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Stabilization of 1:1 phyllosilicate structure due to distortion as investigated by semiempirical molecular orbital method

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Stabilization of a 1:1 dioctahedral phyllosilicate layer structure due to two types of distortion was investigated applying semiempirical molecular orbital method. The discrepancy between the lateral lattice dimensions of octahedral and tetrahedral sheets in their free state structures strains the 1:1 layer structure and causes certain types of its distortion such as rotating the tetrahedra in the sheet, or rolling the 1:1 layer. In order to evaluate the effect of these distortion mechanisms for the stabilization, semiempirical molecular orbital calculations were carried out using MOPAC Ver.6 with a series of model clusters representing the distortion mechanisms. The heat of formation of the model clusters decreased with respect to the progress of both of the distortion mechanisms until certain limits, indicating that these distortion mechanisms could stabilize the 1:1 layer structure effectively.

1.INTRODUCTION

A layer structure of 1:1 dioctahedral phyllosilicate consists of Si-O tetrahedral and Al-OH octahedral sheets combined to each other horizontally. These sheets have different lateral lattice dimensions in their free state; a=5.06Å, b=8.62Å for the octahedral sheet (from a mineral gibbsite $Al(OH)_3$ [1]), and a=5.29Å, b=9.16Å for the tetrahedral sheet (from a hypothetical model). Certain distortion mechanisms should be introduced in order to eliminate the mismatch. Some XRD and TEM works showed that the rotation of tetrahedra in the tetrahedral sheet [2], and the rolling of 1:1 layer making a cylinder shape [3] were the principal distortion mechanisms.

This work aimed at investigating the role of these distortion mechanisms by means of semiempirical molecular orbital method.

2. MODELS AND CALCULATIONS

A six member ring of Si-O tetrahedra was imaginarily cut out of the hexagonal net of the tetrahedral sheet, upon which the octahedral

sheet was made up assuming constant bond lengths; Si-O=1.62Å, Al-O=1.93Å, O-H=0.96 Å. Dangling bonds on the basal O were terminated with H. The basic model cluster was illustrated in Fig.1.

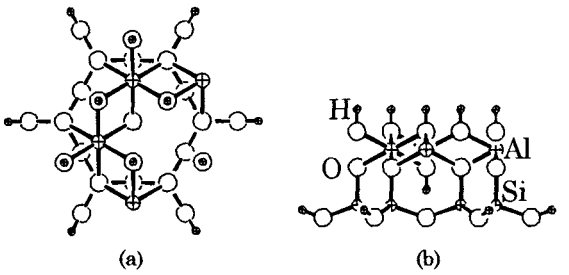

Fig.1 The basic structure of 1:1 dioctahedral phyllosilicate layer, top(a) and side (b) view .

2.1. Rotation of tetrahedra

The adjacent tetrahedra in the tetrahedral sheet were rotated in opposite direction around their individual axes which directed from an apical O to the basal plane perpendicularly [4]. The rotation angle of the tetrahedra was defined as in Fig.2.

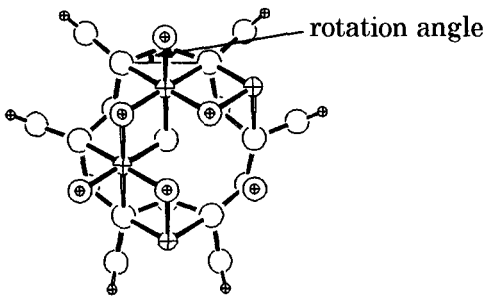

Fig.2 The definition of the rotation angle in the rotation of tetrahedra.

2.2. Rolling of 1:1 layer

The 1:1 layer was imaginarily placed on an inner surface of a cylinder so as to be rolled with the tetrahedral sheet being outside. The radius of rolling and the rotation angle of the rolling axis were determined as those of the hypothetical cylinder and defined as in Fig.3.

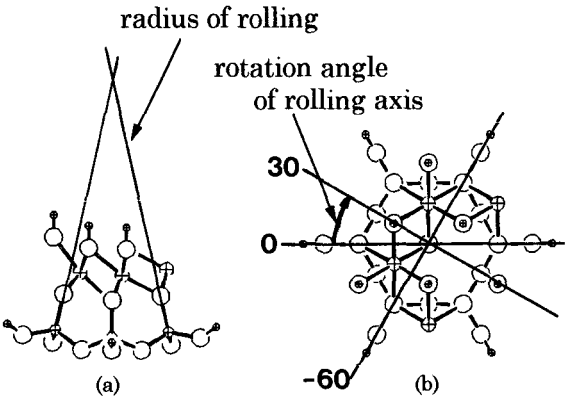

Fig.3 The definition of the radius of rolling (a) and the rotation angle of rolling axis (b).

2.3. Calculations

In this work, a semiempirical molecular orbital calculation program MOPAC Ver.6 [5,6] was employed with PM3 and its original atomic parameters.

3. RESULTS AND DISCUSSIONS

3.1. Rotation of tetrahedra

3.1.1. 1:1 layer

Fig.4 showed that the heat of formation of the 1:1 layer cluster was decreased by the rotation of the tetrahedra rapidly with the local minimum points at $\pm 20^{\circ}$, of which the negative rotation gave lower value showing

that this direction could stabilize the layer more effectively.

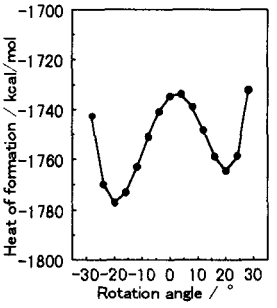

Fig.4 The heat of formation of 1:1 layer at various rotation angle of tetrahedra.

