Experimental and theoretical studies on the intercalation of organics into the Mg_2Al and Zn_2Al Layered Double Hydroxides.

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MOTIVATION

Have a good methodology based on calculations of electronic structure and molecular dynamics, which allow understanding the clay-drug interactions, in addition to being able to reproduce experimental information.

INTRODUCTION

Double Layered Hydroxides (LDH) are layered minerals that provide nanoconfined spaces in the interlayer space being a possible scenario for adsorption of organics in the prebiotic chemistry. Besides, these minerals have been extensively investigated in recent years due to its promising applications in areas such as nanodeposites for drugs delivery

The most widely studied LDHs contain both divalent and trivalent metal cations, a generic formula for these LDHs may be written as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M^{2+} may be Mg^{2+}, Zn^{2+}, or Ni^{2+} and M^{3+} can be Al^{3+}, Ga^{3+}, Fe^{3+}, or Mn^{3+}. A^{n-} is a non-framework charge compensating inorganic or organic anion, e.g. CO_3^{2-}, Cl^-, SO_4^{2-}, RCO_2^-. In this work, ionic form of the non-steroidal anti-inflammatory drug naproxen (NAP) was intercalated by ion exchange reaction from pristine Layered Double Hydroxide (LDH) materials with $Mg_2Al(OH)_6$-Cl and $Zn_2Al(OH)_6$-Cl compositions. Then, atomic modelling calculations were performed at quantum mechanical level based on Density Functional Theory and classical force fields based on empirical interatomic potentials for the sodium naproxen salt.

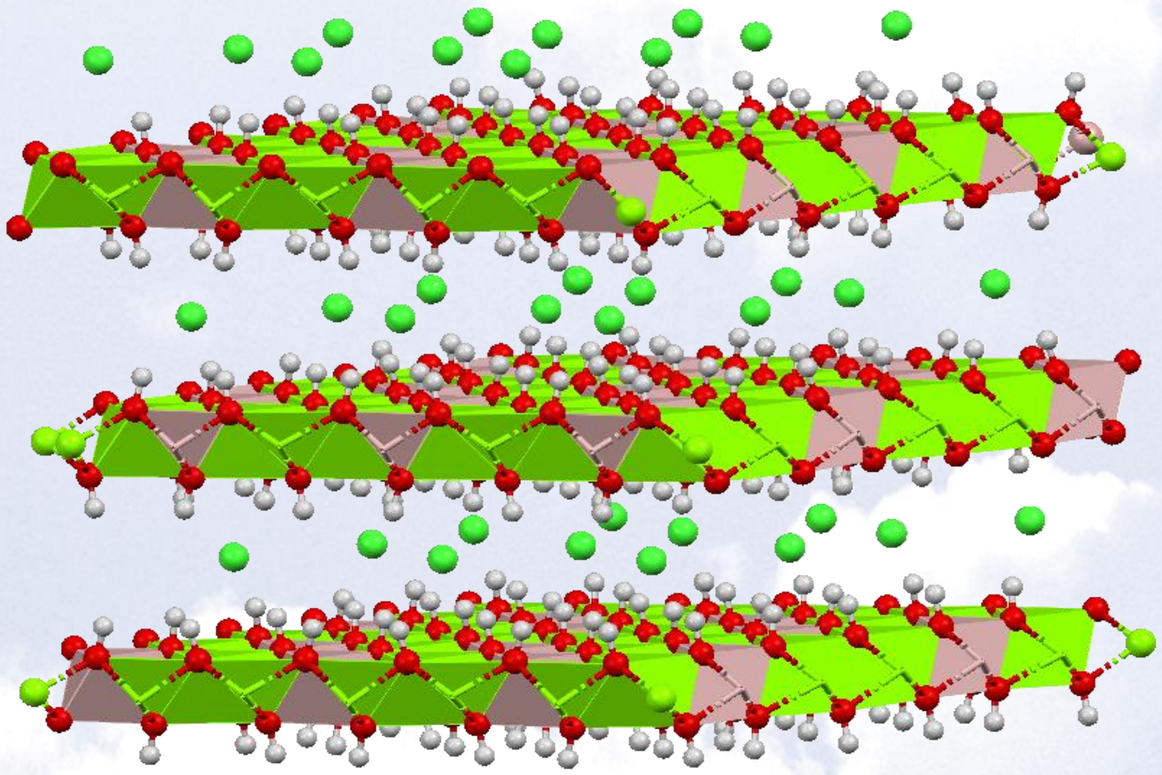

Figure1. Hydrotalcite structure, it is a double layer hydroxide (LDH). The colors magenta, red, white represent aluminum, oxygen and hydrogen. The green atoms inside the sheets represent magnesium, outside they represent chlorine.

The crystalline structures were calculated with Density Functional Theory (DFT) applying periodic boundary conditions based on plane wave conditions using the Quantum-Espresso[1] (QE) code version 6.4 and Materials Studio[2] (MS) with the generalized gradient approximation (GGA), and the Perdew-Burke-Ernzerhof (PBE) functional for exchange correlation potential[3]. PAW (Projector Augmented Wave) planar wave pseudopotentials[4] were used and dispersion corrections were included according to the DFT-D3 scheme. In addition, energy cutoff Ecut(wfc) was of 80 Ry and cutoff for the charge density was of 320 Ry. Finally, molecular dynamics[5] was used for naproxen ions intercalated in the LDL, the force field used was the FF interface.

