



MOLECULAR SIMULATIONS OF HYDROTALCITE INTERCALATED WITH PYRENETETRASULFONATE

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Abstract

Hydrotalcite-like structures were intercalated with pyrenetetrasulfonate anions. The structures were calculated by molecular simulations methods in Cerius² modelling environment. The first initial models were built for 4 different interlayer distances on the base of experimental data (X-ray diffraction and thermogravimetry). For these initial models state space of guests in the interlayer was scanned by Supramol program. The amount of water molecules was randomly inserted into relevant models in agreement with thermogravimetry results. Various calculation techniques were tested. It appeared as optimal to calculate with rigid hydrotalcite layers, cell parameters and with charges estimated separately for every molecule and layer. The intercalated structures were described by following models: (i) interlayer distance 9.83 Å and 0 water molecules (ii) interlayer distance 13.63 Å and 36 water molecules and (iii) two interlayer distances 11.74 Å and 12.81 Å and each with 25 water molecules.

Introduction

Hydrotalcite-like layered structures [1] consist of periodically repeated positively charged layers (usually comprising Zn, Al, and O) and the interlayers containing anions, which compensate the positive charge of the layers. An intercalation causes changes of physical and chemical properties of resulting structures and subsequent design can be directly focused on targeted modification of these materials. It allows for instance changes of optical properties of individual components in the interlayer space. Therefore, the resultant optical properties of intercalated compounds are usually different before and after the intercalation. The intercalated hydrotalcites are very specific and useful materials because set of organic and inorganic anions suitable for their intercalation is very wide.

A knowledge and understanding of the structure-property relationship of the investigated samples is necessary for the development of new materials with interesting properties for industrial applications. The reason is very simple because the material properties always depend on the structure, mainly on relative spatial arrangement of the guests in the interlayer space. The X-ray diffraction analysis is usually the most powerful technique for determination of the crystal structure. Nevertheless, it is not sufficient in the case of powder hydrotalcite samples, thus it is necessary to use computing methods. The hydrotalcite

structures with hundreds or thousands of atoms are quite impossible to be solved by *ab-initio* calculations due to long computer time. From this reason molecular simulations based on the empirical force fields (i.e. the molecular mechanics and the classical molecular dynamics) is good option for solving these disordered structures.

The molecular mechanics search for an optimized structure with the minimum energy. The resultant minimized structure is obtained by geometry modification of an initial model. The crystal energy is calculated for different potential functions on the base of parameters obtained from the empirical force fields. This leads to a necessity to compare the molecular modelling results with experimental measurements (powder X-ray diffraction, infrared spectroscopy, thermogravimetry, etc.) However, experimental data are not used only for validation of calculations but also some constraints and structural parameters in the initial model and also creation of minimization strategies can be estimated on the experimental results.

In this work the molecular strategy includes the building of initial models for Supramol program, the generating a set of initial models, the determining which parameters of the structure should be held fixed and which should be variable, the choosing of the force field, the setting up an expression for calculating the energy, the minimization procedure, etc.

Modelling principles

Principles of molecular simulations [2] lie in calculations of potential energy for a given configuration of atoms on the base of empirical force fields parameters. The total energy of the system is the sum of energies of non bonded and bonded interactions, which are based on mechanical approach, where the atoms are usually described as mechanical oscillators. The energy evaluation carries necessary information for structure minimization and dynamic simulations.

Force field parameters are usually estimated pursuant to known structures and their properties. The special force fields exist for various types of structures and also general ones exist. The specific force field for hydrotalcites has not been derived yet. The Universal force field [3] was used in the calculations because it contains necessary parameters for all atoms of the periodic table. The Ewald summation method [4] was used for calculating of electrostatic interactions in the periodic hydrotalcite system. The Charge equilibration (QEq) method [5] is used for the calculation of charge distribution in the model. This method calculates the charge distribution according to the model geometry and the energy.

