Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Direct comparison among the formation of terephthalate- and carbonate-intercalated Mg-Al-LDH: The influence of the high aluminum content

Inna M. Nangoi[a], Arnaldo C. Faro Jr.[b], Wladmir F. Souza[c], Sandra S.X. Chiaro[c], Alexandre A. Leitão[a,*]

[a] Departamento de Química, Universidade Federal de Juiz de Fora, Juiz de Fora, MG 36033-330, Brazil
[b] Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-972, Brazil
[c] PETROBRAS-CENPES, Ilha do Fundão, Rio de Janeiro, RJ 21941-915, Brazil

ARTICLE INFO

Keywords:
LDH
Terephthalate
DFT
High layer charge
Statistical thermodynamics

ABSTRACT

First principles calculations based on Density Functional Theory (DFT) were used to investigate the standard thermodynamic potentials and also structural and electronic properties of terephthalate (TA) and carbonate intercalated Layered Double Hydroxides (LDH) with molar ratios, $x = Al^{3+}/Al^{3+} + Mg^{2+}$, equal to 0.25, 0.33 and 0.50. Herein we discuss how the interlayer species and formation of the LDH are influenced by the layer charge. Mg-Al-CO_3 with high Al^{3+} content,x over 0.33, is hard to be obtained by synthetic methods in its pure phase, and LDH with high molar ratio is desirable for several applications such as intercalation reactions and obtainment of mixed oxides with better synergistic effects. This structure profile is easily to be acquired by the use of terephthalate as counterion than carbonate. The reason for this behaviour was found to be the competition among water molecules and anions for the interlayer sites. The dehydration process was simulated with excellent agreement with experimental data and showed important structural changes of TA in the interlayer space.

1. Introduction

Layered double hydroxides (LDH) also known as anionic clays and hydrotalcite-like compounds are a family of natural or synthetic layered materials described by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.\ mH_2O$, where A^{n-} is the interlayer charge-compensating anion, and x is the M^{3+} molar fraction. Along with the anion, water molecules are presented in the interlayer domain forming an extensive hydrogen bonding network. These compounds may contain a variety of cations in the layer including: Mn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}, as well as interlayer anions such as CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-} and organic species (Kumar et al., 2007; Rives, 2006). By reason of their capacity of expansion along the c vector, LDH are suitable to intercalate a large number of organic species, making them useful in many fields such as medicine, photochemistry, molecular separation, catalysis, and anion-exchange (Costa et al., 2010; Kloprogge and Frost, 1999; Costa et al., 2011; Costantino et al., 2013).

Hydrotalcites with formula $Mg_{1-x}Al_x(OH)_2(CO_3).mH_2O$ have their values of x generally in the range of 0.20–0.33 presenting a well ordered distribution of the cations in the layer (Richardson, 2013), and higher layer charge is difficult to be obtained by synthetic methods in its pure phase. It occurs because each $Al(OH)_6$ group has only divalent cations as its first neighbours, providing a homogeneous arrangement of the charge in the layer. It has been argued that the presence of M^{3+} - O - M^{3+} linkages, required in LDH with $x > 0.33$, is unfavourable from the point of view of the charge repulsion (Rives, 2006). The charge density of the layer play an important role on the anion-exchange properties (Kooli et al., 1996) and the increase of M^{3+} allows the attainment of mixed oxides with better synergistic effects (Arias et al., 2013).

The terephthalate anion (TA) has been used to provide an expansion of the interlayer space for the intercalation of polyoxometallates in LDH, facilitating the introduction of bulkier anions within the gallery region (Drezdzon, 1988). Also, because of its large and rigid structure, TA has been employed to obtain LDH with high aluminium content, reducing the interlayer electrostatic repulsion energy and stabilizing the structure (Coelho et al., 2015). Depending on the degree of hydration and the layer charge, TA can be found in two main orientations inside the interlayer, perpendicular or parallel to the layer sheets, forming an expanded or collapsed phase, respectively (Greenwell et al., 2010). In our previous work, TA was reported having preferential positioning related to hydroxide layers, restricted by the interlayer hydrogen bonding network, where TA prefers to interact with water