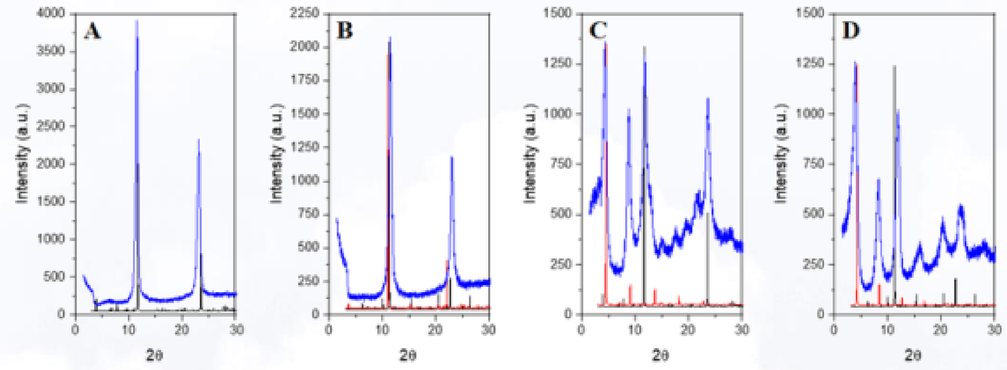

Figure 2. Comparative of simulated and experimental diffractograms of Mg2Al-Cl (A), Zn2Al-Cl (B), 522 Mg2Al-NAP (C), and Zn2Al- NAP (D).

	MgLDH-1NAP	MgLDH-7NAP	MgLDH-12NAP	ZnLDH-12NAP	Exp MgLDH-NAP	Exp ZnLDH-NAP
a **(Å)**	3.044, *3.090*	3.029	3.041 (3.056)	3.044	3.042	3.058
b **(Å)**	3.061, *3.070*	3.047	3.061 (3.073)	3.063	3.043	3.062
c **(Å)**	21.971, *23.780*	45.90	58.538 (55.598)	63.142	60.720	67.618
α (°)	88.8 *92.5*	89.3	88.3 (83.8)	92.4	90	90
β (°)	95.4, *90.4*	93.7	93.7 (107.1)	91.0	90	90
γ (°)	118.2, *120.4*	118.5	118.3 (118.0)	118.5	120	120
d**(003) (Å)**	7.29, *7.93*	15.26	19.47 (17.71)	21.01	20.24	22.54

Table 1. MgLDH-xNAP and ZnLDH-xNAP crystal lattice parameters obtained by the optimization of the 474 LDH 6x6x1 supercell with NAP molecules adsorbed in the interlayers compared with above experimental 475 values. Values from Interface FF calculations being in brackets those from the model with all NAP anions 476 ordered in vertical position MgLDH-12NAPv2; the QE results are in italics. Distances are in Å and angles 477 in degrees (°).

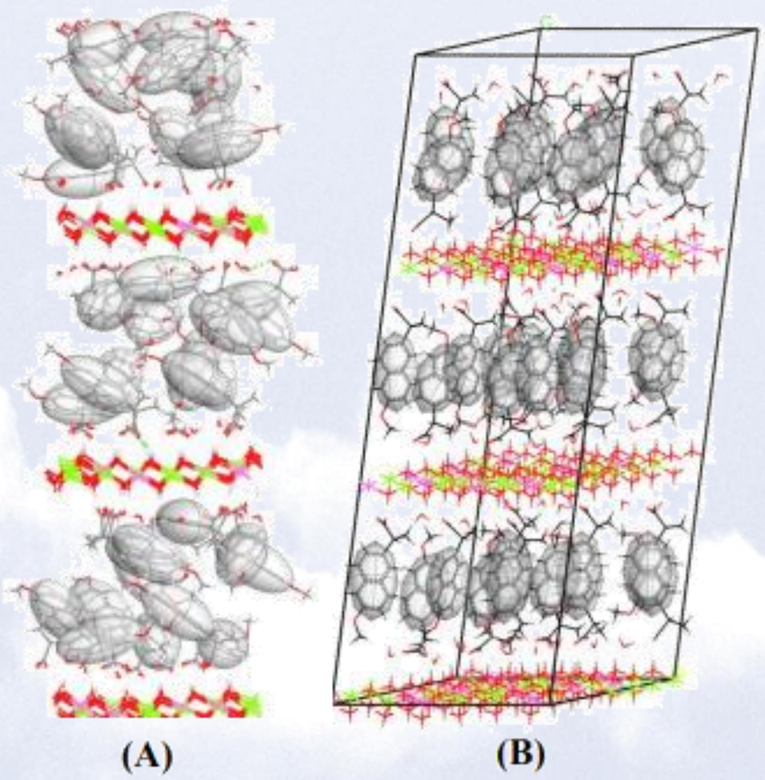

Figure 3. Optimized crystal structure of MgLDH-12NAP with a disordered (A) and ordered 518 MgLDH-12NAPv2 (B) disposition of the NAP anions (highlighted with ellipses) in the interlayers of LDH..

Conclusiones

In this work, a methodology based on classical and quantum mechanics was implemented that allowed the reproduction of experimental information of double-layer hydroxides interspersed with naproxate. In addition, it allowed to obtain possible molecular images of the studied systems.

Bibliografia

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