and [006] reflections of the ZnAl–NO_3–LDH crystal phase appear at 10.06° and 20.18° (2θ), respectively. The basal d-spacing of the ZnAl–NO_3–LDH calculated from the Bragg equation is 0.88 nm, which agrees well with that reported in the literature [35].

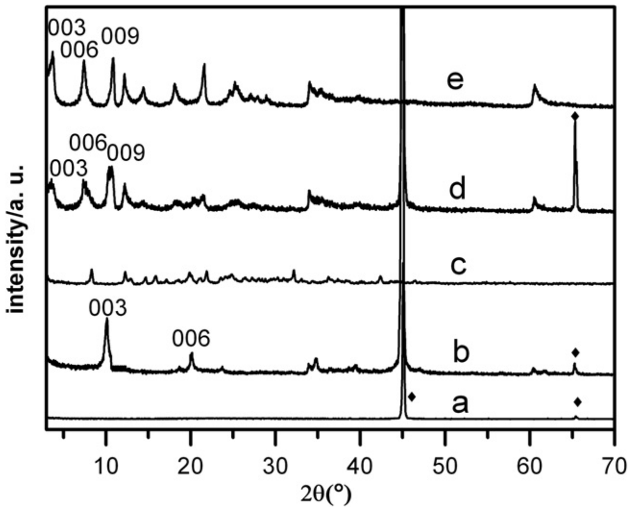

Fig. 2. XRD patterns of the aluminum substrate (a), ZnAl–NO_3–LDH film precursor (b), PPDB (c), ZnAl–PPDB–LDH film (d) and ZnAl–PPDB–LDH powder scraped from the film (e).