Materials Chemistry and Physics 173 (2016) 26–32

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Effects of lamellar reconstruction routes in the release of molybdate encapsulated in Mg–Al layered double hydroxides

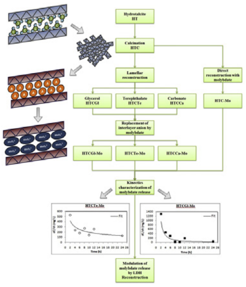
E.V. Bendinelli [a], A.C. Rocha [a], O.E. Barcia [a, c], I.V. Aoki [b], I.C.P. Margarit-Mattos [a, *]

[a] Federal University of Rio de Janeiro, Polytechnic School and COPPE, Department of Metallurgy and Materials, LNDC – Laboratory of Nondestructive Testing, Corrosion and Welding, PO Box 68505, 21941-972 Rio de Janeiro, RJ, Brazil
[b] Polytechnic School of the University of São Paulo, Chemical Engineering Department, CP 61458, 05424-970 São Paulo, SP, Brazil
[c] Federal University of Rio de Janeiro, Institute of Chemistry, Department of Physical Chemistry, 21941-909 Rio de Janeiro, RJ, Brazil

HIGHLIGHTS

- Lamellar reconstruction effect in the release of MO_4^{-2} in Layered Double Hydroxides.
- Choosing the reconstruction route allows to modulate the liberation of MO_4^{-2} by LDH.
- Reconstruction of LDH with terephtalate leads to slower MO_4^{-2} release than glycerol.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form
15 November 2015
Accepted 20 December 2015
Available online 23 January 2016

Keywords:
Coatings
Chemical synthesis
Corrosion
Shape memory effects

ABSTRACT

Effects of lamellar reconstruction methods in the release of molybdate ions encapsulated in Layered Double Hydroxides (LDH) are evaluated. The methodology consisted of two stages: i) treatment of LDHs and interlayer substitution with molybdate; ii) characterization of morphology and kinetics of molybdate release in chloride solution and deionized water. Commercial hydrotalcite (HT) was calcined and then reconstructed in water (HTCCa), terephthalic acid (HTCTe), glycerol (HTCGl) and in molybdate solution (HTCMo). XRD showed that lamellar reconstruction succeeded only with HTCCa, HTCTe and HTCGl. Afterwards, substitution of interlamellar anions by molybdate was done. Molybdate release over time, monitored by ion chromatography, was higher in chloride solution suggesting ion exchange. Increasing temperature to 85 °C doubled the molybdate released by HTCTe-Mo, accelerating the kinetic process compared with room temperature. The kinetics release was different for each LDH doped with molybdate. Gradual liberation of molybdate characterizes HTCTe-Mo while HTCGl-Mo promotes quick release. Therefore by the choice of reconstruction routes it is possible to modulate the liberation of molybdate by LDH.

1. Introduction

The addition of corrosion inhibitors is widely used to increase the service life of anticorrosive organic coatings [1,2]. However, the direct addition of corrosion inhibitors in the coating matrix may result in inhibitor deactivation reactions or coating

---

* Corresponding author.

E-mail addresses: elberbendinelli@metalmat.ufrj.br (E.V. Bendinelli), adrirocha@metalmat.ufrj.br (A.C. Rocha), barcia@metalmat.ufrj.br (O.E. Barcia), idavaoki@usp.br (I.V. Aoki), margarit@metalmat.ufrj.br (I.C.P. Margarit-Mattos).

http://dx.doi.org/10.1016/j.matchemphys.2015.12.049
0254-0584/© 2015 Published by Elsevier B.V.

degradation [3,4]. The coatings aging may occur due to ultraviolet radiation [5], thermal and mechanical stress [6–8] among others. Thermal stress is more important when glass transition temperature is surmounted. The substrate corrosion is favored because polymer chains gain mobility and free volume increases, enhancing permeation of electrolyte. When the temperature decreases below the Tg and there is not enough time for electrolyte desorption, stress and cracks in the coating may occur [8–10]. In this context, the objective is to develop intelligent particles, which allow the release of inhibitor at different rates. Eventually these particles may be used as pigments in anticorrosion coatings formulations in which the availability of the inhibitor would be triggered by the permeation of corrosive agents, namely water and chloride.

The layered double hydroxides (LDHs), natural or synthetic, are known for their ion exchange property [1–3,11]. LDHs have water and anionic species in the interlayer domain to balance the structure electric charge [12]. Such species can be exchanged by others with greatest ability to stabilize the lamellar structure [13,14]. For this reason, the LDHs are used as micro and nanocontainers for anions storage with different applications [12,15–17]. This feature is very attractive for corrosion control because inhibitor release may occur with immobilization of corrosive agent as chloride.

