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First Principle Calculations of Clay-Benzene and Clay-Naphthalene Interaction Energies

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Clay-polycyclic aromatic hydrocarbons (PAHs) interaction energies are estimated by first principle calculation with the SIESTA, a Linear Combination of Atomic Orbitals-Density Functional Theory (LCAO-DFT) program. The results will be referred to in optimization of force field parameters for large-scale classical simulation of clay-water-PAHs system. The background of this study is related with the other paper by the same authors.

Three models of clay minerals were calculated for clay-PAHs interaction energies, which are a pyrophyllite ($\text{Si}_2\text{Al}_4\text{O}_{10}(\text{OH})_2$) as a prototype model for cation substitutions, a beidellite-type model ($\text{X}_{0.33}(\text{Al}_2)(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$) with tetrahedral substitution by Al, and a montmorillonite-type model ($\text{X}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$) with octahedral substitution by Mg (Fig. 1). The calculations were made with DZP basis set in 3-dimensional periodic condition which leads infinite-slab model of clay. Adsorption sites of benzene, naphthalene on the clay basal planes were searched plotting potential curves as a function of the intermolecular distance (Fig. 2 shows the cases of clay-benzene), and further structural optimizations were made at the adsorption sites.

The counterpoise method (Boys and Bernardi, 1970) was used for correction of basis set superposition error (BSSE) to obtain precise interaction energies which is necessary for precise interaction energy in LCAO method. The results are listed in Table 1. Tetrahedral substitution resulted in a remarkable increase of interaction energy (see ΔE_{BSSE}). All values of interaction energies are much larger than the mean translational energy of a molecule (c.a. 0.04 eV at 300 K).

Table. 1. Interaction energies calculated with BSSE correction for clay-benzene and clay-naphthalene systems.

Benzene	E1	E2	E3	E4	E5	BSSE (eV)	ΔE (eV)	ΔE_{BSSE} (eV)	Re (Ang)
	$E_{\text{clay+benz.}}$	$E_{\text{claydummy+benz.}}$	$E_{\text{clay+benz.dummy}}$	$E_{\text{benz.}}$	E_{clay}				
Non Sub	-27453.24	-1023.87	-26428.99	-1023.73	-26429.24	-0.10	-0.27	-0.38	3.156
Oct. Sub	-27384.31	-1023.88	-26360.08	-1023.73	-26359.97	0.26	-0.60	-0.35	3.027
Tet. Sub	-27366.64	-1023.89	not converged	-1023.73	-26342.15	-	-0.76	-	2.919

Naphthalene	E1	E2	E3	E4	E5	BSSE (eV)	ΔE (eV)	ΔE_{BSSE} (eV)	Re (Ang)
	$E_{\text{clay+naph.}}$	$E_{\text{claydummy+naph.}}$	$E_{\text{clay+naph.dummy}}$	$E_{\text{naph.}}$	E_{clay}				
Non Sub	-28104.03	-1674.66	-26429.09	-1674.44	-26429.24	0.08	-0.36	-0.28	3.127
Oct. Sub	-28035.53	-1674.64	-26360.23	-1674.43	-26359.97	0.46	-1.12	-0.66	3.030
Tet. Sub	-28017.86	-1674.66	not converged	-1674.43	-26342.15	-	-1.27	-	3.031

Re: Distance between clay basal oxygen and PAHs

$$\begin{aligned} \Delta E &= E1 - (E4 + E5) \\ \Delta E_{\text{BSSE}} &= E1' - (E4 + E5) \\ &= E1 + \text{BSSE} - (E4 + E5) \\ &= E1 + (E4 + E5 - E2 - E3) - (E4 + E5) \end{aligned}$$

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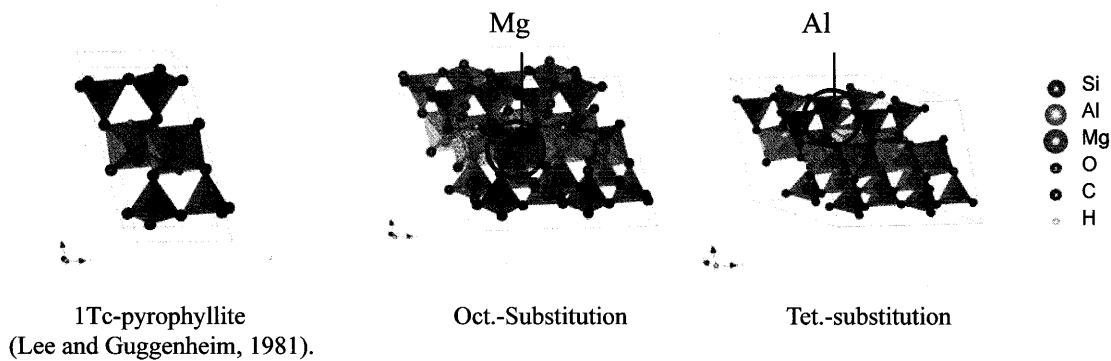


Fig. 1. Structural models of 2:1 clays used in this study. Pyrophyllite has a simple chemical composition. Substitution of octahedral Al for Mg leads montmorillonite-type layer. Substitution of tetrahedral Si for Al leads beidellite-type layer.