3.1.2. Constituent sheets

Model clusters were prepared also for the tetrahedral and octahedral sheets in order to examine individual contributions.

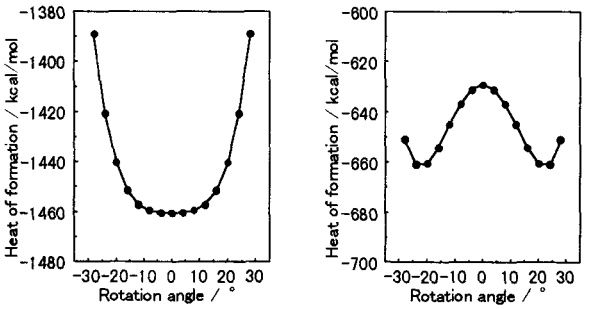

Fig.5 The heat of formation of the tetrahedral (a) and the octahedral (b) sheets at various rotation angle.

In Fig.5, the tetrahedral sheet showed only a slow change over a wide range of rotation angle, while the octahedral sheet showed a rapid decrease with the increase of the rotation angle as the 1:1 layer showed. The results showed that the octahedral sheet could contribute mainly to stabilize the 1:1 layer in this distortion.

3.2. Rolling of 1:1 layer

3.2.1. 1:1 layer

Fig.6 showed that the heat of formation of the 1:1 layer cluster with a fixed axis angle at 0° decreased very rapidly by the decrease of the radius of rolling and had a minimum at 14 Å. It showed that the rolling could stabilize the 1:1 layer effectively. Fig.6 also showed that the heat of formation of the cluster with a fixed radius of rolling at 14Å had local minimum points at 0 and −60° and local maximum at ±30° of the axis angle. The angles which gave the minimum points coincided with the direction of b axis in the 1:1 layer structure.

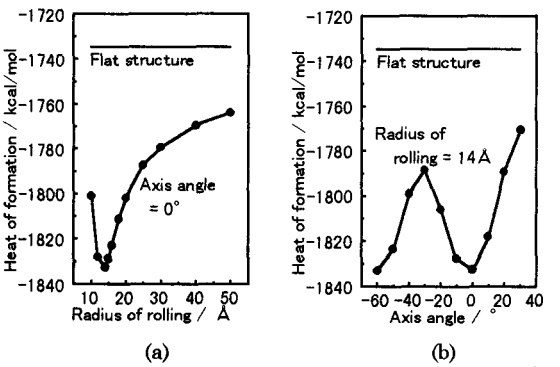

Fig.6 The heat of formation of the 1:1 layer at various radius of rolling with 0° of axis angle (a) and at various axis angle with 14Å of radius of rolling (b).

3.2.2. Constituent sheets

Opposite to the behavior of 1:1 layer, the tetrahedral sheet showed an gradual increase of the heat of formation with the decrease of

the radius of rolling and is almost independent of the rotation angle of the rolling axis in Fig.7. The octahedral sheet, however, showed very similar patterns to the 1:1 layer in Fig.8. It showed that the relaxation of the octahedral sheet caused the stabilization of the 1:1 layer.

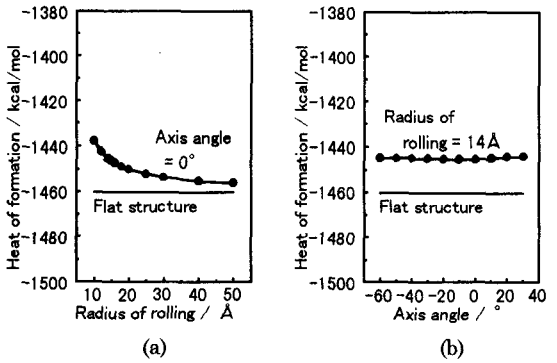

Fig.7 The heat of formation of the tetrahedral sheet at various radius of rolling with 0° of axis angle (a) and at various axis angle with 14Å of radius of rolling (b).

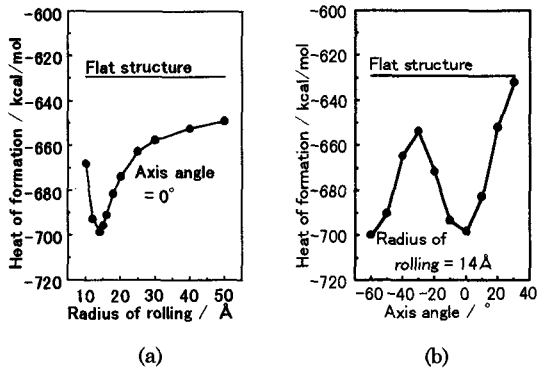

Fig.8 The heat of formation of the octahedral sheet at various radius of rolling with 0° of axis angle (a) and at various axis angle with 14Å of radius of rolling (b).

4. CONCLUSION

The stabilization of 1:1 phyllosilicate layer structure due to the two types of distortion was studied by means of semiempirical molecular orbital method using MOPAC Ver.6.

(1) The rotation of the tetrahedra and the rolling of the 1:1 layer stabilized the 1:1 layer effectively resulting in the similar structures to those observed in natural minerals.

(2) The stabilization could be mainly attributed to the relaxation of the octahedral sheet as the changes of the heat of formation the octahedral sheet model showed were similar to those of the whole 1:1 layer model.

(3) Semiempirical molecular orbital method was successfully applied in this study showing that this method could serve as a very useful tool for the study of crystal structures when certain types of distortions were supposed.

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