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Monte Carlo simulations of surface energy of the open tetrahedral surface of 2:1-type phyllosilicate

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Abstract

Monte Carlo simulations were employed to investigate the surface energy of the open tetrahedral surface of 2:1-type phyllosilicate. Argon was selected as the probe molecule. The adsorption isotherm was simulated and the adsorption potential map was calculated. Both the density and energy distributions of adsorbed atoms were derived at different pressures to explore the adsorption mechanism. It is found that there exist two kinds of energetic sites: minima (−15.5 kJ/mol) corresponding to the centers of six-membered rings and platform points (−8.0 kJ/mol) corresponding to the edges and vertexes of hexagons. They are primary and secondary adsorption sites, respectively. The implications for experiments and future studies are discussed. Current results are applicable for understanding surface energy properties of other clay minerals, since they have very similar basal surfaces.

Keywords: Surface energy; Phyllosilicate; Adsorption isotherm; Monte Carlo; Tetrahedral surface

1. Introduction

2:1-type phyllosilicates, including the pyrophyllite–talc, mica, smectite, and vermiculite groups, are naturally and widely occurring layered minerals. The constituent layer consists of an octahedral sheet sandwiched between two tetrahedral sheets, a T–O–T layer for short [1]. A variety of physicochemical properties, such as high specific surface area, swelling properties, and cation exchangeability, make them very important in many industrial and engineering applications and geochemical processes [2–6]. In those fields, unique surface properties serve as critical roles. For example, adsorption and chemical reactions are commonly controlled by the properties of the external/internal clay surfaces. Among various surface properties, the surface energy heterogeneity is of a central interest. The energy heterogeneity generally originates from the difference in crystal faces, surface functional groups, crystal defects, and pore structures, which influence many interfacial processes to a large extent [7–9]. It is ubiquitous on phyllosilicate surfaces because of their specific crystallochemistry [1,7]. Therefore, good knowledge of energy heterogeneity is greatly important for understanding and handling their behaviors efficiently.

"Molecular probe method" is well proved as a promising characterization technique of surface energy of solids [7–13]. In this method, surface energy heterogeneity is generally expressed by a distribution of adsorbate/adsorbent interaction energy, which could be extracted from the adsorption isotherm of probe gas. Besides adsorption energy distribution, specific surface area, surface fractal, and pore size distribution can also be calculated from the isotherm. Furthermore, superior to microscopic techniques (such as electronic microscopy and atomic force microscopy), molecular probe method commonly produces statistically macroscopic and quantitative information on the whole sample rather than several individual particles. Therefore, the corresponding methodology has been of great interest and long studied.

Lack of sample purity and limits of the available experimental equipment can sometimes make it difficult to understand the

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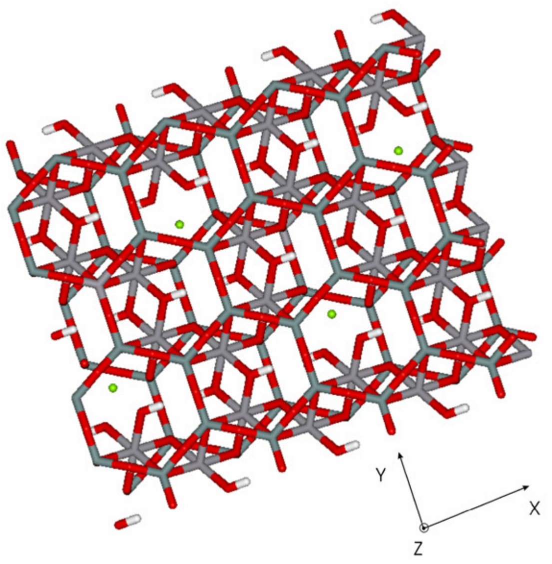
surface energy distributions of solid materials. In general, clay minerals often coexist with quartz, plagioclase, and calcite in soil and sediments, and they generally contain various impurity elements [14], which make the exact interpretation of experimental data very difficult. Similarly, it is difficult to obtain good data on the adsorption of argon at very low pressures by direct measurement. Nevertheless it is important to determine low-pressure adsorption, which can directly reflect the surface energy state [8,9]. Molecular simulation can be used effectively to deal with these issues and indicate how the adsorbed argon probably behaves under these low-pressure conditions. As a result molecular simulation techniques have been developed [15–17] and are commonly utilized for physical adsorption and surface property studies [18–27]. Molecular simulation techniques also provide opportunities to test and improve classical theories [28].

