Supporting Information

Probing Specific Adsorption of Electrolytes at Kaolinite-Aqueous Interfaces by Atomic Force Microscopy

Jing Chang^a, Bo Liu^a, James S. Grundy^a, Huaizhi Shao^b, Rogerio Manica^a, Zhen Li^c, Qingxia Liu^a,* and Zhenghe Xu^{a,d},*

^a Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2V4

^b Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China

^c College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, Shaanxi, China 710054

^d Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China 518055

Corresponding Authors

*E-mail: <u>zhenghe.xu@ualberta.ca</u>; <u>xuzh@sustc.edu.cn</u>; <u>qingxia2@ualberta.ca</u>

1. Spacing between unit cells



Figure S1. Obtaining unit cell spacing on surface lattice image. (a) AFM image of kaolinite Si-basal plane. (b) Height profiles of the blue line and red line (in x and y directions, respectively).

Here, we take the measurement on kaolinite Si-basal plane image captured in Milli-Q water as an example. The spacing between unit cell in x and y directions for kaolinite basal planes was obtained by averaging the horizontal distance of at least 10 unit cells. The horizontal distance was measured using the "section" function built in the Nanoscope Analysis software. In "section" view, draw a line in x and y directions (as indicated in Figure S1(a)), respectively, and the horizontal distance between two valleys on the line is the spacing between two-unit cells.

2. Kaolinite-laden substrate preparation

Kaolinite particles (IMERYS kaolinite, Inc.) with an average particle size of 6.6 µm were used to prepare a kaolinite suspension (3.0 wt%). To fully disperse the kaolinite particles, the suspension of pH 9 adjusted using 0.1 M KOH aqueous solutions was sonicated for half an hour. The kaolinite suspension was left for two hours of gravity settling to remove the coarse particles. The supernatant was centrifuged at 500 g for 30 min in an Ultra Centrifuge (Sorvall WX80, Thermo Scientific Inc.) to remove the super-

fine particles. The sediment was collected, redispersed, and centrifuged at 300 g for another 30 min. The supernatant was decanted again and the centrifuge cake was diluted in Milli-Q water and then sonicated for 20 min to fully disperse the kaolinite particles. The Z-average size of the kaolinite particles prepared as such was determined using a ZetaSizer Nano (Nano ZS, Malvern Instruments Ltd., UK) to be 868 nm. Microscopic glass slides and sapphire wafers were used as substrates for kaolinite particle deposition. Prior to their use, the substrates were cleaned following the standard piranha (96%) H₂SO₄:30% H₂O₂ = 3:1) cleaning procedure (warning: piranha solution is highly dangerous because it is extremely corrosive and is a very strong oxidizer. Standard operating procedure must be followed for anyone who works with piranha solution). One to two drops of the re-dispersed kaolinite suspension with pH adjusted to 5 were carefully spread on the cleaned glass and sapphire substrates to expose the siloxane basal plane and the aluminum oxy-hydroxyl basal plane, respectively.¹ To ensure the particles were kept firmly in place during the experiments, the substrate were placed on a hot plate at 75°C when the suspension drops were placed on the substrates.

3. Surface lattice structures of kaolinite Al-basal plane in 10 mM KCl solution at pH 8 and 11 $\,$



Figure S2. Atomic resolution images of kaolinite Al-basal plane in 10 mM KCl solution at pH 8 (a) and pH 11 (b); Height profiles of kaolinite Al-basal plane in 10 mM KCl solution at pH 8 (c) and pH 11 (d).

In 10 mM KCl background solution, the Al-basal plane of kaolinite carried positive charge at pH 5, which became negative when the solution pH was 8 and 11. To further illustrate the nature of K^+ or Cl^- ions "adsorbed" if any on kaolinite basal plane surfaces, imaging of kaolinite Al-basal planes was performed in 10 mM KCl solutions at pH 8 and 11. As shown in Figure S2, the periodic hexagonal rings remained unchanged on Al-basal planes at these two pHs, which further confirms that K^+ and Cl^- are indifferent ions to these metal oxide surfaces or kaolinite basal planes.

4. Speciation diagram of Ca²⁺

Figure S3 shows the speciation diagram for 10⁻³ mol/L Ca(II), which was constructed using data from Fuerstenau et al.² and Gan et al.³



Figure S3. Concentration diagram for 10⁻³ mol/L Ca(II).

