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Research paper

Comparative Structural, thermodynamic and electronic analyses of $Zn-Al-A^{n-}$ hydrotalcite-like compounds (A^{n-}=Cl^-, F^-, Br^-, OH^-, CO_3^{2-} or NO_3^-): An ab initio study

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ABSTRACT

We have investigated the influence of different anions intercalated in the layered double hydroxides (LDHs). The main aim of this work is to understand the layer-anion and the intermolecular interactions in hydrotalcite-like compounds with F^-, Br^-, OH^-, CO_3^{2-} and NO_3^-. This ab initio study describes the thermodynamics and structural modifications derived from the anion exchange on $Zn_{2/3}Al_{1/3}(OH)_2Cl_{1/3}.2/3H_2O$ LDH. When the Cl^- anion is exchanged by F^-, Br^- or OH^-, any significant structural variation on the material is not observed. Even so, the more strongly bound anions are those with smaller ionic radii, which result in a decreased spacing between the hydroxyl layers. The CO_3^{2-} and the NO_3^- anions have identical symmetry in free state, but their behavior as interlayer anions in LDHs is very different. After the optimization, the carbonate anion kept the orientation parallel to the hydroxide layers. This configuration is energetically more favorable because the three oxygen atoms of the CO_3^{2-} anion can properly interact with hydroxyl groups of hydroxide layers by forming hydrogen bonds. Unlike the carbonate, the nitrate ion has its molecular plane tilted to a direction that forms an angle with *c* vector, which is less than 90°. The orientation of the NO_3^- anion appears to vary depending on the amount of co-intercalated water molecules. The anion-exchange selectivity in the LDH follows the sequence: $NO_3^- < Br^- < Cl^- < F^- < OH^- < CO_3^{2-}$, obtained by the calculation of the Gibbs free energy.

1. Introduction

Layered double hydroxides (LDH) are one of the few clay minerals with significant and permanent anion-exchange capability. These minerals, also known as hydrotalcite-like compounds, or anionic clays, are a class of lamellar compounds that consists of positively charged hydroxyl layers that are charge balanced by hydrated exchangeable anions in the interlayer regions. The hydroxyl layers are charged due to an isomorphous substitution of divalent metal ions, M^{2+}, to trivalent ones, Me^{3+}. The chemical compositions of LDHs are expressed by the general formula $[M^{2+}_{1-x}Me^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$, in which A^{n-} is an exchangeable interlayer anion (Crepaldi and Valim, 1998).

In the LDHs, the distance of the layers is changeable, it may be contracted when the interlayer region is emptied and expanded in presence of the new anions or water molecules. This factor favors the intercalation of additional species, or their interchanges (Lerf, 2004; Lv et al., 2007, 2009; Miyata, 1983; Orthman et al., 2003; Parker et al., 1995). The understanding of the influence of different intercalated anions in the LDH is very important, because the anion-exchange capacity can only be used when the anion that will be introduced has higher affinity with the LDH layer than the precursor anion.

It is reported in the literature that the common anion-exchange capability for the $Mg-Al-LDH$ increases in the following sequence: $ClO_4^- < NO_4^- < Br^- < Cl^- < F^- < OH^- < SO_4^{2-} < CO_3^{2-}$ (Miyata, 1983), but nothing is mentioned about the nature of the chemical interactions. In order to explain this series, the anion-exchange selectivity is usually related to the guest orientation, the ionic radius and the anion charge (Carlino, 1997; del Arco et al., 2000; Fogg et al., 1999; Miyata, 1983; Ogawa and Kuroda, 1995; Wang and Wang, 2007). The expansion of the interlayer space evaluated by X-ray diffraction and the shifting of frequencies in the infrared spectra help to correlate the arrangement of the anion into the LDHs (Bontchev et al., 2003; Khan and O' Hare, 2002), and it is possible to assume some orientations of the intercalated species based on these data. This association can be reasonable because it is well-known that molecules are intercalated on LDHs with preferential orientations, and they are influenced by guest bonds and interactions. Unfortunately, the interpretation of results from those methods and the attribution of the guest orientation are not accurate and have generated some controversy (Wang and Wang, 2007). In addition, the

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ions in question have the ability to reorient with increasing amount of co-intercalated water molecules, or in their absence.

