Research paper

A molecular dynamics framework to explore the structure and dynamics of layered double hydroxides

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ABSTRACT

It is presented a straightforward procedure based on the CLAYFF force field to perform molecular dynamics (MD) computer simulations with the GROMACS open source package of layered double hydroxide (LDH) materials with different intercalated anions. This procedure enables running very long simulations of systems where all atomic positions are allowed to move freely, while maintaining the integrity of the LDH structure intact. Therefore, it has the potential to model different important applications of LDH involving ion-exchange and interlayer equilibrium processes in diverse areas as drug delivery, water purification, and corrosion protection. The magnesium-aluminium based LDH with a metallic ratio 2:1 (Mg_2Al) was chosen to validate our computer simulation framework, because of the comprehensive experimental and computational studies reported in the literature devoted to the understanding of the structure of Mg_2Al LDH. Potential parameters from the literature were used to model the Mg_2Al LDH with different intercalated anions using a new set of atomic point charges calculated with the DDEC6 formalism. Once the model was validated through careful comparisons of the simulated and experimental structures, the procedure was adapted to the Zn_2Al LDH materials. Lennard-Jones parameters had to be developed for zinc (II) cations and calibrated using the experimental structural data found in the literature for Zn_2Al LDH and the height of the galleries determined experimentally in this work for Zn_2Al with intercalated nitrate anions. The consistency of the model is proved by carrying out MD simulations to reproduce in the computer the typical experimental conditions in which the Zn_2Al LDH is immersed in a sodium chloride water solution to act as a nanotrap for aggressive anions in corrosion protection applications. The LDH structure is maintained in the MD simulation in which the LDH is free to move alongside the solution and allowing a natural anion exchange between the LDH and the solution as well as dehydration/hydration of the basal space.

1. Introduction

Layered double hydroxides (LDH) are known as smart macromolecular containers with bifunctional capacity (Richetta et al., 2017). They are capable of hosting functional molecules and release them upon demand, whilst retrieving target species. LDH are constituted by mixed metal cation hydroxide layers held together by interlayers composed of charge compensating anions and water. The interlayers are dominated by electrostatic interactions and complex hydrogen bonding networks. The most widely studied LDH materials have the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}mH_2O$, where M^{2+} and M^{3+} are di- and trivalent cations present in a molar ratio (x) obtained as $M^{3+}/(M^{2+} + M^{3+})$, and A^{n-} is the anion. Singly (M^+) and quadruple (M^{4+}) charged cations such as Li^+ and Ti^{4+} or Zr^{4+} can also be incorporated in the mixed metal cation hydroxide layers. In the present study, M^{2+} is Mg^{2+} or Zn^{2+}, and M^{3+} is Al^{3+}, with a molar ratio of 2:1 of M^{2+} to M^{3+} ($x = 0.33$). The anions considered are Cl^-, NO_3^- or CO_3^{2-} either solvated with one or two water molecules ($m = 1,2$). Depending on the nature of the anions, LDH can be relevant materials with commercial interest to be explored in catalysis, (Lu et al., 2016a) adsorption, (Lu et al., 2016b; Yan et al., 2016) drug delivery (Li et al., 2016; Senapati et al., 2016) or water purification (Yokoi et al., 2016).

The anion-exchange ability of LDH allows them to act as reservoirs for functional anions. The latter can be released upon an external trigger, e.g. a targeted species from the surroundings, which can be temporarily or permanently retrieved by releasing more labile ones. One application in which this property of LDH assumes a fundamental role is in corrosion protection. LDH are able to entrap corrosive species,
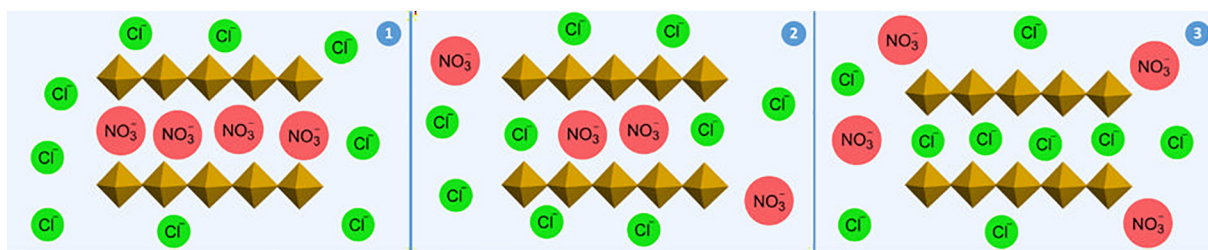

Fig. 1. Scheme with the release of nitrate and intercalation of chloride in the LDH interlayer structure. Green/red circles and yellow polyhedra represent, chloride/nitrate anions and the LDH metal hydroxide layers, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

such as chlorides, (Tedim et al., 2012) and to respond to aggressive electrolyte conditions (Zheludkevich et al., 2012). These layered materials are then ideal macromolecular containers that can be incorporated as additives in functional coatings (Serdechnova et al., 2016), or that can form nanostructured conversion films on top of metallic alloys (Tedim et al., 2011).