5. Free energy change of adsoroption

The change in free energy of adsorption for Ca^{2+} and $Ca(OH)^+$ was calculated according to the thermodynamic model of adsorption by James and Healy⁴. The equations and the values used in the calculations are as follows:

$$\Delta G_{ads_i} = \Delta G_{coul_i} + \Delta G_{solv_i} + \Delta G_{chem_i} \tag{S 3.1}$$

The change in the coulombic energy is given by:

$$\Delta G_{coul_i} = z_i F \Delta \psi_x \tag{S 3.2}$$

where, z_i is the valence of the adsorbing ion; *F* is the Faraday constant, 96485 C/mol; κ is the reciprocal of the Debye length⁵, which is a characteristic parameter describing the thickness of EDL or decay of the electric potential:

$$\kappa^{-1} = \left(\frac{\varepsilon\varepsilon_0 k_B T}{\sum_i n_{i0} e^2 z_i^2}\right)^{1/2}$$
(S 3.3)

where n_{i0} is bulk concentration of electrolyte *i*, ions/m³.

 $\Delta \psi_x$ is the change in the potential ψ_x at x distance out from the adsorption plane into the double layer, with:

$$x = r_{ion} + 2r_w \tag{S 3.4}$$

$$\psi_{x} = \frac{2RT}{zF} \cdot \ln\left(\frac{\left(e^{\frac{zF\psi_{0}}{2RT}}+1\right) + \left(e^{\frac{zF\psi_{0}}{2RT}}-1\right)e^{-\kappa x}}{\left(e^{\frac{zF\psi_{0}}{2RT}}+1\right) - \left(e^{\frac{zF\psi_{0}}{2RT}}-1\right)e^{-\kappa x}}\right)$$
(S 3.5)

where, r_{ion} and r_w are the radii of adsorbing ion and water, respectively; z = 1 for 1:1 background eletrolyte; T is the absolute temperature; R is the gas constant, 8.314 J/mol·K; κ is the ψ_0 is the surface potential of the solid surface (in this case, the kaolinite Si-basal plane).

Using the Grahame equation,⁶ one can convert the surface charge density to the surface potential:

$$\sigma_0 = \sqrt{8c_0\varepsilon\varepsilon_0k_BT}\sinh\left(\frac{e\psi_0}{2k_BT}\right)$$
(S 3.6)

where c_0 is the bulk concentration of the salt; ε is dielectric constant of the medium; ε_0 is the permittivity of vacuum, 8.85×10^{-12} C/V·m; k_B is the Boltzmann constant, 1.38×10^{-23} J/K; and *T* is the absolute temperature.

The calculation of the change in the solvation energy is given by:

$$\Delta G_{solv_i} = \left(\frac{z_i^2 e^2 N}{16\pi\varepsilon_0}\right) \left(\frac{1}{r_{ion} + 2r_w} - \frac{r_{ion}}{2(r_{ion} + 2r_w)^2}\right) \left(\frac{1}{\varepsilon_{int}} - \frac{1}{\varepsilon_{bulk}}\right) + \left(\frac{z_i^2 e^2 N}{32\pi\varepsilon_0}\right) \left(\frac{1}{r_{ion} + 2r_w}\right) \left(\frac{1}{\varepsilon_{solid}} - \frac{1}{\varepsilon_{int}}\right)$$
(S 3.7)

with

$$\varepsilon_{int} = \left(\frac{\varepsilon_{bulk} - 6}{1 + (1.2 \times 10^{-17})(d\psi/dx)_x^2}\right) + 6$$
(S 3.8)

$$\frac{d\psi}{dx} = -2\kappa \frac{RT}{zF} \sinh\left(\frac{zF\Delta\psi_x}{2RT}\right)$$
(S 3.9)

where, N is the Avogadro number, $6.02 \times 10^{23} \text{ mol}^{-1}$; ε_{solid} is the dielectric constant of the solid surface, ε_{bulk} is the dielectric constant of bulk water, 78.5.

6. DFT calculation

In the paper "Adsorption mechanism of hydroxyl calcium on two kaolinite (001) surface",⁷ the authors used DFT plane-wave pseudopotentials program to study the adsorption mechanisms of calcium hydroxyl ions on the two basal planes of kaolinite. The results of their calculations are in good agreement with our experimental results. Since this article is not written in English and for the convenience of future readers, the investigation methods and main conclusions are summarized here (please note the following is interpreted from reference 38 in the manuscript, not from the current work). We also show our respect and sincere appreciation to the authors (Han et al.) who conducted the work of this article.

