

## 陽이온이 支持된 Layer Silicate 上에서의 水分의 吸着

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## Adsorption of Water on Cation Supported Layer Silicates

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요 약.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$  이온이 포화된 montmorillonite 상에 여러 온도에서 일어난  $\text{H}_2\text{O}$ 와  $\text{D}_2\text{O}$ 의 氣相吸着에 관하여 연구하였다.

吸着으로 인하여 생긴 OH의 IR 신축진동 band를 computer에 의하지 않고 4개의 Gauss 성분으로 나누었다. 물과 silanol OH 기와의 共鳴理論은  $3625\text{ cm}^{-1}$ 와  $2680\text{ cm}^{-1}$ 로 증명되었다.  $3400\text{ cm}^{-1}$ 와  $2475\text{ cm}^{-1}$ 에서의 broad한 吸收는 吸着된 물과 水素結合을 일으키고 있는 silanol OH의 신축진동에 의한 것이었고  $3650\text{ cm}^{-1}$ 와  $2345\text{ cm}^{-1}$  band는 吸着된  $\text{H}_2\text{O}$ 와  $\text{D}_2\text{O}$ 에 의한 것이었다. 吸着水와 表面 OH 사이의 水素結合은 靜電氣的 相互作用에 의한 것이임이 밝혀졌다.

**ABSTRACT.** The adsorptions of gaseous  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  on  $\text{Na}^+$ -,  $\text{Ca}^{2+}$ -, and  $\text{Al}^{3+}$  montmorillonites at various temperatures were undertaken. Break down of ir hydroxyl stretching bands into four Gaussian components was made by means of manual technique.

Resonance theory of water to form silanol hydroxyl group was supported by  $3625\text{ cm}^{-1}$  band for OH and  $2680\text{ cm}^{-1}$  band for OD which depend on amounts of water adsorbed. The broad bands at about  $3400\text{ cm}^{-1}$  and  $2475\text{ cm}^{-1}$  were assigned to stretching band of silanol OH hydrogen bonded to adsorbed water. The prominent  $3230\text{ cm}^{-1}$  band together with component around  $2345\text{ cm}^{-1}$  were attributed to adsorbed  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively. The chemical nature of the hydrogen bonding between adsorbed water and neighboring surface OH was explained adequately in terms of electrostatic interaction.

## INTRODUCTION

A few workers<sup>1</sup> have given indications that the nature of the surface of a silica or silicate depends greatly on the water content and the conditions under which the water is taken from the catalyst to function as a good cracking catalyst. It is

illustrated that a typical silica-alumina catalyst retains approximately 0.8 % water even after it is evacuated at  $500^\circ$ . These "fixedly adsorbed water" molecules seem adsorbed tightly with sufficiently high heat of adsorption. This type of adsorption presumably takes place primarily on the surface of silica alumina complexes which

have active acid sites located in the neighborhood of their four coordinated aluminum ions, but on the surface of silica.

The dehydration of alcohol, over alumina was investigated<sup>2</sup> from the aspects of catalytic reaction mechanisms and attributed to the surface acid sites of alumina catalyst. Proton on an oxide surface of such a typical acidic solid catalyst as silica-alumina is known to behave as an acid when adsorbate molecules come into contact with such an acidic site<sup>3</sup>. And adsorption of water on the site may take place according to the neutralizing effect which eventually may induce charge transferring.

The band assignments of i.r. spectra of adsorbed water on silica in carbon tetrachloride and in vacuum state were made recently<sup>4-6</sup>.

Break down of the hydroxyl stretching band was made using a curve resolver. In order to obtain the best fit area under the peaks, the Lorentzian analytical function was introduced into the computer<sup>7</sup>.

On the careful spectral studies of water at various temperatures by means of a computer, the four Gaussian librational components revealed the best fit of the Raman and infrared contours<sup>8</sup>.

The nonacidic component that appeared at about  $3520\text{ cm}^{-1}$  with the Y zeolite was explained as due to hydroxyl groups located at aluminum deficient points in the lattice. The actual frequency of these hydroxyl groups depends on the nature of the associated cations, electrostatic properties and size of the cations in hydroxyl cations<sup>9</sup>.