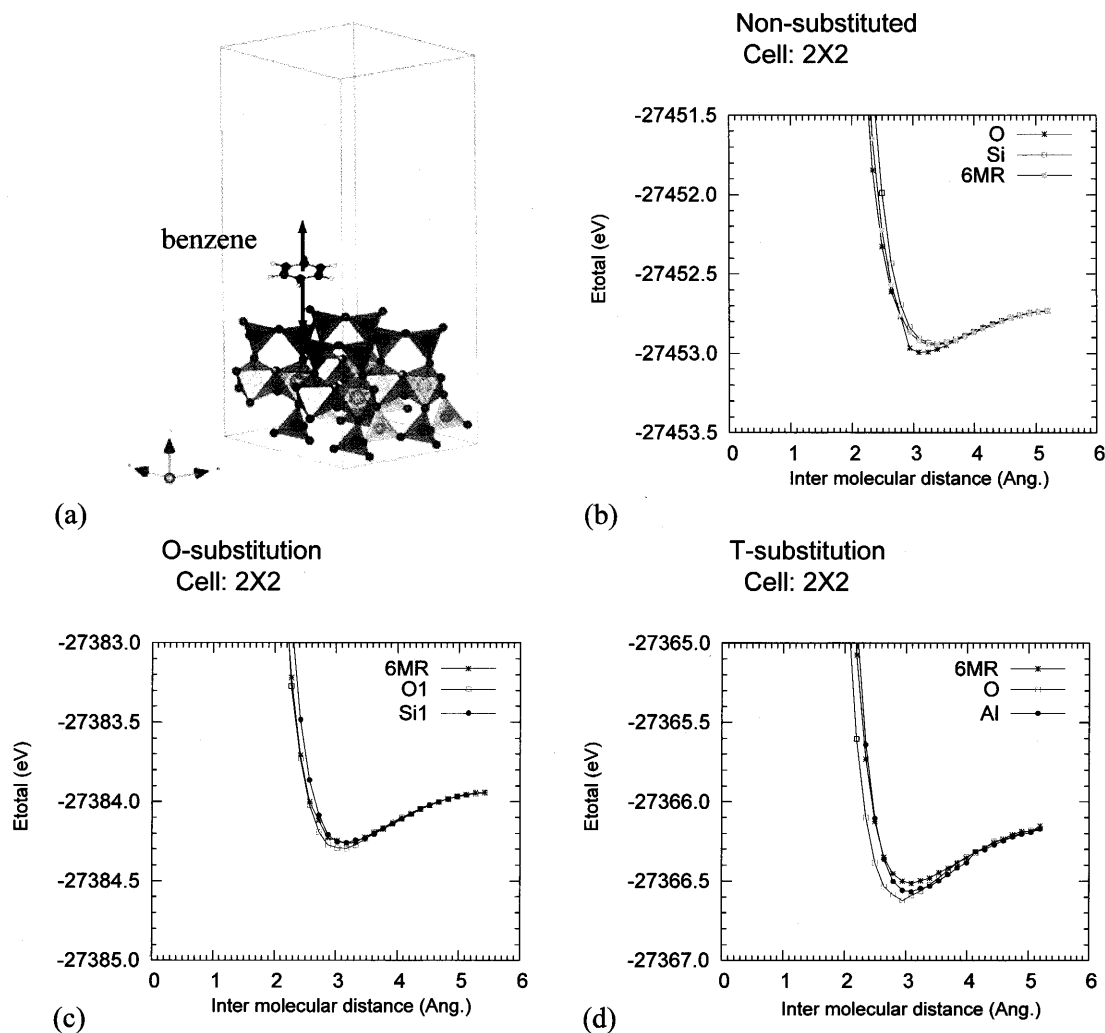


Fig. 2. Simulation model and calculated intermolecular potential curve in the clay-benzene systems. (a) Illustration of simulation model. An example of the pyrophyllite-benzene system. (b) Pyrophyllite. The horizontal axis indicates distance from basal plane to benzene molecule. (c) Montmorillonite-type layer. (d) Beidellite-type layer.

The energies estimated here are not converged in relation to basis set size. These values may be unsuitable for referential data to which the force field parameters for the large-scale simulation are fitted. Higher precision could be obtained by introducing an extrapolation technique (Feller, 1992) to calculate interaction energies at basis set limit.