Chapter 22
Molecular Dynamics Simulation of Interlayer Structure and Hydration Properties of Glycine Intercalated Layered Double Hydroxides

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ABSTRACT
Interlayer structure, hydrogen-bond, hydration and swelling properties of glycine intercalated layered double hydroxides (LDHs-Gly) were investigated with molecular dynamics (MD) methods. The results show that the interlayer spacing $d_c$ increases as hydration level increases. The computed hydration energies reach the most negative values at low water contents and change rapidly over the range $1 \leq N_W \leq 6$, and slowly and gradually approach the potential energy for bulk SPC water at $N_W > 6$. But there are no local minima in the energy over the entire hydration range. This result suggests that LDHs-Gly tend to absorb water continuously in water-rich environments and enhance swelling to delaminate the hydroxide layers. The interlayers of LDHs-Gly exhibit complex hydrogen-bond network. With water content increasing, the glycine molecules progressively change their orientation from parallel to the

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layers to nearly perpendicular. Water molecules firstly form hydrogen-bond with M-OH layers at low water contents. While the hydroxide layers gradually get to saturation state at \( N_w > 3 \). And then water molecules continuously fill the interlayer to expand interlayer spacing.

**INTRODUCTION**

Layered double hydroxides, also known as anionic clays or hydrotalcite-like compounds (HTLcs), may be considered as analogous to the magnesium hydroxide mineral brucite. In the largest group of anionic clays some of the Mg\(^{2+}\) is substituted by a M\(^{3+}\) species, for example Al\(^{3+}\), Fe\(^{3+}\) or Ga\(^{3+}\). Other varieties of anionic clays exist where the M\(^{2+}\) species is for example Zn\(^{2+}\) or Ni\(^{2+}\), giving rise to the family of compounds of general formula \( M^{2+}_{1-x}M^{3+}_x(OH)_2A^{x-} \cdot nH_2O \). In each case the resulting structure consists of layers bearing a net positive charge, which is compensated by the introduction of anions in the interlayer region, as well as at the edges and surfaces of layered double hydroxides (Cavani et al., 1991).

Incorporation of bio- and organic species into LDHs interlayers using ion-exchange method has gained significant attention in recent years. Amino acids, as important components of proteins, enzymes and biomolecules, can serve as pillars in cationic and anionic clays. Intercalation compounds of amino acids offer the perspective applications in separation science as chiral catalyst, as well as in drug delivery systems.

In recent times there has been a growing interest in anionic clays although, historically, attention has been focused almost exclusively on the cationic clay materials. Experimental techniques have been used to determine or at least to infer the local structure of the clay sheet or intercalated material. However, clays are polycrystalline materials and precise experimental location of interlayer species is extremely difficult. Because of these limitations, interest in and the use of computational methods for studying these layered solids has increased in order that observed physical and chemical properties may be rationalised and even predicted.

By applying initial velocities to a configuration of atoms and solving Newton’s equations of motion the potential energy surface may be traversed in a deterministic fashion and the temporal evolution of a system followed. This is known as molecular dynamics (MD). In this technique thermal energy is included using a thermostat, which allows potential energy barriers to be overcome in a realistic manner. The main advantage of the method is that the dynamical evolution of a system, with time, may be followed, which allows comparison with additional experimental techniques such as NMR and quasi-elastic neutron scattering. It still remains a challenge, however, to follow the evolution of a system beyond the timescale of 1–10 ns, even when using classical mechanics simulations.

Force-fields are often parameterised to fit a set of experimental data, or based upon detailed electronic structure calculations. However, there are relatively few force-fields able to reliably model both the interlayer (often organic) species and the octahedral metal ion environments peculiar to the clay structure, particularly in the case of anionic clays. Force-fields that are specifically parameterised to model clay–organic interactions (Teppen et al., 1997; Cygan et al., 2004). The more generic Dreiding force-field has also been utilised, in a modified form, for modelling clay systems, especially LDHs (Newman, et al., 2001). Force-field based molecular dynamics simulations have been used to determine the elastic properties of clay sheets, an important property for the prediction of bulk materials properties.

Recent experimental studies have shown that glycine intercalated layered double hydroxides (LDHs-Gly) can be obtained via hydrothermal synthesis, and enhanced swelling leading to delamination of the LDHs layers can be achieved in a solution environment (Li et al., 2006; Aisawa et al., 2006).