A discussion on the importance of charge transfer interaction in H-bonding with the correlation of band shift and ionization potentials of adsorbed molecules on the silica surface was made. And a correlation between the frequency shifts of the surface silanol OH band and the ionization potentials of similar compounds such

as benzene, toluene, was reported<sup>10</sup>.

However, many questions on the shift of the silanol OH band due to hydrogen bonding with adsorbed water and the mechanisms of water adsorption on the layer silicates exchanged by polyvalent cations are not clearly answered so far.

## EXPERIMENTAL

The self-supported films of  $\text{Na}^{+}$ -,  $\text{Ca}^{2+}$ -,  $\text{Ni}^{2+}$ -, and  $\text{Al}^{3+}$ - montmorillonite were prepared as described in the previous report<sup>11</sup>. The ir spectra of the substrates and adsorbed compounds were obtained with a Hitachi Model EP1-G3 ir spectrophotometer equipped with a 5X expansion unit and modified heatable gas cell. The equilibrium temperatures within the gas cell, 25, 50, 80, 110, 140, 170, 200 and  $230^{\circ}$ , were maintained by a Hitachi Model IRC-2 cell heating controller with  $\pm 2^{\circ}$  accuracy.

$17.5 \pm 3$  torrs of  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  were supplied from the vapour supplying unit specially designed to control vapour pressure by means of water circulation through the double jacket as shown in Fig. 1. In order to protect the KBr window from cracking at high temperature, the gas cell was modified to have a double wall so that circulation of a coolant was possible. The volume of the vapour supplying unit was made to be nearly 5 times larger than that of the gas cell to minimize the effect of temperature variation within the gas cell on the vapour pressure of water.

Water used as an adsorbate was well distilled.  $\text{D}_2\text{O}$  which is known to be 99 % pure, was obtained from Tokyo Kasei Chemical Co. Prior to the injection of 50 ml of either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  into the vapour supplying unit, complete evacuation of the gas cell, as well as the gas supply unit, at  $10^{-4}$  torr by a Welch diffusion pump for half an hour was undertaken.

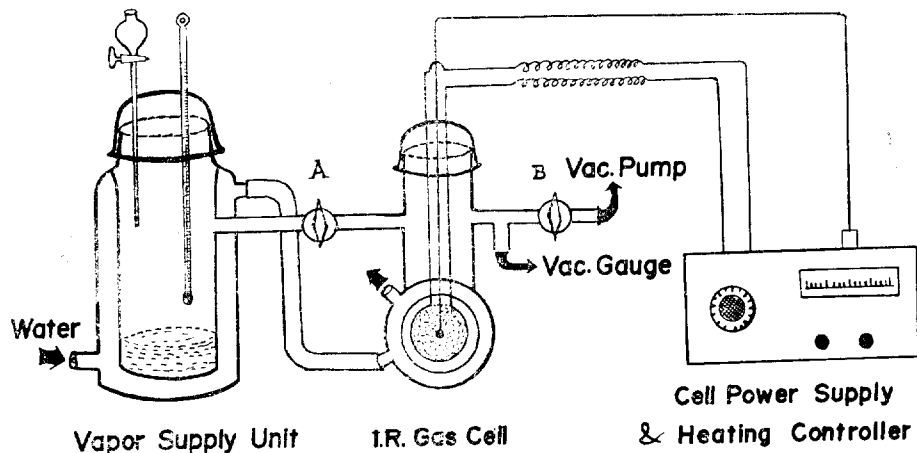


Fig. 1. The ir gas cell and vapour supply unit.

The montmorillonite film within the gas cell connected to the vacuum system was evacuated at  $10^{-4}$  torr and  $250^\circ$  for 3 hours prior to the adsorption process. The vapour of either  $H_2O$  or  $D_2O$  was allowed to fill the gas cell and to maintain the pressure of  $17.5 \pm 3$  torr regardless of the variation of cell temperature by opening cock A. It took half an hour before the adsorption process reached the equilibrium state for the ir spectra. To manage consistent intensities on spectra quantitatively gain control of the instrument was carefully checked by using reference polystyrene film. The areas of the absorption peak were measured utilizing the cutting out and weighing method. Dividing the measured area by the weight of the film, the absorption area per mg substrate were computed to correlate with amounts of water adsorbed.

