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Development and Application of the Nano-Kaolinite Molecular Cluster Model

Ph.D. THESIS

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Introduction

“Molecular Engineering” is an interdisciplinary research strategy, which is based on fundamental basic science, engineering concepts and practices with the potential to develop new technologies in a bottom-up, molecular approach. An important component of this strategy is the development and application of realistic theoretical models that are not just mimic the structure and composition, but also behave like a real chemical system with respect of chemical reactivity. These models have the potential of rationalizing experimental observations, directing experimental work, and generating experimentally testable hypotheses. The design, optimization, and execution of experimental work involving clay minerals and nanoparticles have major obstacles due to our limited atomic level knowledge and understanding of processes taking place at the outer surface (adsorption) and the inner surface (intercalation). Although many experimental methods are available for interrogating nano-clays, we need atomic level approach to understand structural changes and reactivity. We can increase the reactivity and in parallel the industrial value of crystalline kaolinite by modifying its structure and surface properties. Upon elimination of crystallinity order (delamination and exfoliation), the commonly employed experimental techniques, such X-ray diffraction or Raman spectroscopy, are no longer applicable although infrared spectroscopy can provide some indirect information about the chemical environment of specific groups and ions. Therefore, we do not have any direct analytical method that is able to determine, for example the position of atoms in nano-kaolinite to date. This would be essential in understanding the differences between the periodic crystalline kaolinite and molecular exfoliated nano-kaolinite and in turn, this could assist the development of industrially valuable raw materials.

Computational Methods

In modeling crystalline and nano-kaolinite both periodic and molecular cluster models were employed. A new approach to define molecular cluster models was developed by applying the coordination chemical principles related to of inner and outer coordination spheres. The models of nano-kaolinite particles are based on the crystal structure and they correspond to defect free, ideal structures. Corresponding mathematical rules were formulated in order to create models with an arbitrary size or generation. In order to define the most appropriate theoretical method with respect of accuracy and computational time, a wide range of levels of theory were employed from *ab initio* wave function method, Hartree-Fock (HF), and density functional theory (DFT) with different double- ζ (D95, Lanl2DZ, 6-31Gd, SVP) and triple- ζ (def2TZVP) quality basis sets. In addition, semi-empirical methods, such as MNDO

approximation (PM6, PM7) and density functional based density functional tight binding method (SCC-DFTB) were also applied for models with several thousands of electrons.

Scientific Insights and Development of Molecular Engineering Tools

1. Thesis

The literature examples to date employed in studying exfoliated nano-kaolinite particles fall short of accuracy and reliability in reproducing even qualitative chemical trends expected from theoretical considerations and experimental measurements.

Using the highly truncated molecular cluster models from literature and employing a commonly used theoretical (B3LYP hybrid functional and double- ζ basis set) the adsorbed and intercalated structures and binding energies for various reagents (urea, ethylene glycol, potassium acetate) were determined. It was found that while the molecular structures appeared to be reasonable; however, the calculated binding energies did not correlate with even qualitative theoretical trends or with any experimental observations.

A conclusion was drawn that both the composition and size of computer model and the adequacy of used theoretical method need to be improved.

2. Thesis

A more holistic computational model can be developed when considering the principles of coordination chemistry for the reactive site of nano-kaolinite formed by Al- and Si-honeycombs.

Molecular cluster models were developed by focusing on what the inner, outer, and peripheral coordination spheres contain. As first approximation, a neutral cluster model was created by replacing the dangling Al^{3+} and Si^{4+} ions at the periphery with Na^+ and Mg^{2+} counter ions.

It was shown that the coordination chemistry based molecular cluster models describe a much more complete chemical environment of the central Al- and Si-honeycombs than any previously published, truncated molecular cluster model.

3. Thesis

In addition to a more complete computational model, validated theoretical level of theory assists in recognizing the most reactive groups by their sensitivity to the variation of external chemical environment to nano-kaolinite.

A search of validated theoretical methods was carried out using both crystalline and molecular cluster models. The sensitivity of the reactive groups of nano-kaolinite and related structure

changes were defined as function of the applied level of theory and the nature of the external chemical environment.

Initially, it was found that regardless of the applied density functional, the triple- ζ (def2TZVP) basis set was initially promoted to be the optimal to describe the correct molecular structure of nano-kaolinite. Later it was recognized that the use of a smaller double- ζ (SVP) basis set turned out to be also acceptable with a significant reduction of computational time (to 5%) with some compromise in relative energies.

