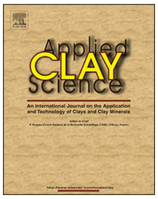
Applied Clay Science 162 (2018) 428–434

Contents lists available at ScienceDirect

Applied Clay Science

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



Research Paper

Investigation on sustainable phosphate release in agriculture: Structural and thermodynamic study of stability, dehydration and anionic exchange of Mg-Al-HPO_4 layered double hydroxide by DFT calculations

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ARTICLE INFO

Keyword:
Layered double hydroxides
Density functional theory
Phosphate
Thermodynamic
Fertilizer

ABSTRACT

This work is mainly focused on investigating the conformation of the interlayer $HPO_4{}^{2-}$ anions in a Mg-Al layered double hydroxide, as well as their characteristic interactions, and the thermodynamic features of the dehydration process and the anion exchange of these phosphate-intercalated structures. Different anion conformations were tested and compared by means of DFT calculations. It could be observed that the anion configuration in the interlayer region affects the basal spacing of these layered materials, also presenting a clear distinction between their electronic energies. The phase diagram of the studied material indicated a strong stabilization of the hydration water molecules in the interlayer region, mainly driven by hydrogen bonds. Thermodynamic potentials for the anion exchange reaction with $CO_3{}^{2-}$ were calculated in order to investigate the possible nutrient release of this material. The process was thermodynamically spontaneous for the studied LDH, thus making it suitable for agricultural applications.

1. Introduction

The recent global population growth increased the demand for food, fuel and energy, prompting the innovation of production methods. In this context, the agricultural development of worldwide food production depends on soil fertility, i.e., on the presence of important macronutrients such as nitrogen, phosphorus and potassium (NPK fertilizers) (de Castro et al., 2015). NPK fertilizer elements are present in the composition of ammonia, phosphate and potash rock, which are extracted directly from natural resources. These nutrients are essential for the plant growth, production and health (Timilsena et al., 2014). For instance, phosphorus is crucial for some physiological and biochemical processes such as plant development, production and transport of nutrients in the whole plant (Simpson et al., 2011; Schachtman et al., 1998). The phosporus availability in soil for nutrient uptake is tremendously low due to the precipitation of $PO_4{}^{3-}$ (Schachtman et al., 1998), which compromises the growth and development of crops. Phosphorus fixation is also a complication in many tropical soils because the fertilizer can bind with iron and aluminum oxides, thus compromising its availability. Therefore, farmers need to increase the amount of inorganic fertlizer to enhance their crop produtivity (Roy et al., 2016).

On the other hand, the excessive use of fertilizer and leaching effects may cause environmental pollution. Thus an appropriate fertilizer management is necessary for maximizing productivity and minimizing pollution, concomitantly. Another major issue is related to the phosporus depletion in 50–100 years caused by the current extraction rates, as reported by some studies (Abelson, 1999; Rasul and Thapa, 2004; Sattari et al., 2012). For this reason, many solutions were found for this problem, such as the improvement of phosphorus recycling (Withers et al., 2015), the development of new technologies like nutrient recovery from waste water (Guaya et al., 2018), and the design of slow release fertilizer (SRF) and controlled release fertilizer (CRF) (Shaviv and Mikkelsen, 1993) and new materials with potential application for agriculture (Liu and Lal, 2014, 2015).

Layered Double Hydroxides (LDHs) or hydrotalcite-like compounds (Cavani et al., 1991; de Roy et al., 1992) are synthetic or naturally occurring anionic clays, whose structure is similar to brucite ($Mg(OH)_2$). The LDH structure can be simply regarded as a modification of brucite by the exchange of certain divalent cations for trivalent ones. The chemical formula of hydrotalcite can be written as $[Me_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A_{x/m}{}^{m-}\cdot nH_2O)$, where Me $^{2+}$ is a divalent cation, M $^{3+}$ is a trivalent cation, A $^{m-}$ is the intercalated anion with charge $m\ -$, n is the amount of water molecules and x is the molar fraction between the trivalent cation and the total amount of cations. This compound was explored in the literature for many applications like