The break down of the hydroxyl stretching band was attempted by a manual technique that we developed. The original spectra were drawn on a horizontal baseline by the spectrophotometer itself. The hundreds of plastic ruler of Gaussian curves which follow the function;

$$A_p = A_0 \exp(-\alpha x^2)$$

where  $A_p$  is the absorbance at frequency  $\nu$ ,  $A_0$  the absorbance at the band center,  $x$  a measure

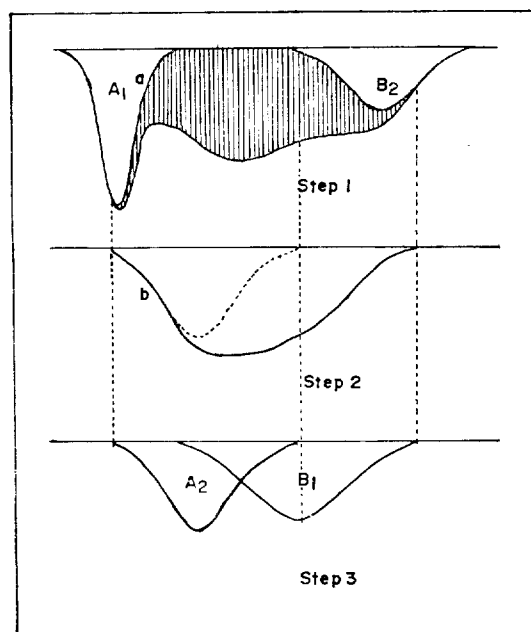


Fig. 2. The break down of contours in three steps.

of the wave number from the band center and  $\alpha$  the constant varied from 0.001 to 0.00006, were made to assist manual technique. The four main bands were analysed in three steps as follow. Two symmetrical bands  $A_1$  and  $B_2$  were drawn on each side of the curve using Gaussian curves which fit the outer side of the curves. Secondly, the remaining part of the peak area was redrawn by plotting the absorbance left after point sub-

traction at each frequency.

Thirdly, two more peaks,  $A_2$  and  $B_1$ , were analysed using selected Gaussian curves which just fit leaving no appreciable gaps. Careful study of the spectra taken throughout various temperatures such as the shoulder of the peak help to determine each band center. In order to separate each peak area continuous curves of the broader side, such as  $b$  in Fig. 2, should be drawn first and the adjacent curve  $a$  in Fig. 2 followed according to this curve  $b$ . A great deal of practice on addition as well as subtraction of curves is required to develop the technique so as to minimize the error to 3~5 %.

## RESULTS and DISCUSSION

**$A_1$  band.** The ir bands of layer silicates exposed to  $H_2O$  or  $D_2O$  were obtained at various temperatures as shown in Fig. 3. The ir absorption bands were broken down to four components,  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ .

Among these the  $A_1$  bands always observed at

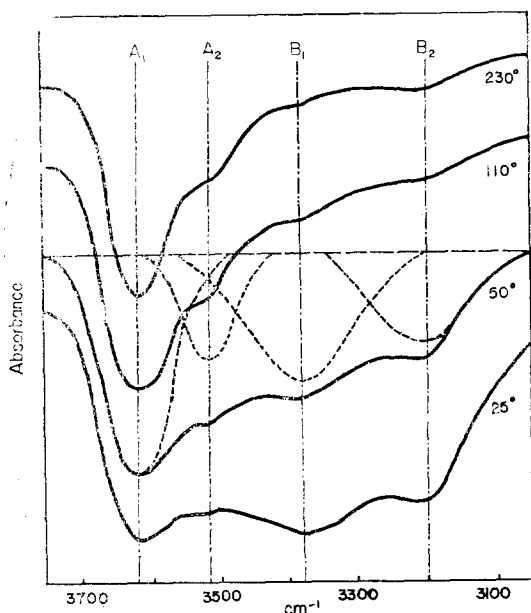


Fig. 3. The ir bands of  $Ca^{2+}$ -layer silicates exposed to  $H_2O$  at different temperatures.

