Supporting information for

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

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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
Inorganic Crystal Structure Database code 168601

5x5x3 lattice of kaolinite

Cartesian coordinates: XYZ

Structural optimizations for the 1x1x1 unit cell of kaolinte
Experimental structure for crystalline kaolinite with selected internal coordinates

PW91/DZ optimized structure

PW91/DZ* optimized structure

BP86/DZ* optimized structure
Molecular cluster model for the [6Al-6OH] honeycomb-line unit of the octahedral (Al) sheet of exfoliated kaolinite

Models evaluating the effect of the levels of theory

- effective core potential at HF or B3LYP level
- effective core potential with polarization at B3LYP level
- double-zeta all electron basis set at B3LYP level
- DZ with an additional polarization function at B3LYP level
- DZ with an additional diffuse and polarization functions at B3LYP level

Models evaluating the effect of the chemical environment

- inclusion of an explicit solvent molecule at B3LYP level
- inclusion of an explicit Mg2+ ion (fixed) at B3LYP level
- inclusion of an explicit Mg2+ ion (relaxed) at B3LYP level
- embedding into a water polarizable continuum at B3LYP 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: XYZ
- Na+ and Mg2+ counter ions: XYZ
- No counter ions, but water PCM: XYZ
- K+ and Mg2+ counter ions and water PCM: XYZ

exfoliated kaolinite model embedded into a filed of point charges

Cavity formed by field of point charges

Point charge embedded model
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: XYZ
- Mixed basis set 4 ((O3Si)2O..H-O{Al(OH)3(O)2}2 at TZ level, rest DZ* level), HF calculations: XYZ

Functional dependence with the largest basis set (TZ)
Artistic rendering of the implications of the computational results with regards of adsorption and intercalation

Animated illustrations of computational results programmed by
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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=a1IRRGNjov0](https://www.youtube.com/watch?v=a1IRRGNjov0))

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](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. (https://www.youtube.com/watch?v=7ZRmouwiLyM)

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 OT-layer relative to a pristine kaolinite surface. This creates a polarization of chemical bonds through the OT-layer that weakens the interlayer hydrogen-bonding 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)