Quantum calculations can help these investigations, for instance, by evaluating the energetically preferred orientation of guest species and assisting the interpretation of experiments. It also allows detailed atomic-level understanding of the interactions that control the exchange capacity of LDHs. Unfortunately, the majority of DFT studies of anion-exchange capability for the LDH were performed with anhydrous minerals (Li et al., 2006; Trave et al., 2002; Xu et al., 2009), which may have compromised some analyses, because the structure, the dynamics and the stability of intercalated species are influenced by their interactions with water molecules (Costa et al., 2011; Hou et al., 2003; Lombardo et al., 2005, 2008).

We have investigated the properties of lamellar compounds (Costa et al., 2008, 2010, 2011; Vaiss et al., 2009). Our recent results have indicated that the water molecules play an important role in many elementary steps of the reaction of HF molecules with brucite, $Mg(OH)_2$, which leads to the formation of the $Mg(OH)_{2-x}F_x$ compound (Vaiss et al., 2009), they contribute to stabilize the lamellar structure via hydrogen bond involving anions and hydroxyl groups of the layers (Costa et al., 2010), and the water molecules act cooperatively to maximize the hydrogen bonding between the layers and the intercalated species, restricting the mobility of molecules intercalated (Costa et al., 2011). We have found that multiple interactions are more prominent in hydrated LDHs than in anhydrous minerals, indicating that the interaction of intercalated anions is stronger with co-intercalated water molecules than with hydroxyl layers. Thus, some calculations can underestimate the interaction energy of intercalated species with respect to the experiment, resulting in a prediction error. Therefore, a good knowledge of the intermolecular interactions is essential for the reliable theoretical determination of the properties of the anion-exchange of the LDH.

Our previous paper described the overall effect of the water molecules on the LDH compounds (Costa et al., 2011). Here, we concentrate on the intercalated anions and the influence of water molecule on the structural properties and stability of layered materials. The objective of the present work is to understand the intermolecular interactions in hydrotalcite-like compounds intercalated with simple univalent anions, such as F^-, OH^-, Br^- and inorganic anions having D_{3h} symmetry, like CO_3^{2-} and NO_3^-. In this investigation, the van der Waals interactions were not properly included, because the lamellar packing and the intercalations among the intercalated species are mainly dominated by the Coulombian interactions and the hydrogen bond. This ab initio study discuss the thermodynamics and the structural modifications derived from anion exchange on $Zn_{2/3}Al_{1/3}(OH)_2Cl_{1/3}.2/3H_2O$ LDH, which was abbreviated as Zn – Al – Cl. The Cl^- ion in the LDH precursor is exchanged for a series of anions, F^-, Br^-, OH^-, CO_3^{2-} and NO_3^- by using the single-layer model (Costa et al., 2011). The Gibbs energy, the enthalpy and the charge density difference are evaluated.

2. Theoretical methodology

Calculations were performed in the framework of DFT using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996). We used ultrasoft pseudopotentials (Vanderbilt, 1990). KohnaSham orbitals were expanded in a plane-wave basis set up to a kinetic energy cutoff of 30 Ry (240 Ry for the charge-density cutoff). Monkhorst–Pack (Monkhorst and Pack, 1976) meshes of 3×3×2 and 2×3×2 k-point sampling in the first Brillouin Zone were used for $\left(\sqrt{3}\times\sqrt{3}\right)R30°$ and $\left(2\sqrt{3}\times\sqrt{3}\right)R30°$ supercells, respectively. All these parameters were tested and found to be sufficient to ensure that the total energy and stress tensor were well converged. The criterion of convergence for the total energy was 10^{-6} Ry. All calculations were done using the PWscf code from the Quantum ESPRESSO distribution (Baroni and Dal, 2001), while molecular graphics were produced by the XCRYSDEN graphical package (Kokalj, 1999; Kokalj and Causà, 2003).