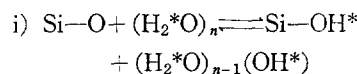
about  $3625\text{ cm}^{-1}$  made us attribute them to the stretching vibrations of the surface silanol OH groups. The sharpness of the band indicates that the surface hydroxyl groups are relatively homogenous. Angell and Schaffer<sup>12</sup> had also found a band at about  $3640\text{ cm}^{-1}$  with zeolites which were allowed to contact water in stepwise and a small variation with different cations as due to the OH group responsible for the water adsorption. At elevated temperatures the water apparently attacks the zeolite structure by hydrolysis and forms more hydroxyls than there were present originally.

On the other hand, the intensities of the bands depend on the cations, particularly positive charges of the cations. This fact makes it rather difficult to correlate quantitatively the intensities of the bands with the nature of the silanol OH group.

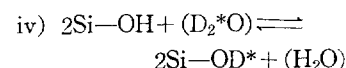
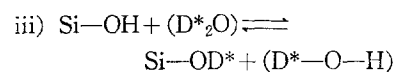
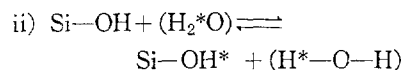
However, a comparison of the intensities of  $A_1$  and  $B_1$  which is supposed to be related to adsorbed water seems to indicate roughly that the amounts of silanol depend on the amounts of water adsorbed.

In other words, the  $A_1$  band must be due to the surface Si—O group so placed as to accept protons migrated from the water adsorbed on cations through the mechanism proposed as follow.

Proton migration (parenthesis indicates adsorbed state) :



proton exchange:



The proton migration process and proton ex-

change mechanism seem very reasonable to explain the cationic effects on the amounts of silanol OH, as well as adsorbed water as shown in the Fig. 4. The reported stabilities of the

surface silanol OH even at high temperatures seems in good agreement with the result shown in Fig. 4, 5, and 6 as well as highly dehydrated

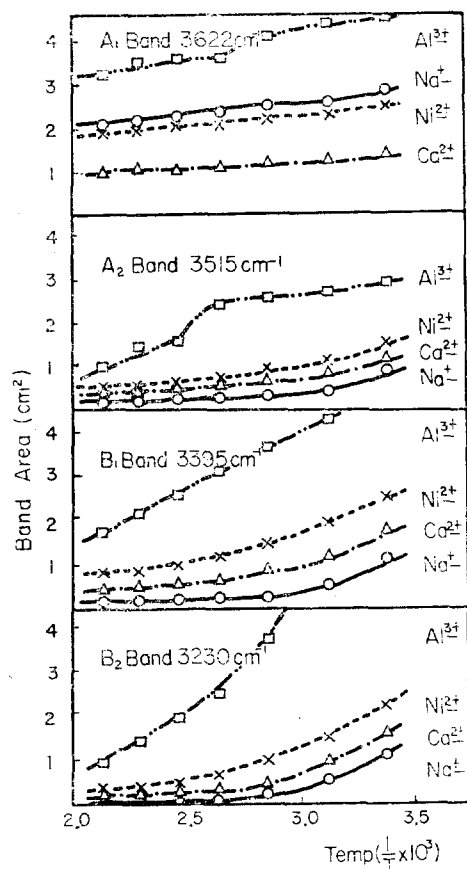


Fig. 4. The ir band areas of each component of cation supported layer silicates exposed to H<sub>2</sub>O at different temperatures.