* Corresponding author.
E-mail addresses: inna@ice.ufjf.br (I.M. Nangoi), alexandre.leitao@ufjf.edu.br (A.A. Leitão).

http://dx.doi.org/10.1016/j.clay.2017.10.011
Received 18 May 2017; Received in revised form 6 October 2017; Accepted 12 October 2017

molecules than layer hydroxides. Also, electronic calculations demonstrated the stronger interaction between water molecules and hydroxide sheets as the layer charge increases (Nangoi et al., 2015). Recent works concerning DFT calculations of intercalation of organic molecules in layered materials have reported the good results, reinforcing the use of theoretical tools in analyzing these kind of materials (Tavares et al., 2017a,b; Maruyama et al., 2016)

The metal hydroxide layers bonding are covalent-type, whereas the interlayer is governed by Coulombic and hydrogen bonding interactions. The nature of the weak forces between the layers has been the subject of considerable controversy in the literature with different importance being attached to contributions from dispersion forces and hydrogen bonding (Evans and Slade, 2006). Hydrogen bonds are said to be the dominant interaction in the interlayer environment, where the anions seem to prefer to accept hydrogen bonds from water (Kumar et al., 2006).

The LDH simulated in this paper are $Mg_{(1-x)}Al_x(OH)_2TA_{x/2}.mH_2O$ and $Mg_{(1-x)}Al_x(OH)_2(CO_3)_{x/2}.mH_2O$ named by Mg-Al-TA and Mg-Al-CO_3 respectively. Their dehydrated forms are $Mg_{(1-x)}Al_x(OH)_2TA_{x/2}$ and $Mg_{(1-x)}Al_x(OH)_2(CO_3)_{x/2}$ identified as D-Mg-Al-TA and D-Mg-Al-CO_3 respectively. The LDH-Mg-Al notation is used for general structure. The aim of the present work is to provide sufficient data to understand the formation of Mg-Al-TA with with $x = 0.25$, 0.33 and 0.50, and more specifically discuss the difficulty of synthesized Mg-Al-CO_3 with $x = 0.50$ (Kukkadapu et al., 1997; Kooli et al., 1996; Arias et al., 2013). All solid-state DFT calculations are well supported by previous work with layered materials published by this workgroup (Costa et al., 2008, 2010, 2011, 2012a,b; Tavares et al., 2017a,b; Maruyama et al., 2016; Moraes et al., 2016).

2. Theoretical methodology

First principles calculations were performed using the codes available in the Quantum-Espresso (QE) package (Giannozzi et al., 2009), which implements the DFT (Hohernberg and Kohn, 1964; Kohn and Sham, 1965) framework employing plane-wave basis set, periodic boundary conditions and pseudopotentials. Generalized gradient approximation, GGA-PW91 (Perdew and Wang, 1992), was adopted for the exchange-correlation functional and the Vanderbilt ultrasoft pseudopotentials (Vanderbilt, 2011) were used to describe the ion cores of H, O, Mg, Al and C atoms. The Kohn-Sham one-electron states were expanded in a plane wave basis set until the kinetic cutoff energy was 60 Ry and 360 Ry for the density. To reach these values, energy cutoff tests were performed for each structure as well as k-point sampling (Monkhorst and Pack, 1976) in the first Brillouin zone. The k-points sampling used for the systems are the Monthorsk-Pack meshes of $3 \times 3 \times 1$ for LDH with $x=0.33$ and $x=0.25$ and $4 \times 4 \times 2$ for LDH with $x=0.50$. Then a full optimization including unit cell parameters were carried out for all the structures so as to display forces smaller than 0.001 Ry/bohr. All the molecular graphics have been generated by the XcrysDen graphical package (Kokalj, 1999).

Mg-Al-TA structures were constructed as described by Nangoi et al. (2015) and Mg-Al-CO_3 followed the procedure adopted by Costa et al. (2010). Considering a layer reconstruction $n \times m$ based on brucite sheet, three supercells were built with different molar ratios (Table 1),

Table 1
Supercells size per molar ratio.

