Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2014

Supporting information for

The Positions of Inner Hydroxide Groups and Aluminium Ions in Exfoliated Kaolinite as Indicators for Outer Chemical Environment

Attila Táborosi, Róbert Kurdi and Róbert K. Szilágyi*

Surfaces and Nanostructures Group, Department of Analytical Chemistry, Faculty of Engineering, University of Pannonia, Veszprém, H-8201, PO Box 10. Hungary E-mail: szilagyi@almos.uni-pannon.hu Homepage: http://analitika.mk.uni-pannon.hu/ and

na

Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717 E-mail: szilagyi@montana.edu

Experimental structural information for crystalline Kaolinite

Literature reference for the combined X-ray diffraction, neutron diffraction and computational work:

 Lubomir Smrcok, Daniel Tunega, Anibal Javier Ramirez-Cuesta, Eva Scholtzova

 The combined inelastic neutron scattering and solid state DFT study of hydrogen atoms dynamics in a highly ordered kaolinite

 Physics and Chemistry of Minerals (2010) 37(8):571-579 DOI 10.1007/s00269-010-0358-3
 PDF

 Inorganic Crystal Structure Database code 168601

5x5x3 lattice of kaolinite



Cartesian coordinates: XYZ

Structural optimizations for the 1x1x1 unit cell of kaolinte











Models evaluating the effect of the levels of theory

- effective core potential at <u>HF</u> or <u>B3LYP</u> level
- effective core potential with polarizaton at <u>B3LYP</u> level
- double-zeta all electron basis set at <u>B3LYP</u> level
- DZ with an additional polarization function at $\underline{B3LYP}$ level
- DZ with an additional diffuse and polarization functions at <u>B3LYP</u> level

Models evaluating the effect of the chemical environment

- inclusion of an explicit solvent molecule at <u>B3LYP</u> level
- inclusion of an explicit Mg2+ ion (fixed) at <u>B3LYP</u> level
- inclusion of an explicit Mg2+ ion (relaxed) at <u>B3LYP</u> level
- embedding into a water polarizabale continuum at <u>B3LYP</u> level

Counter ion effects

- No counter ions: XYZ
- Cs+ and Ba2+ counter ions: XYZ
- K+ and Ca2+ counter ions: XYZ
- Li+ and Be2+ counter ions: <u>XYZ</u>
- Na+ and Mg2+ counter ions: <u>XYZ</u>
- No counter ions, but water PCM: <u>XYZ</u>
- K+ and Mg2+ counter ions and water PCM: XYZ





Performance of mixed basis sets

- Mixed basis set 1 (O.H-O at TZ level, rest DZ* level), HF calculations: XYZ
- Mixed basis set 2-Al (O..H-OAl2 at TZ level, rest DZ* level), HF calculations: XYZ
- Mixed basis set 2-Si (Si2O..H-O at TZ level, rest DZ* level), HF calculations: XYZ
- Mixed basis set 3-Al (O.H-O{Al(OH)3(O)2}2 at TZ level, rest DZ* level), HF calculations: XYZ
- Mixed basis set 3-Si ((O3Si)2O..H-O at TZ level, rest DZ* level), HF calculations: <u>XYZ</u>
 Mixed basis set 4 ((O3Si)2O..H-O{Al(OH)3(O)2}2 at TZ level, rest DZ* level), HF calculations: <u>XYZ</u>

Functional dependence with the largest basis set (TZ)





Becke's 3-parametric hybrid exchange and Lee-Yang-Parr correlation



Becke's pure GGA exchange and Lee-Yang-Parr correlation



Perdew and Wang's pure GGA exchange and correlation (with 5% HFX for convergence)

Artistic rendering of the implications of the computational results with regards of adsorption and intercalation

Animated illustrations of computational results programmed by Gergõ Roth software engineer Veszprém, H-8200, Hungary email:gergo.roth91 at gmail.com; web site:http://www.muleengine.com **Urea adsorption and desorption at the O-sheet of exfoliated kaolinite** Urea molecules collide with the O-sheet surface of the exfoliated kaolinite sheet and become trapped by hydrogen bonding interactions formed between the surface hydroxide groups and the carbonyl groups of the urea. This results in a structural rearrangement within the a fused octahedral(O) and tetrahedral (T) sheets or OT-layer. The displacements are exaggerated in the animation to emphasize the structural displacements that will enable the intercalation process. (https://www.youtube.com/watch?v=al1RRGNjov0)

Urea adsorption and desorption at both O- and T-sheets of exfoliated kaolinite

Urea molecules collide with the surface of the exfoliated kaolinite sheet and become trapped by hydrogen bonding interactions between the surface hydroxide groups and the carbonyl group of urea or the bridging oxide groups and the amide groups of urea at the O- and T-sheets, respectively. This results in a structural rearrangement within the a fused octahedral(O) and tetrahedral (T) sheets of the OT-layer. The movements of atoms are exaggerated to emphasize the structural displacements that will enable the intercalation process. (https://www.youtube.com/watch?v=PZSHdxa7Eb4)

Urea adsorption and desorption at the O-sheet of on crystalline kaolinite

Urea molecules collide with the outer surface of kaolinite and become trapped by hydrogen bonding interactions between the surface hydroxide groups and the carbonyl groups of urea. This results in a structural rearrangement within the a fused octahedral(O) and tetrahedral (T) sheets of the OT-layer. The displacements are exaggerated to emphasize the structural displacements. Upon the intralayer swelling, the hydrogen bonding interactions weaken between two adjacent OT-sheets, which facilitates the intercalation process. (<u>https://www.youtube.com/watch?</u> <u>v=7ZRmouwiLyM</u>)

Urea intercalation of kaolinite (a concerted process)

Urea molecules attack the kaolinite simultaneously both on the outer surface and by entering the interlayer space between two adjacent fused octahedral(O) and tetrahedral (T) sheets of OT-layers. Once the kaolinite structure has undergone a considerable structural reorganization, the urea molecules continue to increase the basal plane distance, thus swelling to a degree that matches values measured by crystallographic measurements. (https://www.youtube.com/watch?v=xBTiA9viIQo)

Urea intercalation of kaolinite (a stepwise process)

Urea molecules adsorbed at the surface of kaolinite modify the chemical bonding within a fused octahedral(O) and tetrahedral (T) sheet of the OTlayer relative to a pristine kaolinite surface. This creates a polarization of chemical bonds through the OT-layer that weakens the interlayer hydrogenbonding interactions between the upper and the lower OT-layers. This in turns allows for urea molecules to enter through the edges of the kaolinite sheets. Upon entering between the layers, the conformational changes allows for adapting the most likely position, as can be deduced from crystallographic and vibrational spectroscopic measurements. (https://www.youtube.com/watch?v=MJBKtNVddak)