4. Thesis

The validated level of theory allows for specifically identifying the most sensitive, hence reactive groups and ions of the nano-kaolinite in comparison to the crystalline kaolinite.

A systematic series of levels of theory were employed to interrogate the response of inner-hydroxide, surface-hydroxide, bridging-oxide to variation in the polarity of the external chemical environment, presence of crystalline phase, being submersed into a low-to-high dielectric solvent environment, with the presence of explicit solvent molecules. The structural changes and energetic relationships were practically unanimous among all examined levels of theory to a varying degree of confidence.

The orientation of the inner-hydroxide groups was determined to be greatly depends on the external chemical environment, which contradicts the literature examples of using the inner-hydroxide stretching bands as a reference in FTIR spectra. The surface-hydroxide groups can adopt electrophilic/hydrogen-bond and nucleophilic/hydrogen-bond acceptor orientations in contrast to the crystalline kaolinite with only electrophilic/hydrogen-bond donor orientation. The orientation of surface-hydroxide groups as a function of the external chemical environment in a unique function of the polarity of external chemical environment and the nature of the explicit solvent molecules. The positions of the Al^{3+} ions of the octahedral sheet also drastically changes relative to either of the O- or T-sheets during the formation of nano-kaolinite, which greatly contribute to the tantalizing morphology and formation of nanotubes.

5. Thesis

For structure/function studies of nano-kaolinite particles, the use of alkali and alkaline earth metals must be avoided that hinder unconstrained full structural optimizations as a key for potential energy surface mapping. Furthermore, an algorithm needs to be set up for generating any arbitrary sized nanoparticle for modeling secondary structure features such as experimentally observable morphology and reactivity.

Utilizing mathematical rules for molecular cluster model structure and composition, an algorithm was developed for constructing model generations or “families” ($G_1, G_2, G_3, \dots, G_i$) of molecular cluster models that enable to describe the surface properties of the nano-kaolinite at the molecular level with experimental fidelity. For charge neutrality, the kaolinite nanoparticle edges were protonated at surface-hydroxide, apical-oxide, and bridging-oxide peripheral groups in order to create an ideal defect free nano-particle. Due to the size of the higher generation models, the applicability of semi-empirical methods (PM7, SCC-DFTB) was also invoked.

It was found that semi-empirical methods provide acceptable stationary structures, but for accurate energetic results they need to be further parameterized and specialized for nano-kaolinite in order to be approximate the results of the *ab initio* method calculations and experimental observations. However, density functional based methods with saturated basis set and employment of implicit solvation models allows for the full and unconstrained optimization of second generation molecular cluster models for nano-kaolinite.

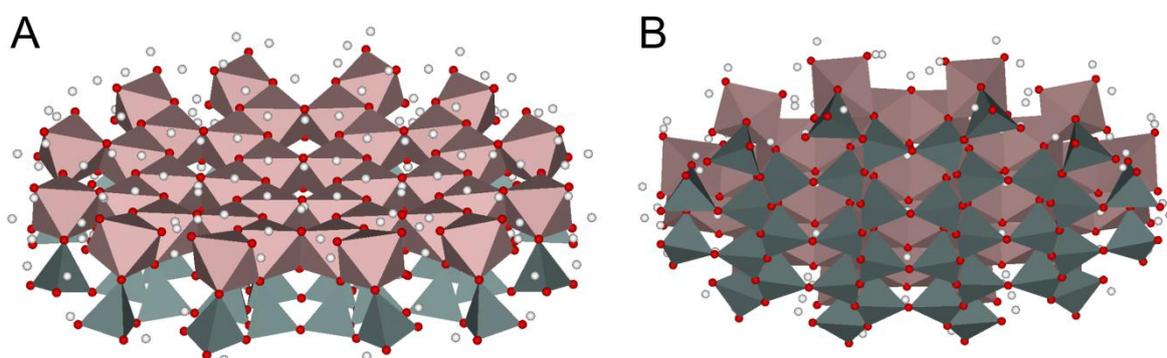


Figure 1: Second generation (G_2 , 414 atoms and 2700 electrons) molecular cluster model for exfoliated nano-kaolinite with the views of octahedral (A) and tetrahedral (B) sheets. The charge neutrality of the model was achieved by employing protonation rules for the edges.

6. Thesis

Development of a well defined, experimentally validated molecular engineering technology allows for a direct connection between experimental observables and atomic level modeling for nano-kaolinite.