The aim of molecular mechanics strategies is to find a local minimum on the potential energy surface for a given

initial model. The atom coordinates (in periodic models eventually cell parameters) are optimized by various iterative algorithms. A cascade of various methods (steepest descent, conjugate gradient, Newton methods) with different convergent parameters was used for calculations.

The molecular dynamics is based on evaluations of forces acting on the atoms and moving the atoms according to these forces. It is a calculation of classical Newton equations for a system of N atoms. It is ordinarily used for determining some statistical characteristics of the model evolving in some statistical ensemble. But in this work, the dynamics is used for the optimal geometry seeking. The dynamics enables the model to get over a potential barrier so that the calculated structure should come to some better nearby local minimum which is inaccessible for the minimization. This technique is known as quenched dynamics.

The quenched dynamics is suitable still only for effective exploring of the local state space for given conformation and is not sufficient for seeking for the structure with global minimal energy. Hence the program Supramol which scans the entire potential energy surface was used. The scanning produces a plenty of rough initial models. Then the most feasible ones, each separately, are minimized and subsequently optimized by molecular mechanics calculations.

Results

The model of pyrenetetrasulfonate acid anion $C_{16}H_6O_{12}S_4$ was built in the 3D sketcher module in Cerius² modelling environment. The minimization and the recounting of charges were iteratively executed until stable energy of molecule was reached. It refined the molecular geometry.

The model of layers was built according to crystallographic data which was provided by Prof. U. Costantino from University di Perugia, Italy:

- Trigonal cell system, space group $R\bar{3}m$.
- Cell parameters: $a = b = 3.07598 \text{ \AA}$; $c = 23.2048 \text{ \AA}$.
- Atomic coordinates:

Element	x/a	y/b	z/c
Zn (Al)	0.0	0.0	0.0
O	0.0	0.0	0.37700

It was necessary to add hydroxyl groups to the model of the host framework and create a supercell by linking 25 (5*5) primitive cells so that its charge would equal to the charge of two guest anions which would be placed into the interlayer space. The formula of the resulting structure is as following:



where n is a number describing amount of water in individual samples.

The distribution of Zn and Al atoms is as random as possible without any preferred location. A basic model for follow-up calculations originates from optimization. This

is consisted from (i) the charge recounting individually for each layer and from (ii) the minimization with fixed all parameters and positions, only hydroxyl groups were free. The extra model was created for each structure with different interlayer distance.

The Supramol program [6] written by Bohdan Koudelka at KChFO MFF UK was used for generating of initial models. Its use is restricted to the motion of only two independent units. Those units were pyrenetetrasulfonate anions, which were placed into one interlayer space of the model (Fig.1). The positions and orientations of rigid units represent degrees of freedom. The state space was defined by proper range option of the inner coordinates with consideration of symmetry. A set of 12 billion initial models for each structure was generated with various positions of guests and with their various mutual orientations in the interlayer space. Models with an overlap of guests were primarily excluded. After that the models with a higher value of vdW energy were excluded from about 50 million remaining models. About 10 essentially different initial models for the next molecular mechanics calculations were selected from remaining 300–600 models.

The configuration of molecules in one interlayer space was identically replicated to other two interlayers. The water molecules in proper amount were randomly placed into the interlayers of the models representing the samples: into models 9.83 Å added 0 water molecules per one interlayer, into models 13.63 Å added 36 water molecules, into models 11.74 Å + 12.81 Å added 25 water molecules.

The layers for each model (except hydroxyl groups) were taken as rigid units or they were fixed.