Layer reconstruction[a,b]	x
4×2	0.25
$(2\sqrt{3} \times \sqrt{3})R30°$	0.33
2×2	0.50

[a] (Costa et al., 2010)
[b] (Nangoi et al., 2015)

Table 2
Gibbs free energy and enthalpy formation at 25°C and 1 atm of Mg-Al-CO_3, in kJ/mol.

	Molar fraction, x			
	0.25	0.33	0.50	Exp. ($x=0.25$)[a]
$\Delta H°$	−5.13	−5.58	19.01	−7.81
$\Delta G°$	−10.26	−8.19	17.60	−8.82

[a] (Allada et al., 2005)

Table 3
Gibbs free energy and enthalpy formation at 25°C and 1 atm of Mg-Al-TA, in kJ/mol.

	Molar fraction, x		
	0.25	0.33	0.50
ΔH°	−6.94	−8.48	−12.83
ΔG°	−16.71	−18.36	−18.56
ΔZPE	2.51	2.48	1.50
−T Δ S °	9.77	9.88	5.73

to maintain the neutrality of the system. All the models can be found in Appendix A.

The relative position of hydroxide layers is determined by a stacking vector that generates the desired polytype of the LDH. For Mg-Al-TA, Mg-Al-CO_3 and D-Mg-Al-CO_3, the stacking vector of $(a/2, \sqrt{3}a/6, c/3)$ was applied, where a and c are the cell parameters for $3R_1$ polytype, while D-Mg-Al-TA has a stacking vector of $(0,0,c/3)$ to give a 1 H polytype. These vectors produce the correct stacking for the LDH structure and define a unit cell with only one layer and one interlayer space. Thus, this single layer model was used to reduce the number of atoms and the stacking sequence is recovered by a sloped c vector where the periodic boundary condition allows the recovery of the polytype. The initial c parameter of 42.6 Å(Mg-Al-TA), 22.66 Å(Mg-Al-CO_3 and D-Mg-Al-CO_3) and 25.2 Å(D-Mg-Al-TA), based on experimental values (Benito et al., 2009; Greenwell et al., 2010; Costa et al., 2010), were employed for the initial structures.

The number of water molecules were introduced according to experimental data, where each Mg-Al-TA supercell having 6, 4 and 3 water molecules, respectively (Drezdzon, 1988; Kooli et al., 1996; Newman et al., 1998; Maxwell et al., 1999), and Mg-Al-CO_3 supercell having 3, 4 and 2 water molecules, respectively (Tsuji et al., 1993; Allada et al., 2005).

Thermodynamic properties of formation reactions of Mg-Al-TA and Mg-AlCO_3 were calculated using the following equations

$$\Delta E = E_{LDH} - \sum n_R E_R \quad (1)$$

where E is the enthalpy (H °) or Gibbs energy (G °) calculated for LDH, respectively, and R and n_R are the index and the stoichiometric coefficient for any reactant.

Intercalated water was calculated based on ice *Ih* structure, and thermodynamic potentials were corrected by adding the experimental liquefaction enthalpy and Gibbs free energy of the ice in structure *Ih* to liquid water at 25°C and 1 bar, where $\Delta H(ice \rightarrow water)$ is 6.91 kJ/mol and $\Delta G(ice \rightarrow water)$ is −0.59 kJ/mol (Mercury et al., 2001). All minerals used to calculate the formation energy had their geometries optimized, including the unit cell parameters, with the same tolerance as for LDH structures.

The chemical equation used to calculate the energy associated with dehydration process is shown below

$$Mg_4Al_2(OH)_{12}(A^{n-})\cdot 4H_2O_{(s)} \rightarrow Mg_4Al_2(OH)_{12}(A^{n-})_{(s)} + 4H_2O_{(g)} \quad (2)$$

Where the following equations were employed:

$$\Delta G°(T) = ((G°_{dehyd} + mG°_{H_2O}) - G°_{hyd})/N_{Al+Mg} \quad (3)$$

$$\Delta H°(T) = ((H°_{dehyd} + mH°_{H_2O}) - H°_{hyd})/N_{Al+Mg} \quad (4)$$