The second generation (G_2 , **Figure 1**) molecular cluster model constructed based on coordination chemistry rules was utilized in merging experimental observations and theoretical modeling in a molecular engineering approach. The morphology of the calculated

structures reproduced the experimental curvature of the nanotubes from TEM measurement with remarkable agreement. The theoretically predicted vibrational spectra of the inner Al- and Si-honeycombs of nano-kaolinite gave the most accurate results to date with respect to experimental FTIR results. Application of the most accurate theoretical method (PW91+D/SVP/PCM) and model (G_2) enabled the atomic-level description of the dehydration and dehydroxylation processes of nano-kaolinite. All possible proton-transfer and dehydration steps were mapped out along the reaction coordinate of meta-kaolinite formation. The theoretical mass loss curves matched well the experimental thermogravimetric results.

The good agreement in location of stationary structures, curvature of the potential energy surface, and energetics contributed to a notable breakthrough in modeling nano-kaolinite particle structure/function relationship. These unambiguously indicate that the computational models and experimental observation work shoulder to shoulder. This is the requirement for establishing a molecular engineering technology

In closing, the development of a new computational model and validation of the theoretical levels allowed for describing at the atomic level molecular structural and energetic features that we cannot measure in the laboratory and *vice versa* we can use experimental measurement to further tune and enhance the predictive power of the molecular engineering technology. Further advancement of this technology is expected for Al- and Si-NMR spectra, photochemical properties and solar energy conversion from UV-vis excited state description. The quantum chemical results are absolutely essential for developing molecular mechanical force fields, and as a long term goal, coarse grain models that capable of describing structures at the micrometer scale and millisecond dynamic simulation range.

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1. **Attila Táborosi**, Róbert Kurdi, Róbert K. Szilágyi: Adsorption and intercalation of small molecules on kaolinite from molecular modeling studies, *Hungarian Journal of Industry and Chemistry*, 42(1), 19-23, **2014**
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3. **Attila Táborosi**, Róbert K. Szilágyi: Realistic molecular cluster models for exfoliated kaolinite, *Clay Minerals*, 50, 307-327, **2015**
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5. Balázs Zsirka, **Attila Táborosi**, Péter Szabó, Róbert K. Szilágyi, Erzsébet Horváth, Tatjana Juzsakova, Dávid Fertig, János Kristóf: Surface characterization of mechanochemically modified exfoliated halloysite nanoscrolls, *Langmuir*, 33(14), 3534-3547, **2017**
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Oral presentation in English with only abstract appearance:

1. Róbert K. Szilágyi, Róbert Kurdi, Attila Táborosi: Development of molecular cluster models for structure/property relationships of clay, *7th Mid-European Clay Conference*, **2014**
2. **Attila Táborosi**, Róbert K. Szilágyi: In silico examination of the exfoliated kaolinite, *2015 Montana ACS Spring Meeting*, **2015**
3. Róbert K. Szilágyi, Orsolya Fónagy, Mercedész Kiss, Balázs Zsirka, **Attila Táborosi**: A journey into the world of “molecules” in clay minerals: synthesis, spectroscopy, and computation, *Whitman College seminar*, **2015**
4. **Attila Táborosi**, Róbert K. Szilágyi: In silico examination of pyrite mineral structure, *Montana State University, Graduate Research Seminar*, **2015**

5. Róbert K. Szilágyi, Attila Táborosi: A discussion of molecular engineering and computational modeling of nano-clays, *Montana State University – College of Engineering Research Seminar*, **2016**
6. Róbert K. Szilágyi, Attila Táborosi, Balázs Zsirka, Scott Spring, Tacey Hicks, Takahide Yamaguchi: Quantum mechanical engineering of exfoliated kaolinite, *8th Mid-European Clay Conference*, **2016**

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1. **Táborosi Attila**, Kurdi Róbert, Szilágyi K. Róbert: Kaolinit-komplexek interkalációs és adszorpciós vizsgálata kvantumkémiai módszerekkel, *X. Kárpát-medencei Környezettudományi Konferencia*, **2014**

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1. **Attila Táborosi**, Róbert Kurdi, Róbert K. Szilágyi: Investigation of the kaolinite inner-OH and outer surface-OH with new molecular cluster model using quantum chemical methods, *7th Mid-European Clay Conference*, **2014**
2. **Attila Táborosi**, Róbert K. Szilágyi: Development of molecular cluster models for nano-kaolinite from crystalline structures, *8th Mid-European Clay Conference*, **2016**
(the best poster certificate)