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水合 $Pb(OH)^+$在高岭石(001)晶面的吸附机理

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Adsorption Mechanism of Hydrated $Pb(OH)^+$ on the Kaolinite (001) Surface

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Cell parameters for initiative cell of kaolinite:

a=0.51535 nm, b=0.89419 nm, c=0.73906 nm; α=91.926°, β=105.046°, γ=89.797°.

Space group: $C1$

Atomic coordinates:

Atom	*x/a*	*y/b*	*z/c*
Al(1)	0.289	0.4966	0.466
Al(2)	0.793	0.3288	0.465
Si(1)	0.989	0.3395	0.0906
Si(2)	0.507	0.1665	0.0938
O(1)	0.049	0.3482	0.3168
O(2)	0.113	0.6599	0.3188
O(3)	0	0.5	0
O(4)	0.204	0.2291	0.030
O(5)	0.197	0.7641	0.001
OH(1)	0.050	0.9710	0.325
OH(2)	0.960	0.1658	0.607
OH(3)	0.037	0.4726	0.6046
OH(4)	0.038	0.8582	0.609
H(1)	0.145	0.0651	0.326
H(2)	0.063	0.1638	0.739
H(3)	0.036	0.5057	0.732
H(4)	0.534	0.3154	0.728

Equilibrium geometries of $Pb(OH)(H_2O)_{1\text{-}5}^+$ and the corresponding structural parameters:

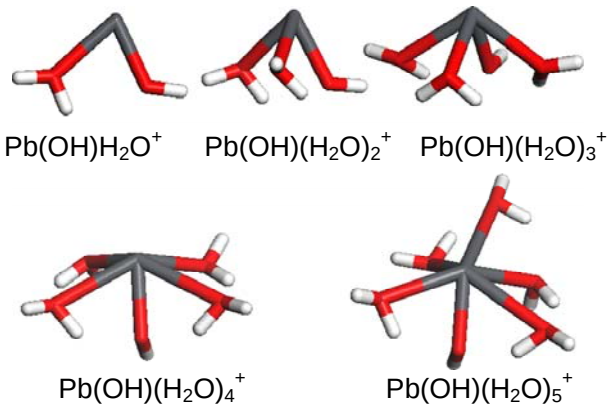

Fig.S1 Equilibrium geometries of $Pb(OH)(H_2O)_{1\text{-}5}^+$ from periodic DFT calculations. Atoms of Pb, O and H are colored grey, red and white, respectively.

Table S1 Equilibrium geometrical parameters and binding energies of $PbOH(H_2O)_n^+$

n	Pb–O_H /nm	Pb–O_w /nm	Pb–O_m /nm	$\Delta E_{binding}$ /(kJ·mol^{-1})	∠O_HPb$O_{w,1}$ /(°)	∠O_HPb$O_{w,2}$ /(°)	coordination geometry
1	0.208	0.238	0.223	-345.50	73.55	------	hemi-directed
2	0.215	0.244, 0.242	0.234	-440.18	71.71	70.48	hemi-directed
3	0.221	0.256, 0.243, 0.258	0.245	-514.97	66.82	66.01	hemi-directed
4	0.222	0.248, 0.252, 0.270, 0.283	0.255	-581.24	61.26	64.18	hemi-directed
5	0.222	0.244, 0.256, 0.264, 0.296, 0.363	0.274	-641.65	58.88	67.77	holo-directed

Pb–O_H and Pb–O_w, the distances of Pb to the O centers of "OH" and "H_2O" ligands, respectively. Pb–O_m, the average value of Pb–O bond lengths in $PbOH(H_2O)_n^+$. $O_{w,1}$ and $O_{w,2}$ are the oxygen atoms of aqua ligands neighboring to the hydroxyl ligand. -------, no corresponding datum. $\Delta E_{binding}$, the binding energy of $PbOH(H_2O)_n^+$, is calculated according to the reaction: $Pb^{2+} + x\ H_2O = Pb(OH)(H_2O)n^+ + (x\text{-}n\text{-}1)\ H_3O^+$, and defined as the energy difference between the products and reactants.

Equilibrium geometries of $[S(OH)_2(O)Pb(OH)(H_2O)_m]$ and the corresponding structural parameters:

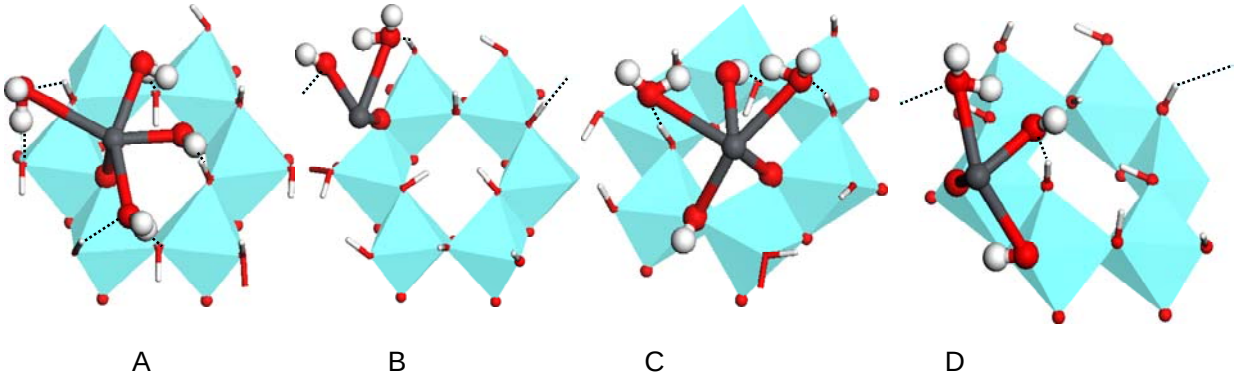

Fig.S2 Equilibrium geometries of monodentate complexes on "O_u" (A) and "O_l" (B) sites and bidentate complexes on "O_uO_l" site of the same Al center (C) and two neighboring Al centers(D). AlO_6 octahedra are indicated by green polygons. Black dashed lines denote the hydrogen bonding interactions

Table S2 Structure parameters and binding energies (ΔE_{bind}) of mono- and bidentate complexes of $Pb(OH)^+$ on the Al(o) (001) surface of kaolinite

Complexes	*N*	Pb–O_m/nm	Pb–O_s/nm	Pb–O_H/nm	Pb–O_w/nm	Pb–Al/nm	O_l…H/nm	O_H…H_u/nm	ΔE_{bind}/ (kJ·mol^{-1})
A	5	0.266	0.224	0.229	0.346, 0.267, 0.263	0.361	0.167, 0.159, 0.166	0.167	-182.60
B	3	0.248	0.215	0.234	0.296	0.313	--	0.179	-79.46
C	5	0.267	0.216, 0.277	0.233	0.320, 0.290	0.326	0.189	--	-121.91
D	4	0.253	0.215, 0.281	0.232	0.282	0.365	--	0.170	-55.23

N, the coordination number of Pb(II) in the complex. Pb–O_s, Pb–O_H and Pb–O_w represent the distances of Pb to the O centers of Al(o) surface, hydroxyl and aqua ligands, respectively. Pb–O_m, average value of Pb–O bond lengths in the adsorption complex. Pb–Al, distance of Pb to the nearest Al center of the (001) slab. O_l…H, hydrogen bond length between surface O_l and H of hydroxyl or aqua ligands. O_H…H_u, hydrogen bond length between O of hydroxyl ligand and H of surface "O_uH". -------, no corresponding data.