The role of several anions on LDHs behavior is well known [12,14,18,19], but the effects of the routes of synthesis on the rate of inhibitor liberation can hardly be found. There are many routes for synthesis [20–24]. Lamellar reconstruction [22] and replacement of interlayer anion [12,15,23,24] is focused in this paper. This method is based on the LDHs type [Mg–Al] and [Zn–Al] “memory effect” [19,22,25,26]. Intermediate anions commonly used are carbonate, terephthalate and glycerol [27–32]. In this work, lamellar reconstructions using such anions, followed by replacement with molybdate corrosion inhibitor were used as routes of synthesis of doped LDHs for evaluation of molybdate kinetics release.

2. Materials and methods

Hydrotalcite (HT), general formula $Mg_6Al_2(CO_3)OH_{16}.4H_2O$, Sigma–Aldrich 185361 with ratio Mg^{2+}/Al^{3+} 4.0 to 5.0 was used. The experimental procedure adopted was based on the protocol described by Mitchell and Wass [32].

2.1. Calcination and reconstruction

Conditions for calcinations were investigated by thermogravimetric analysis carried out on Instruments Specialists Incorporated 1500 STAI model. The heating rate was 1 °C min^{-1} with dry nitrogen flow of 100 cm^3 min^{-1}, from room temperature to 800 °C. The amount of samples used was 5 mg. HT was calcined at 500 °C for 3h under pure Argon flow for removal of interlayer carbonate anion. The heating ramp was 10 °C min^{-1}. After calcination, HTC was stored in desiccators with N_2 to avoid contact with atmospheric CO_2. Afterwards, based on shape memory effect of HT, lamellar reconstruction of HTC was tried using glycerol, terephthalate, molybdate and carbonate from water as interlayer anions (Fig. 1).

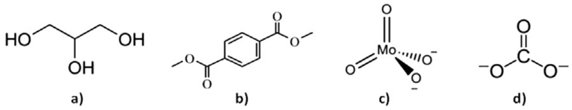


Fig. 1. Structural formulas: a) glycerol; b) terephthalate; c) molybdate and d) carbonate.

2.1.1. Glycerol

HTC reconstructed with glycerol (HTCGl) was obtained with 13 g of HTC, 100 mL of glycerol and 200 mL of carbon dioxide-free deionized water. This system was maintained at 50 °C under stirring and nitrogen bubbling for 72 h. Lastly, HTCGl was filtered and dried in an oven at 50 °C for 24 h.

2.1.2. Terephthalic acid

HTC reconstructed with terephthalate (HTCTe) was obtained with 11.24 g of HTC, 11.24 g of terephthalic acid, 24.48 g of sodium hydroxide and 200 mL of carbon dioxide-free deionized water. This system was maintained at 70 °C under stirring and nitrogen bubbling for 24 h. Lastly, HTCTe was filtered and dried in oven at 50 °C for 24 h.

2.1.3. Carbonate from water

HTC reconstructed with carbonate (HTCCa) was obtained with 10.0 g of HTC and 200 mL of deionized water containing CO_2 from atmosphere. This system was maintained at room temperature under stirring for 24 h. Lastly, HTCCa was filtered and dried in oven at 50 °C for 24 h.

2.1.4. Molybdate

HTC reconstructed with molybdate (HTC-Mo) was obtained with 10.0 g of HTC, 10.9 g of sodium molybdate and 100 mL of carbon dioxide-free deionized water. This reconstruction is called “direct reconstruction” because molybdate is the anion of interest. The system was maintained at room temperature under stirring and nitrogen bubbling for 24 h. Lastly, HTC-Mo was filtered and dried in oven at 50 °C for 24 h.

2.2. Replacement of interlayer anion

The intermediate anions of HTCGl, HTCTe and HTCCa, except HTC-Mo, were replaced by molybdate. Inside glass flasks 10.0 g of each reconstructed LDH, 10.9 g of sodium molybdate and 100 mL of carbon dioxide-free deionized water were added. The pH of HTCTe suspension was adjusted to 4.5 with nitric acid. All flasks were maintained at room temperature under stirring and nitrogen bubbling for 24 h. At the end, three different LDHs doped with molybdate were obtained: HTCGl-Mo, HTCTe-Mo and HTCCa-Mo.

2.3. Nitrogen physisorption

The specific areas of HT, HTC, HTC-Mo, HTCCa-Mo, HTCGl-Mo and HTCTe-Mo were determined by nitrogen physisorption technique at −196 °C using equipment ASAP (Accelerated Surface Area and Porosity). The amount of sample used was approximately 500 mg. Before analysis, samples were conditioned under vacuum of 1×10^{-6} mmHg and helium flow of 50 mL min^{-1} at 60 °C for 15 h. The specific areas of the LDHs were obtained by the BET method with duplicate samples.

2.4. X-ray diffraction

XRD was carried out in Bruker D8 Discover model type Bragg-Brentano diffractometer (theta-2theta) with cobalt tube and wavelength 1.78 Å. The detector used was type Point Scanning (PSD) with radiation K beta suppressor filter and maximum distortion of 2.5°. The scan rate used was 0.2 s/increment with scan range (2θ) from 5° to 110°. XRD was employed to evaluate the degree of crystallinity of the different LDHs and check the entrance