Han et al. used the Materials Studio CASTEP⁸ and built a unit cell of kaolinite crystals to obtain a good exchange-correlation function and plane-wave cutoff energy. The results were optimized by LDA (local density approximation) and GGA-PBE (Perdew-Burke-Ernzerh of generalized gradient approximation),⁹ and compared with unit cell parameters of kaolinite obtained by simulation and experiments reported previously.¹⁰⁻¹² The authors used ultrasoft pseudopotential to describe the interaction between the valence electron and the core electron to optimize the model and perform the calculation. The surface model adopted the (001) surface of kaolinite lattice, which is also the surface of most easily delamination. Han et al. started with building a 15×15×15 Å³ periodic simulation box with Ca(OH)⁺ in it, followed by an optimization process of the (001) surface and the Ca(OH)⁺ ion using Dmol.³ Based on the research on the impact of fixed atom layers on surface relaxation¹³ and combined with the frontier orbital theory, the models of the Sibasal plane and the Al-basal plane of kaolinite were successfully constructed.

Simulation results by Han et al. showed that $Ca(OH)^+$ can adsorb on both the Si-basal plane and the Al-basal plane of kaolinite. For the kaolinite Si-basal plane, the most likely mode of adsorption was Ca atom from $Ca(OH)^+$ on the O atom from the surface. For the Al-basal plane, the strongest adsorption site was found in the hollow surrounded by the H atoms from the Al-basal surface, with the O atom from Ca(OH)⁺ adsorbing on the H atoms from the surface. The initial adsorption configuration was obtained based on the above-mentioned simulation model. Considering the surface configuration of the kaolinite Si-basal surface and Al-basal surface after relaxation and the structure symmetry, the initial adsorption sites of Ca(OH)⁺ can be confirmed. For the Si-basal surface, Ca is the adsorbing atom binding with the O atoms on the basal surface, from which one top site, one bridge site and two hollow sites were built. For the Al-basal surface, the adsorbing atom is the O and the binding atoms are the H on the Al-basal surface, from which three top sites, three bridge sites and 6 hollow sites were built. The positions of the unfixed atoms and the distance among the atoms were changed continuously while calculating the corresponding energy until convergence was reached. The whole configuration optimization process is looking for the lowest energy state, e.g., the preferred adsorption state of Ca(OH)⁺ was evaluated by the value of the adsorption energy (see Eq. (1)).

$$E_{ads} = E'_{ads/slab} - (E'_{ads} + E_{slab})$$
(1)

Analyzing the adsorption configurations and the Mulliken bond population (the higher the value, the stronger the covalency of the bond) after Ca(OH)⁺ was stably adsorbed on kaolinite basal surfaces and the Mulliken charge of atoms before and after the adsorption,

the authors concluded that hydroxyl calcium could adsorb stably on both basal surfaces of kaolinite, but the adsorption mechanisms were different.

(1) For the Si-basal surface of kaolinite, the most stable configuration is the Ca atom siting on top of the twelve-fold hollow center consisting of Si and O atoms. The Ca atom carries more positive charges and the Si-basal surface carries negative charges, leading to a relatively strong electrostatic attraction between them. In the meantime, the covalency between the Ca atom and the O atom from the $Ca(OH)^+$ ion becomes stronger.

(2) For the Al-basal surface of kaolinite, the $Ca(OH)^+$ ion prefers to be perpendicular to the Al-basal surface with the O atom from $Ca(OH)^+$ interacting with the H atoms from the Al-basal surface via strong hydrogen bonds. The most stable adsorption site for $Ca(OH)^+$ is the threefold hollow enclosed by the three H atoms from the Al-basal surface. The 1s orbit of the H atom and the 2p orbit of the O atom from the Ca(OH)⁺ form a hybrid orbit. In the meantime, Ca(OH)⁺ transfers a few electrons to the surface and has a weak electrostatic attraction with the Al-basal surface. The distance between the Ca atom and O atom in the Ca(OH)⁺ becomes larger, the covalency of the bond reduces, and the Ca atom has a tendency of leaving the Ca(OH)⁺ ion.

7. Depth profile of kaolinite Al-basal plane in Milli-Q water



Figure S4. Atomic resolution image (a) and height profiles (b) of kaolinite Al-basal plane

in Milli-Q water.