Tedim et al. (Tedim et al., 2012) demonstrated that when dispersed in a polymeric coating commonly used in the automotive industry for corrosion protection, zinc-aluminium LDH, with a metallic ratio of 2:1 and intercalated nitrate anions (Zn_2Al-NO_3 LDH), can decrease the permeability of the coatings to chlorides in solution. The choice of the nitrate anion was based on its lower affinity to the LDH interlayers when compared to that of the chloride anion (Miyata, 1983; Israëli et al., 2000). Due to this differential affinity, chloride anions in solution enter the LDH interlayer distance (the so-called galleries or basal space) and replace the nitrate species. As it is schematically illustrated in Fig. 1, when the Zn_2Al-NO_3 LDH material is in contact with a corrosive chloride solution Fig. 1 panel 1, the lower affinity of NO_3^- anions to stay in the galleries when compared with that displayed by Cl^- anions, promotes their exchange Fig. 1 panel 2 until all the nitrate species are displaced from the galleries Fig. 1 panel 3. The ion-exchange equilibrium between trapping chlorides and releasing nitrates was proved experimentally, (Tedim et al., 2012) and Zn_2Al-NO_3 LDH were suggested as concentration responsive materials.

In the present study, a framework is developed to carry out molecular dynamics (MD) simulations with the aim to analyse the mechanism associated with the equilibrium and to establish the baseline for future ion-exchange studies. The computational work was performed for zinc-aluminium and magnesium-aluminium LDH, with a metallic ratio of 2:1 (zinc/magnesium:aluminium), and with solvated nitrate, chloride or carbonate anions intercalated between the metal hydroxide. The magnesium based LDH was chosen to benchmark the quality of the simulation framework here presented against the information available from the noticeable number of computational and experimental studies found in the literature for this system (Lombardo et al., 2005; Cunha et al., 2016; Wang et al., 2009; Galvão et al., 2016; 2017; Costa et al., 2010; Radha et al., 2007). Then, a similar simulation protocol was extended to the zinc-aluminium LDH materials with the same intercalated anions.

Computer simulations in these materials have been a matter of great interest (Rad et al., 2016; Tsukanov and Psakhie, 2016). However, the studies reported in literature were developed following different approaches, based on diverse Lennard-Jones (LJ) parameters, partial charges and software, thus a unique computational protocol that can be extended to different LDH materials incorporating different anions is still lacking. Importantly, as far as we know, none of the previous computational models are able to reproduce the archetypical experimental conditions where the LDH immersed in solution as nanocontainers of corrosion inhibitors (Tedim et al., 2012; Zheludkevich et al., 2012; Serdechnova et al., 2016; Tedim et al., 2011; Galvão et al., 2016; Poznyak et al., 2009).

Herewith, we are reporting a model that takes into account the

periodic expansion of the LDH structure in the directions parallel and perpendicular to the cationic layers with different anions inside the galleries (Thyveetil et al., 2008; Makaremi et al., 2015; Lv et al., 2012). Based on the very satisfactory comparison of calculated and experimental data, it is expected that the model will serve for applications in a wide range of fields, having the potential to predict the controlled release of functional anions, such as corrosion inhibitors (Poznyak et al., 2009) or pharmaceuticals, (Senapati et al., 2016) the trapping of undesired anions (Lu et al., 2016b) or to simulate the influence of pH or other electrolytes (Carneiro et al., 2015). As a test case, the Zn_2Al LDH with intercalated nitrate anions was introduced into a sodium chloride water solution. Encouragingly, it was found that the layered structure of the LDH was not destroyed within the time of a long MD simulation, providing the closest way so far to study an ion or water exchange between the LDH and the solution.

2. Computational methods

2.1. Periodic structures

The LDH crystallographic structure corresponds to the *R-3c* space group. For structures with zinc/aluminium cationic layers, the supercells were described by two lattice parameters, a and c, that were used to define the vectors of the supercell according to: $\overrightarrow{v_x}(2\sqrt{3}a, 0, 0)$, $\overrightarrow{v_y}\left(-\sqrt{3}a/2, 3a/2, 0\right)$ and $\overrightarrow{v_z}\left(a/2, \sqrt{3}a/2, c/3\right)$.(Costa et al., 2010; Radha et al., 2007; Costa et al., 2012). The lattice parameter a is defined by the size and ratio of metal cations in the LDH cationic layers. This parameter was obtained in a previous work (Wang et al., 2009) from the position of the (110) reflection of the powder X-ray diffraction (XRD) pattern. In the case of magnesium/aluminium LDH, the atomic coordinates and lattice parameters of the cationic layer were those described in literature for a natural occurring magnesium/aluminium LDH (Krivovichev et al., 2010) and were taken directly from the powder diffraction file (PDF)-4+ 2016 database of the International Center for Diffraction Data (ICDD). The c lattice parameter depends on the interlayer distance occupied by the anions and was taken from literature (Lombardo et al., 2005; Cunha et al., 2016; Wang et al., 2009; Galvão et al., 2016; 2017; Costa et al., 2010; Radha et al., 2007).

Both magnesium/aluminium and zinc/aluminium LDH models with nitrate, chloride, and carbonate anions were built within the supercell approach for periodic repetition in the three dimensions, i.e., Mg_2Al-Cl, Mg_2Al-NO_3, and Mg_2Al-CO_3 or Zn_2Al-Cl, Zn_2Al-NO_3, and Zn_2Al-CO_3 LDH, which are named from now on as MI, MII, and MIII or ZI, ZII, and ZIII, respectively. The systems, the supercells and notations used in this work are summarized in Table 1, while Fig. 2 displays the corresponding structural representations. In the present work, the number of water molecules per charge was fixed to the ratio 2:1, which yields two water molecules per chloride or nitrate anion and four water molecules per carbonate species (Table 1). The number of solvating water molecules per anion was chosen according to experimental results presented in literature (Lombardo et al., 2005; Cunha et al., 2016; Ay et al., 2009; Latterini et al., 2007). It should be noted at this point that in the case of