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https://doi.org/10.1016/j.clay.2018.06.036
Received 27 March 2018; Received in revised form 14 June 2018; Accepted 25 June 2018

exfoliation/delamination (Mao et al., 2017), pollutant removal (Goh et al., 2008), catalisys (Cavani et al., 1991) and phosphorus recovery (Das et al., 2006). Recently, several works reporting LDHs for agricultural use were published. Most of them were related to slow and controlled release of plant nutrients (Komarneni et al., 2003; Ureña–Amate et al., 2011; Silva et al., 2014; Everaert et al., 2016; Benício et al., 2016) and sustained release of agrochemicals (Cardoso et al., 2006; Bruna et al., 2009).

Computational calculations such as DFT (Density Fuctional Theory) are a remarkable tool to provide information unobtainable experimentally, to assist the characterization of materials and to predict some interesting properties. The literature presents many DFT simulations of LDHs with different exchange-correlation functionals like PBE (Costa et al., 2010; Yan et al., 2010) and PW91 (Nangoi et al., 2015; Moraes et al., 2016), restricted and unrestricted calculations, and with Hubbard correction (Xu et al., 2015; Moraes et al., 2016; Xu et al., 2017). All these calculations showed a good agreement with the available experimental data and could help the interpretation of complex experimental results. For example, in the case of LDHs, the nature of the interlayer region could be better understood, as can be shown in the works of (Costa et al., 2012a, 2012b). In general, the advances in the computational methodologies provided precise structural, electronic and thermodynamic results for layered materials (Tavares et al., 2018).

In this work, the main objective is to investigate, by means of *ab initio* calculations, the interlayer region of $HPO_4{}^{2-}$-intercalated LDH and to elucidate how the anion conformation can affect the basal spacing and the electronic structure of these materials. The thermodynamic simulation of the dehydration process and of the anion exchange reaction between phosphate and carbonate is also one of the goals of the present paper. These anion exchange reactions aim to enquire into the potential use of these LDHs as fertilizers.

2. Computational details

2.1. Phosphate-intercalated LDH structural models

The synthesis of phosphate-intercalated hydrotalcites is usually performed by anion exchange. The layer charge density can also modify the arrangement of the intercalated anion, thus affecting the basal spacing (Olfs et al., 2009). The work of Everaert et al. (2016) showed that the compounds with molar fraction Mg:Al = 2 had the highest P uptake. Lower molar ratios also increase the stability of the LDH and favor stronger interactions between the layer and the anions. The structural models of the monohydrogen phosphate-intercalated LDHs used in this work correspond to the $(2\sqrt{3} \times 2\sqrt{3})R30^{\circ}$ 3R $_1$ polytype supercell, as reported by Costa et al. (2010). The chemical formulas of the structures were $[Mg_8Al_4(OH)_{24}][(HPO_4)_2 \cdot 6H_2O]$. Three structures with this chemical formula were built, with two different orientations of phosphate anions in the interlayer region of layered double hydroxides. The first structure with face and corner sharing anions with the hydroxide layer, the other one with edge sharing anions with both hydroxide layer and the last one with face and corner sharing and other edge sharing anions with the layer. These types of stable orientations of the phosphate anion in the interlayer region of LDH were described in the Supporting Information of the work of Everaert et al. (2016). $HPO_4{}^{2-}$ was chosen for this work because it is one of the anionic forms absorbed by plants (Timilsena et al., 2014). Furthermore, the simulation of monohydrogen phosphate-intercalated LDHs does not require the construction of large unit cells for the accomodation of the anions and the water molecules. It should be mentioned that the co-intercalation of different phosphate forms is possible depending on the synthesis conditions (Benício et al., 2015). For the sake of simplicity, these models will be called as: [Mg-Al-$HPO_4\Delta$], [Mg-Al-HPO_4 ×] and [Mg-Al-$HPO_4\Delta$ ×], as depicted in Fig. 1. The carbonate-intercalated LDH model was also based on the work of Costa et al. (2010), with the following chemical formula $[Mg_4Al_2(OH)_{12}][(CO_3) \cdot 4H_2O]$. The adopted supercell was $(2\sqrt{3} \times \sqrt{3})R30^{\circ}$ belonging to the 3R $_1$ polytype.