To further study the nature of specific adsorption, it would be interesting to investigate the protruded height of adsorbed ions. The blue and red profiles in (f) of Figure 3 corresponding to the traces marked in (d) show clearly different depth profiles (see Figure S4) corresponding to the surface topology of kaolinite Al-basal plane in Milli-Q water as shown in Figure 1 (e) in the Manuscript. The absolute heights measured by AFM depth profile (80 pm) in these two marked directions in Figure S4 (b) are much lower than the corresponding heights of 250 pm and 220 pm in (f) of Figure 3. Much higher absolute heights (~3 times) of the protruded ions in (f) of Figure 3 than in Figure S4 (b) show clearly the dramatic difference between the specifically adsorbed ions in (f) of Figure 3 and the original surface lattice ions (atoms) of kaolinite Al-basal plane shown in Figure S4. However, it is important to note that the protruding heights we were probing with the atomic resolution imaging technique do not represent the absolute size of adsorbing ions, as part of hydrated monohydroxy cations could be sunk in the lattice vacancy of original Al-basal planes. Subtracting the size of one water molecule (270 pm) in the protruding (z) direction, the measured height of specifically adsorbing ions on the top of Al-basal planes would be 550 pm, which is double the measured protrusion height (250 pm) of specifically adsorbed monohydroxy calcium cations. The difference could be attributed to the sinking of the adsorbed ions in the vacant space among the lattice ions on the Al-basal plane surfaces.

8. Image processing



Figure S5. Image processing procedure. (a) Original atomic resolution image after being flattened; (b) Spectrum 2D image; (c) inverse FFT image; (d) zoomed-in view of (c).

The atomic resolution image of the kaolinite Si-basal plane taken in Milli-Q water was used to show the image processing procedure. The original figure was 2nd-order flattened using NanoScope Analysis Version 1.8 (Bruker Corporation) and shown in Figure S5 (a). Lowpass filtering can be used to further improve the image clarity if noise is high. Spectrum 2D function was then used to transform the image data to frequency domain via a 2D fast Fourier transform (FFT), as we can see in Figure S5 (b). By passing selected frequencies, the image was filtered and certain surface features (in this case, the surface lattice structure) were isolated, as shown in Figure S5 (c). Finally, a zoomed-in view was provided to see the surface lattice structure image more clearly.

References

(1) Gupta, V.; Miller, J. D. Surface Force Measurements at the Basal Planes of Ordered Kaolinite Particles. *J. Colloid Interface Sci.* **2010**, *344*, 362-371.

- (2) Fuerstenau, M. C.; Miller, J. D.; Kuhn, M. C. *Chemistry of flotation*. Soc of Mining Engineers of AIME: **1985**.
- (3) Gan, W.; Crozier, B.; Liu, Q. Effect of Citric Acid on Inhibiting Hexadecane–quartz Coagulation in Aqueous Solutions Containing Ca²⁺, Mg²⁺ and Fe³⁺ Ions. *Int. J. Miner. Process.* **2009**, *92*, 84-91.
- (4) James, R. O.; Healy, T. W. Adsorption of Hydrolyzable Metal Ions at the Oxide water Interface. III. A Thermodynamic Model of Adsorption. J. Colloid Interface Sci. 1972, 40, 65-81.
- (5) Israelachvili, J. N. *Intermolecular and surface forces;* Academic Press: Burlington, MA, **2011**.
- (6) Grahame, D. C. The Electrical Double Layer and the Theory of Electrocapillarity. *Chem. Rev.* **1947**, *41*, 441-501.
- (7) Han, Y.; Liu, W.; Chen, J.; Han, Y. Adsorption Mechanism of Hydroxyl Calcium on Two Kaolinite (001) Surface. *China Coal Soc* **2016**, *41*, 743-750.
- (8) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I.; Refson, K.; Payne, M. C. First Principles Methods using CASTEP. Z. Kristallogr. Cryst. Mater. 2005, 220, 567-570.
- (9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (10) Wang, J.; Xia, S.; Yu, L. Adsorption Mechanism of Hydrated Pb(OH) on the Kaolinite (001) Surface. *Acta. Phys. Chim. Sin.* **2014**, *30*, 829-835.
- (11) Hu, X. L.; Michaelides, A. Water on the Hydroxylated (0 0 1) Surface of Kaolinite: From Monomer Adsorption to a Flat 2D Wetting Layer. *Surf. Sci.* **2008**, *602*, 960-974.
- (12) Hou, X.; Li, H.; Li, S.; He, P. Theoretical Study of the Intercalation Behavior of Ethylene Glycol on Kaolinite. J. Phys. Chem. C. 2014, 118, 26017-26026.
- (13) Wang, J.; Xia, S.; Yu, L. Adsorption of Pb (II) on the Kaolinite (0 0 1) Surface in Aqueous System: A DFT Approach. *Appl. Surf. Sci.* **2015**, *339*, 28-35.