The methods of charge calculations had a significant effect on the results of minimization because the QEq method of charges recounting does not take into account the bonds. Charges recounting in the case of bigger groups was tested in order to speed up the calculations but it always led to a higher redistribution of the charges mutually among the molecules and the results were significantly affected. Thus,

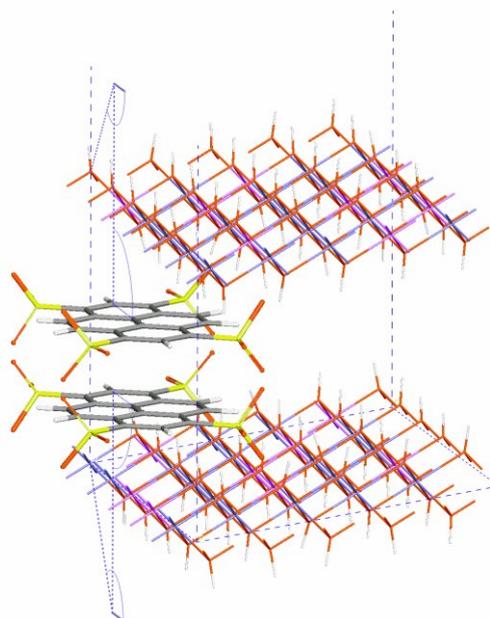


Figure 1. The initial model prepared for Supramol.

the charges had to be recounted for each water molecule and each acid molecule and each layer separately.

The results were also affected by methods of limiting interaction range. A direct cut-off could be used for short-range vdW interaction but it was found out that this faster method cannot be used in any case for evaluation of electrostatic interactions. It was proved by applying the Ewald summation that results were not different as far as an energy precision of 10^{-4} kcal/mol was reached.

The minimization procedure consisted of iteration of charge recalculating and 500-step minimization until convergence criteria were reached.

The molecular dynamics calculations were carried out in an NVT statistical ensemble (N—constant number of particles, V—constant volume (fixed cell size), T—constant temperature) at the temperature of 300 K, one step duration was 0.001 ps, which is the longest acceptable time step for a model with hydrogen atoms. Tens up to hundreds thousands steps of dynamics were carried out, whereas at least half of them had already been in equilibrium. Every the hundredth step of dynamics the model was minimized and was saved. 200 steps of minimization were done. It is sufficient for appreciation of energetic pertinence of the states. The most energetic expedient states were subsequently properly minimized.

The models with different interlayer distances and amount of co-intercalated water depending on relative humidity were optimized on the base of experimental measurements made at University of Pardubice by X-ray diffraction and thermogravimetry.

Discussion

Sample 9.83 Å

9 models were selected from Supramol results—each model with both acid molecules positioned in one layer parallel with hydrocalcite layers or alternatively with acid molecules only slightly tilted and/or little moved out from the layer. During minimization the interlayer distance expanded for all models with free cell parameter c . Even the minimization under a pressure or optimization by quenched molecular dynamics did not turn this trend. The model with molecules in one level expanded the interlayer distance at the least. For this model the systematic changing of the angles of sulfonates and turning them was also tested (thanks to tiny modification in Supramol). The best model obtained by these modifications showed nearly the same characteristics as the original one. It can be concluded that these modifications of sulfonates turning did not have significant influence on the result.

Therefore, the models were calculated with fixed cell parameters until the convergence criteria were reached. Final energies differed at the most in percent units. Nevertheless, the calculations showed that changes of energy in percents are also possible to be gained by adjustment of sulfonates or by dynamics. Thus, all minimized models have similar probability with respect to energy to occur in real sample. (One selected model is shown at Fig. 2.).

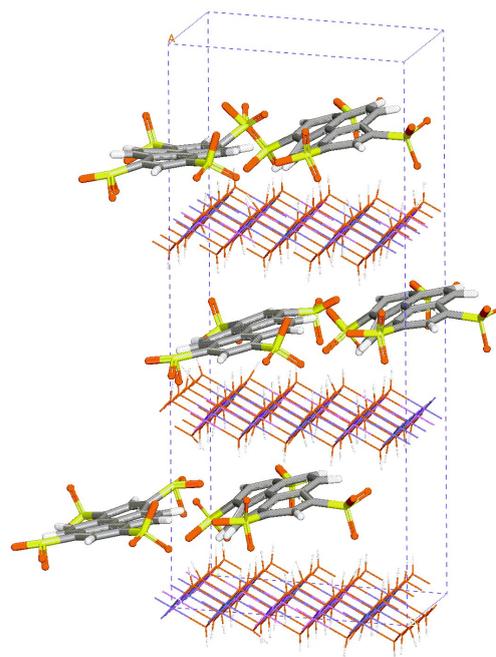


Figure 2. One selected model with interlayer 9.83 Å.