In this study, the surface energy of the open tetrahedral surface of 2:1-type phyllosilicate was studied using molecular simulation. Argon was selected as the probing molecule, and Monte Carlo techniques were employed to simulate the adsorption isotherm. An adsorption potential map was also calculated to explore stationary energy sites of the open basal surface. Both structural and energetic properties of the adsorbed phase were derived to study the adsorption mechanism.

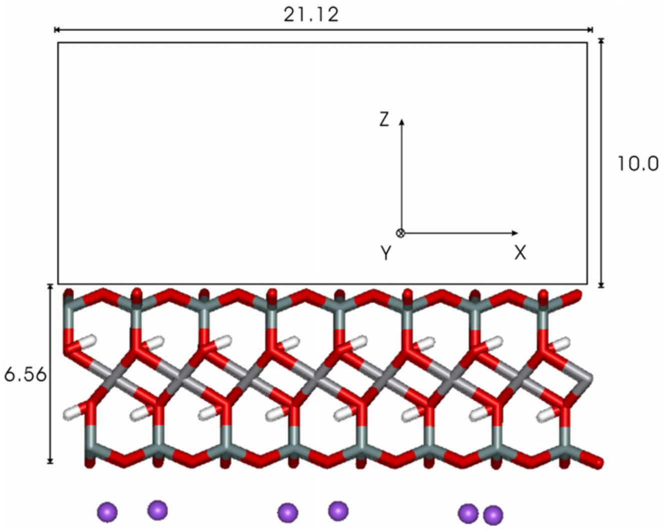
2. Methodology

2.1. Model

Fig. 1 shows the T–O–T model and the simulation box. This model corresponds to the Wyoming smectite developed by Skipper et al. and is often used as a prototype of 2:1 phyllosilicates [29,30]. It consists of eight unit cells with the structural formula $Na_{0.75}$ $[Si_{7.75}Al_{0.25}][Al_{3.5}Mg_{0.5}]O_{20}(OH)_4$. In this model, one out of 32 silicon atoms in the tetrahedral sheets are replaced by aluminum atoms, and one in 8 aluminum atoms in the octahedral sheet are replaced by magnesium. Sodium ions are placed at distances of about 2 Å from the surface of T–O–T layer, close to the midplane of the interlayer space in dry clay [30]. The dimensions of the T–O–T sheet are 21.12, 18.28, and 6.56 Å, respectively. The basal surface, i.e., the (001) facet, is selected to study. The height of the simulation box above the surface was defined to be 10 Å. Thence, the simulation box size is 21.12 × 18.28 × 10.00 Å.



(a)



(b)

Fig. 1. (a) The T–O–T layer: projection on (001). (b) Simulation box above the open basal surface. The length is in the unit Å. Si: dark brown stick, Al: greenish blue stick, O: red stick, H: silver stick, Na: purple sphere, Mg: green sphere. (For interpretation of the reference to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Potential calculation

The total potential of an adsorbate atom includes two parts, adsorbate–surface and adsorbate–adsorbate interactions, both of which are exhibited by the simple pairwise potential

$$u(r_{ij}) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right), \tag{1}$$

where r_{ij}, ε_{ij}, and σ_{ij} denote site–site separation, LJ well depth, and LJ diameter, respectively. For argon–argon interaction, two typical LJ parameters were taken [31]. Parameters of clay atoms were taken from the universal force field (UFF) [32]. For argon–clay interaction, Lorentz–Berthelot combining rules were used [16] and the interaction parameters are listed in Table 1. In all potential calculations, Eq. (1) is truncated at a cutoff of 9 Å.

2.3. Calculation of potential map

The adsorption potential map on the studied surface was calculated with the following procedure. An argon atom was placed on each mesh point on the surface and its energy was minimized with respect to the distance to the surface. Here the mesh interval is set at 0.02 Å. Once the minimum was attained, the energy value and the distance (i.e., z co-