The incorporation of different species should be investigated by considering the balance between the forces that the anion experiences within the LDH framework with respect to that in aqueous solution. Thus, the anion-exchange energies for the studied systems were calculated considering the following reaction:

$$Zn{-}Al{-}Cl(s) + A^{n-}(aq) \rightarrow Zn{-}Al{-}A_{1/n}(s) + Cl^-(aq) \qquad (R1)$$

where A^{n-} represents an anionic species F^-, OH^-, Br^-, CO_3^{2-} or NO_3^- which can replace the intercalated Cl^-.

The variation of entropy, enthalpy and Gibbs free energy related to the exchange reaction, were obtained from the calculated thermodynamic property of each solid or isolated ionic species. The enthalpy and the entropy of minerals in solid state were calculated through the following approximation:

$$H(T) = E^{el} + E^{ZPE} + E^{vib}(T) \qquad (1)$$

$$S(T) = S^{vib}(T) \qquad (2)$$

where E^{el}, E^{ZPE}, $E^{vib}(T)$ and $S^{vib}(T)$ are the electronic energy, the zero point energy, which is a linear sum of the fundamental harmonic frequencies, and the vibrational contributions of enthalpy and entropy, respectively. The vibrational analyses of all the optimized structures were done at the Gamma-point and by using the harmonic approximation. The vibrational data were also used to calculate both the contribution of the lattice thermal vibration to the total energy and the zero point energy (ZPE) as shown in our previous work (Costa et al., 2011).

The ions in gas state are treated according to the formalism described in our previous work (Costa et al., 2011). In this case, the enthalpy and the entropy contributions were calculated as:

$$H(T) = E^{el} + E^{ZPE} + E^{vib}(T) + E^{trans}(T) + E^{rot}(T) + RT \qquad (3)$$

where $E^{trans}(T)$ and $E^{rot}(T)$ are the translational and rotational contributions of enthalpy. RT is equivalent to PV term, that is necessary to obtain the enthalpy of a gas.

$$S(p,T) = S^{trans}(p,T) + S^{rot}(T) + S^{vib}(T) \qquad (4)$$

where $S^{trans}(p,T)$ and $S^{rot}(T)$ are the translational and rotational contributions of entropy.

We have still considered an additional contribution to the electronic energy in order to remove the long-ranged Coulomb interaction between the periodic images of charged molecules. This effect, was compensated with the Makov–Payne correction (Makov and Payne, 1995). To obtain the contributions of H, S and G of the anions in the aqueous solution ($H_A^{(aq)}$, $S_A^{(aq)}$, $G_A^{(aq)}$, respectively), we considered the formation of a hydrated ion from gas state, as it is shown in the following equation:

$$A^{n-}(g) \rightarrow A^{n-}(aq) \quad \Delta E_A^{\circ(hyd)}. \qquad (R2)$$

Thus, we considered:

$$H_A^{(aq)} = \left(H_A^{(g)} + \Delta H_A^{\circ(hyd)}\right) \qquad (5)$$

$$S_A^{(aq)} = \left(S_A^{(g)} + \Delta S_A^{\circ(hyd)}\right) \qquad (6)$$

$$G_A^{(aq)} = \left(G_A^{(g)} + \Delta G_A^{\circ(hyd)}\right) \qquad (7)$$

where, $H_A^{(g)}$, $S_A^{(g)}$, $G_A^{(g)}$, the calculated enthalpy, entropy and the Gibbs free energy of the anions in the gas phase and $H_A^{\circ(hyd)}$, $S_A^{\circ(hyd)}$ and