Sample 13.63 Å

11 models were selected from Supramol—one with tilted acids, others with acids in two layers horizontally located and variably turned and shifted with respect to each other. Various optimization methods (preliminary minimization with fixed parameters, pressure, dynamics, less random water distribution) were tested during calculations with free cell parameter c . Still the interlayer distance expanded. Nevertheless it was shown that starting distribution of water did not have a significant influence on resulting structure because the optimization, especially by the dynamics, finally sorted water molecules to similar positions in the minimized models.

The models were subsequently minimized with fixed cell parameters. The total energy of all resultant models differs only in several percents so the configuration of acids is very variable in the frame of tested models where acids are positioned arbitrarily above themselves (both molecules stay in its half of interlayer, roughly in thirds of whole interlayer). It is clearly obvious from modelling results that water molecules form triple level organization, one level in the middle, other ones in quarters of the interlayer space (whereas oxygen are turned towards the layers). Fig. 3 shows a selected minimized model describing positions of molecules in the interlayer.

Sample 11.74 Å + 12.81 Å

Both phases of the sample were modelled separately. 9 models were selected from Supramol for each phase. Models were minimized with fixed cell parameters. The energies of phases differed up to 10 %. It can be deduced from this the sample is not constituted separately from 2 phases.

It can be supposed that the interlayers could be randomly alternated. Therefore, a model with six layers It can be supposed that the interlayers could be randomly al-

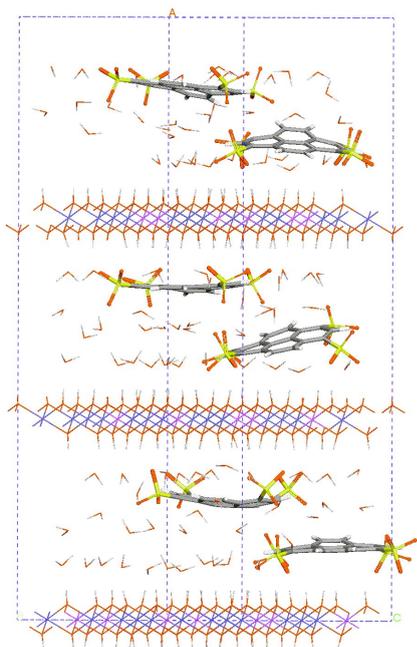


Figure 3. One selected model with interlayer 13.63 Å.

ternated. Therefore, a model with six layers was constructed where the interlayer distances 11.74 Å and 12.81 Å alternated periodically. Molecule configurations were copied from the most expedient models of both phases. The model energy after minimization appeared just in the middle of energies of relevant one-phase models. Thus, the model with alternating interlayers was not energetically better than the one-phase ones and there is no explanation or reason for two phases. The most probable is that the sample was not yet stabilized after preceding changes of environmental conditions.

Conclusion

The results show an applicability of molecular simulations for solving hydrotalcite structures intercalated with pyrenetetrakisulfonate anions and similar structures. The

strategies of molecular modelling suitable for solving the hydrotalcite layer structures were developed on the base of combination of experimental results and results from modelling. Interlayer space of 9.83 Å and 13.63 Å models is characterized by planar arrangement of pyrenetetrakisulfonate anions with a disorder in mutual position and orientation with respect to each other. One layer of pyrenetetrakisulfonate anions is typical for 9.83 Å sample and two layers for 13.63 Å sample with water in the interlayer. Water molecules in the interlayer space create three-layer arrangement parallel to hydrotalcite layers. Model 11.74 Å + 12.81 Å was calculated as two single phases but energy difference does not support this prediction. Subsequently the alternation of layers for two phases was calculated but the result was not energetically better. It can be concluded that this sample was not yet stabilized.

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