Differently from the LDHs containing phosphate, the carbonate- and nitrate-intercalated LDHs were vastly studied in the literature (Costa et al., 2010; Costa et al., 2012a; Moraes et al., 2016; Nangoi et al., 2018). In the present work, the simulations of the $CO_3{}^{2-}$-containing LDH were carried out for the thermodynamic study of the anion exchange processes to release nutrients ($HPO_4{}^{2-}$). Our calculated basal spacing of this LDH was of 7.58 Å, showing a good agreement with the experimental value reported by Tyagi et al. (2011).

2.2. Methodology

The ab initio calculations were performed using the Quantum ESPRESSO package (Giannozzi et al., 2009), which is based on the DFT framework (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) under periodic boundary conditions (Makov and Payne, 1995). A plane wave basis set was used to expand the one-electron wave functions of Kohn-Sham equations. The geometry and the cell optimizations of the LDH structures were performed with the generalized gradient approximation (GGA/PW91) (Perdew and Wang, 1992) by minimizing the total energy gradient. The relative ion positions were relaxed until all of the force components were smaller than 0.001 Ry/bohr.

The ion cores were described by Vanderbilt ultrasoft pseudopotencials (Vanderbilt, 1990) and the Kohn-Sham orbitals were expanded up to a kinetic energy cutoff of 60 Ry (480 Ry for the charge density cutoff). The integration in the Brillouin zone was determined by the Monkhorst-Pack method (Monkhorst and Pack, 1976) with meshes of 2 × 2 × 2 for the LDHs containing monohydrogen phosphate and carbonate. The full relaxation of atomic positions and cell parameters was performed during the structural optimizations. All of the molecular graphics were generated by the XCRYSDEN graphical package (Kokalj, 2003).

The calculation of the Gibbs free energy, entropy and the enthalpy of the dehydration process and the anion exchange was carried out with the vibrational modes obtained from phonon calculations. This calculation was based on the harmonic approximation by the density functional perturbation theory (DFPT) (Baroni et al., 1987, 2001) at the Γ-point. These calculations were also used to characterize the optimized structures as minimum points. The Gibbs free energy (G) can be calculated using the following equation: G = H - TS. The enthalpy and the entropy were calculated for the LDH models in the solid state by the following approximations, in the same way it was done for other materials in previous works (Vaiss et al., 2009; Costa et al., 2010; Vaiss and Leitão, 2011; Alvim Jr. et al., 2011; Costa et al., 2012a; Tavares et al., 2014; Moraes et al., 2016; Tavares et al., 2018).

$$H_{solid}(T) = E_{ele} + E_{ZPE} + E_{vib}(T) \tag{1}$$

$$S_{solid}(T) = S_{vib}(T) \tag{2}$$

where E_{ele}, E_{ZPE}, E_{vib}(T) and S_{vib}(T) are, respectively, the total electronic energy at 0 K, the zero point energy and the vibrational contributions for the enthalpy and the entropy. The water molecule was considered in the gas state, i.e., the term *pV* and the contributions related to the translational and rotation degrees of freedom had to be evaluated. Therefore, the enthalpy and the entropy were treated according to the Eqs. 3 and 4, respectively.

$$H_{gas}(T) = E_{ele} + ZPE + E_{vib}(T) + E_{trans}(T) + E_{rot}(T) + RT \tag{3}$$

$$S_{gas}(p, T) = S_{vib}(T) + S_{trans}(p, T) + S_{rot}(T) \tag{4}$$

where E_{trans}(T) and E_{rot}(T) are, respectively, the translational and the rotational contributions to the enthalpy, S_{trans}(T), S_{rot}(T) and S_{vib}(T) are, respectively, the translational, rotational and vibrational contributions to the entropy. RT comes from the ideal gas law. The water molecule was optimized and calculated in a cubic cell of 20 Å.

In the case of the anion exchange reactions, the anions were also considered in a cubic cell of 20 Å. The long-range Coulomb interaction