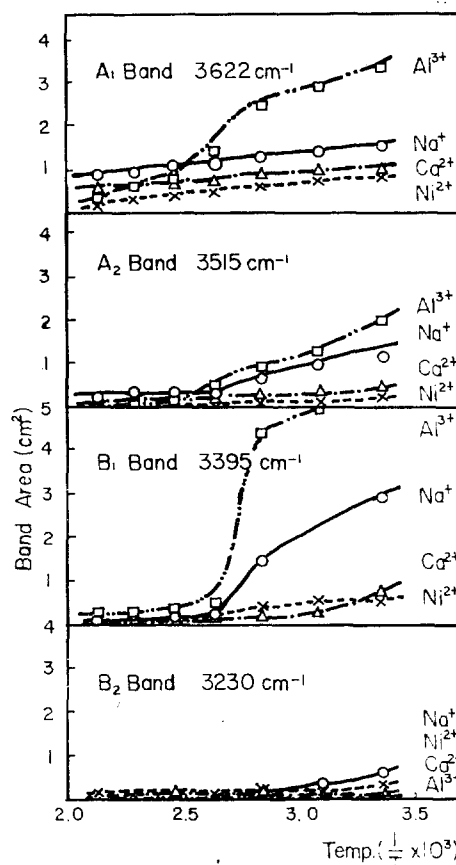


Fig. 5. The ir band areas of each component of cation supported layer silicates exposed to D<sub>2</sub>O at different temperatures (3700~3000 cm<sup>-1</sup>).

Table 1. The band center of ir spectra of layer-silicates treated by H<sub>2</sub>O or D<sub>2</sub>O.

		A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>	C
a) H <sub>2</sub> O treated	Na <sup>+</sup> -	3622	3517	3395	3230	1620
	Ca <sup>2+</sup> -	3627	3520	3390	3200	1585
	Ni <sup>2+</sup> -	3625	3510	3360	3165	1610
	Al <sup>3+</sup> -	3627	3515	3380	3185	1560
b) D <sub>2</sub> O treated	Na <sup>+</sup> -	2680	2580	2475	2345	1430
	Ca <sup>2+</sup> -	2680	2580	2471	2345	1420
	Ni <sup>2+</sup> -	2680	2583	2475	2345	1425
	Al <sup>3+</sup> -	2678	2585	2475	2345	1430

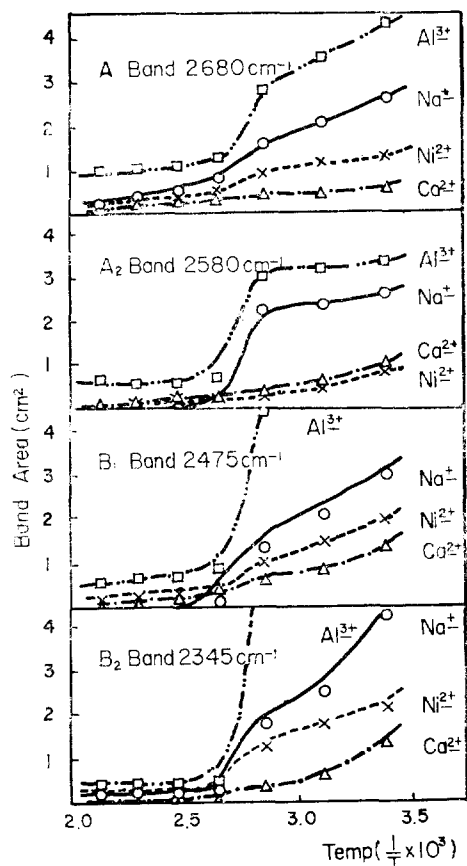


Fig. 6. The ir band areas of each component of cation supported layer silicates exposed to  $D_2O$  at different temperatures ( $2800 \sim 2000 \text{ cm}^{-1}$ ).

states at  $10^{-4}$  torr and  $300^\circ$  for 4 hours.

This evidence apparently supports resonance theory reported previously<sup>11</sup>. Otherwise it could hardly explain the consistent ir absorption at  $2675 \text{ cm}^{-1}$  due to the Si—OD stretching vibration with samples exposed to  $D_2O$  vapour throughout the temperature range and the relative intensities of the OD bands appeared very similar as OH bands. Such deuteration mechanism of silanol OH through proton exchange as illustrated in the reaction iii~iv should eventually support resonance reaction theory.

Nevertheless, what can accounts for the fact that the intensities of the free silanol band ( $3740$

$\sim 3690 \text{ cm}^{-1}$ ) was always negligible which supposed to be very intense with silica? What causes this band to appear at  $3625 \text{ cm}^{-1}$  instead of  $3660 \text{ cm}^{-1}$  for the hydrogen bonded silanol even at the highly dehydrated states? These questions quite clearly point out the unfavourable situation of surface silanol groups of layer silicates to exist either as free or weakly hydrogen bonded. This probably due to the specialities in structure of layer silicates which consist of several silicate layers facing each other to form inter-layers.

**$A_2$  Bands.**  $A_2$  Bands were observed at about  $3530 \text{ cm}^{-1}$  with all cation supported silicates (Table 1). It was reported that the  $3540 \text{ cm}^{-1}$  band was associated with the interaction between two neighboring OH groups presumably through hydrogen bonding, lowering the OH stretching frequency and broadening the band<sup>12</sup>. However, this particular hydrogen bonding was hardly differentiated from those associated with the  $3625 \text{ cm}^{-1}$  band. The remarkable change in  $A_2$  bands according to the elevation of temperature which eventually caused dehydration of adsorbed water makes it seem that this band is directly related with the water adsorbed.

$A_2$  Band would be ascribed to the OH bands whose interactions diminish as dehydration takes place as the temperature is increased. However, these were not sufficient to visualize the mechanism related to the OH band.

**$B_1$  Band.** All the perturbed peaks resolved at  $3395 \text{ cm}^{-1}$  were found to consist of a single, symmetrical Gaussian band. It seems of some interest to refer to the opposing theories about this broad band. Bertsch and Habgood<sup>14</sup> observed a broad band at  $3400 \text{ cm}^{-1}$  and attributed it to the OH of water molecules hydrogen bonded to a surface oxygen which increased on the addition of water on NaX zeolite. Bascom<sup>4</sup> had also obtained a result that the intensity of the free silanol OH band at  $3700 \text{ cm}^{-1}$  was reduced.

relative to the dried silica and the hydrogen bonded  $\text{H}_2\text{O}$  band at  $3400\text{ cm}^{-1}$  increased as the samples were rehydrated. Walrafen<sup>8</sup> assigned two Gaussian components at  $3435$  and  $3247\text{ cm}^{-1}$  to vibrations of lattice water. Two significant ir absorption at  $3430$  and  $3240\text{ cm}^{-1}$  for  $\text{H}_2\text{O}$ ,  $2530$  and  $2390\text{ cm}^{-1}$  for  $\text{D}_2\text{O}$  were observed and assigned the absorption at higher wave numbers to the antisymmetric OH stretching vibrations of the symmetrically hydrogen bonded complex<sup>4</sup> and the rest to those of asymmetrically hydrogen bonded complex. McDonald had also noticed a sharp band at  $3749\text{ cm}^{-1}$ , increased in intensity, and a broader band at  $3400\text{ cm}^{-1}$ , decreased in intensity until ultimate elimination as the silica was degassed<sup>5</sup>. And he attributed this broad band to the perturbed silanol OH band due to the water adsorption on the surface. We have observed, however, this broad band  $B_1$  fitted by a single Gaussian peak always at  $3395\text{ cm}^{-1}$  with little variation according to cations and its integrated area under this peak exhibited a correlation with  $A_2$  and  $B_2$  except in the case of  $3230\text{ cm}^{-1}$  after  $\text{D}_2\text{O}$  was added (Fig. 5). If the  $B_1$  band at  $3395\text{ cm}^{-1}$  is due to the water molecules hydrogen bonded, how can we explain the prominent component even when  $\text{D}_2\text{O}$  was added as an adsorbate instead of  $\text{H}_2\text{O}$  as shown by  $B$  bands in the Fig. 5. On the basis of these remarks, we believe that the  $B_1$  band may not be related entirely with adsorbed water, but with the hydrogen bonded silanol OH band. The quick decrease of intensity at the temperature range,  $80\sim 110^\circ$ , on which dehydration become active being simply due to the liberation of the OH from hydrogen bonding with water.

**$B_2$  Band.** The integrated area under this peak apparently depends on the water adsorbed as indicated in the Fig. 4~6.

It is known that  $\nu_1$  and  $\nu_3$  stretching vibration of free water, having similar magnitude, cannot

perturb each other since they belong to different symmetry species,  $A_1$  and  $B_1$ . For the liquid, however, the broad absorption of  $\nu_1$  is reported<sup>13</sup> to overlap  $\nu_3$  having the absorption maxima at  $3363\text{ cm}^{-1}$ . The ir spectra of  $\text{SiO}_2$  that have been repeatedly dried at  $750^\circ$  and exposed to  $\text{H}_2\text{O}$  vapour is known<sup>14</sup> to have absorption maxima at  $3370\text{ cm}^{-1}$ . And it makes it difficult to give some insight into how the water is held on the silicate surface to have such a shift as  $B_2$  Band. We noticed a couple of bits of evidence to support our theory about the band  $B_2$ . First, correlations have been found between the intensities of these bands and the temperature of the cell, as well as cations. The intensities reduced significantly at the temperature range  $80\sim 110^\circ$ . Secondly, entire missing of this band in the ir absorption spectra of the sample allowed to contact  $\text{D}_2\text{O}$  after dehydration (Fig. 5). Thirdly, the value of peak area ratio,  $B_1$  and  $B_2$  divided by  $C$ , bending vibration, as shown in Table 2 indicated gradual increase at low temperature and equilibrated value at elevated temperature. This final result implies that adsorption probably takes place in at least two stages, the polymerized state at which bending vibrations are highly restricted at low temperatures and the molecular adsorption at which bending vibrations are partly restricted at high temperatures. The slight increment at the temperature above  $200^\circ$  is probably due to the weak interaction between hydrogen and surface entities. These results leads us to conclude that the frequency  $B_2$  can be assigned adequately to the stretching frequencies of water adsorbed and the tendency to be polymerized is prominent at lower temperatures than  $80^\circ$  and related to the nature of the cations.

The amount of water adsorbed on the adsorbent was illustrated in the Table 3. This result point out that the ionization potential of the cation probably plays an important role in the hydrogen

Table 2. The peak area ratio of ir frequencies of water adsorbed on cation supported layer silicate at different temperatures.

		25°	50°	80°	110°	140°	170°	200°	230°
$B_1/C^*$	Na <sup>+</sup>	1.6443	1.2542	0.6927	0.9460	1.1528	1.1816	1.4459	1.4163
	Ca <sup>++</sup>	2.2890	2.0732	1.7915	1.6032	1.6507	2.0709	1.9915	2.5436
	Ni <sup>++</sup>	4.6956	5.0328	4.0649	5.1685	4.5658	4.6530	6.2437	9.3852
	Al <sup>+++</sup>	3.0086	3.4115	3.0830	3.7229	4.0011	4.5494	5.9797	5.0732
$B_2/C$	Na <sup>+</sup>	1.7825	1.3498	0.4526	0.5515	0.4915	0.4973	0.6113	
	Ca <sup>++</sup>	2.2581	2.4483	1.0350	0.8356	0.7906	0.9812	1.0628	1.4459
	Ni <sup>++</sup>	4.3654	4.1276	3.1005	3.1886	2.8136	2.4068	3.0050	4.3074
	Al <sup>+++</sup>	9.0134	7.7374	3.3522	3.1043	3.0437	3.0968	3.4651	3.1047

\*C indicates area under the bending frequencies around 1620 cm<sup>-1</sup> for H<sub>2</sub>O or 1425 cm<sup>-1</sup> for D<sub>2</sub>O.

Table 3. amounts of water adsorbed on he cation supported. layer silicates(g/g).

		Na <sup>+</sup>	Ca <sup>2+</sup>	Ni <sup>2+</sup>	Al <sup>3+</sup>
I. P		5.12	11.82	18.20	28.30
H <sub>2</sub> O	25°	0.071	0.094	0.129	0.906
	110°	0.009	0.019	0.041	0.142
D <sub>2</sub> O	25°	0.2374	0.074	0.121	0.613
	110°	0.011	0.016	0.030	0.126

bonding of water adsorbed particularly at elevated temperature. In other words, hydrogen bonding of water could be explained adequately in terms of electrostatic interaction and charge transfer hydrogen bonding.

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