

Layer Silicate 에 지지된 양이온상에서 일어나는 Alkyl Ketones 의 흡착기구. 水酸基의 Link 形成理論

金 涼 澤 · 孫 宗 洛
慶北大學校 工科學 應用化學科
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Adsorption Mechanism of Alkyl Ketones on Cation Supported by Layer Silicate. Link Formation of Hydroxyl Group

Jong Taik Kim and Jong Rack Sohn

Department of Applied Chemistry, Kyungpook National University, Taekoo, Korea

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요 약. Li^+ , Na^+ , K^+ , Ca^{2+} , Ni^{2+} , Al^{3+} , 과 F^{3+} 의 양이온을 포화시킨 Wyoming montmorillonite 에 acetone, methyl-ethyl ketone, diethyl ketone 을 加熱用 i.r. gas cell 內에서 各各 다른 壓力 아래 吸着시켜 $4000\sim 1200\text{ cm}^{-1}$ 의 범위에서 spectra 를 얻었다. 두가지 형태의 $\text{C}=\text{O}$ 결합변화가 1713 cm^{-1} 과 1690 cm^{-1} 에서 나타났으며 이들은 양이온의 水酸基 및 吸着水와 그리고 表面水酸基와 水素結合을 이끄는 결과로 나타났다. OH 吸收 spectra 의 強度는 양이온의 水酸基의 resonance 理論을 뒷받침 해 주었다. coordinate bond 를 이끄는 경향은 計算한 $\text{C}=\text{O}$ 基의 酸素의 formal charge 의 크기와 잘 맞았다.

Abstract. The self supported film specimen of Wyoming montmorillonite as a layer silicate saturated by cations, Li^+ , Na^+ , K^+ , Ca^{2+} , Ni^{2+} , Al^{3+} and Fe^{3+} , were allowed to contact acetone, methyl-ethyl ketone and diethyl ketone within the heatable gas cell. The i.r. spectra between $4000\sim 1200\text{ cm}^{-1}$ at different pressures of adsorbates indicated bond formation through carbonyl oxygen. Two types of carbonyl bond shift with maxima at 1713 and 1690 cm^{-1} are attributed as coordinate bond formation of carbonyl with either surface hydroxyl or cationic hydroxyl group. The intensity of the νOH was analyzed and resonance form of cationic hydroxyl was proposed as an adsorption site. The tendency to form coordinate bond was in good agreement with calculated formal charge of carbonyl oxygen in an increasing order, acetone < methyl-ethyl ketone < diethyl ketone. As an additional mechanism of adsorption, weak hydrogen bonding of methyl hydrogen with surface oxygen was observed.

Introduction

In order to obtain a clearer understanding of many close correlations between the catalytic

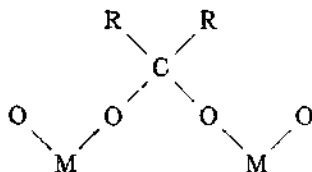
activities and adsorption mechanisms of organic compounds on cations supported by minerals and of holding capacities of clay minerals, the infrared spectroscopic technique has been utili-

zed. However, due to the complicated states of cations exchanged at the clay mineral surface as well as the existence of various types of adsorption sites the bonding characters of adsorbed species are not as simple as those in ionic crystal or homogeneous solution. Particularly, the probable bonding types of organic compounds which have carbonyl group have been expressed in a number of ways.

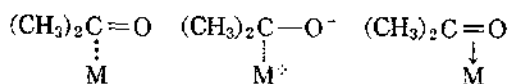
Blyholder and his co-worker¹ studied the orientation of adsorbed species of C_2H_4O over an oil supported metal surface, and observed a lowering of the $C=O$ stretching frequency as much as 40 cm^{-1} and attributed it to acyl formation as a general phenomenon. They expected the formation of some $Ni=C$ double bond character which would reduce the bond order of carbonyl to lower its frequency. The effect of stabilizing acyl derivatives of transition metals by resonance contribution of two structures was suggested by King².



Young and Sheppard³ recently reported formation of acetate ion groups on the surface, studying the adsorption of aldehyde on the silica supported nickel. Another bridge structure for the carboxylate surface species was proposed by Kagel⁴ and others.^{5,6} It is also



reported that the metal atom utilizes π -electrons from a suitable organic ligand to form the isoelectric with the next rare gas atom and formulate such surface species in electronic structure as partway between σ -complexed species and π -complexed species.



Young and Sheppard⁷ concluded that the moderate shifts of CO band implied that the carbonyl group interacts with the surface through a surface hydroxyl group. Occurrence of a surface hydroxyl ion which performs as probable sites of catalytic activity was reported earlier by Bradley.⁸ And a fully hydrated silicate is known to chemisorb organic compounds recently.⁹ Canwelaert¹⁰ and others¹¹ considered surface hydroxyl groups as the most important adsorption sites and distinguished two different hydroxyl groups, "geminal" and "vicinal", according to their interaction behavior with surface species. Pinnavia and Mortland¹² found that two types of complex formation of Cu(II) ion supported by layer silicates were greatly influenced by the amount of water involved. The formation of a strong hydrogen bond between organic compounds and montmorillonite supported cations by means of a water bridge was discovered by Farmer¹³ and the present author.¹⁴ Other theories such as alkoxide formation¹ and diadsorbed alkoxide form³, CH_3CHMOM , have been also reported. It is the purpose of this paper to examine the effect of pretreatment of cation saturated montmorillonite at different temperatures to clarify the water and hydroxyl group involvement to the bonding mechanism and to understand the nature of interaction behavior of alkyl ketones at the surface of the adsorbent.

Material and Method

The Wyoming montmorillonite used was obtained from Archer Daniels Midland Co. Cleveland, Ohio. Three alkyl ketones, acetone (ACT), methyl ethyl ketone (MEK) and diethyl ketone (DEK) were obtained from Wako pure chemical industry L. T. D., Japan. Ketones

were dehydrated by molecular sieve and redistilled until regarded as sufficiently pure for spectroscopic purposes. The fractions of less than 1μ size Wyoming montmorillonite whose cation exchange capacity was known to be 69 meq/100 g were saturated by the cations, Li^+ , Na^+ , K^+ , Ca^{2+} , Ni^{2+} , Al^{3+} , and Fe^{3+} , as described in a preceding publication¹⁴. The self-supported film specimens of those cation saturated montmorillonite, approximately 0.003g in weight, were prepared by air-drying fresh suspensions within a circular aluminum dish 2 cm in diameter.

The nickrome wire installed in the i.r. gas cell was used as a sample holder as well as sample heater. Specimens were put in the gas cell connected to the vacuum system and were heated at a temperature of about 200 °C by the sample heater and evacuated at 10^{-4} Torr for 4 hours at the same time prior to each adsorption process. The i.r. spectra of the film specimen and the specimen with gaseous adsorbates at 40, 20 and 0 Torr were taken. To halve the pressure of gas in the cell by degassing through the diluter, the diluter was designed to have the same volume as the gas cell. The final stage of the dilution, 0 Torr, was conducted by evacuating the cell 10^{-3} Torr for 20 minutes.

In order to remove adsorbed water existing

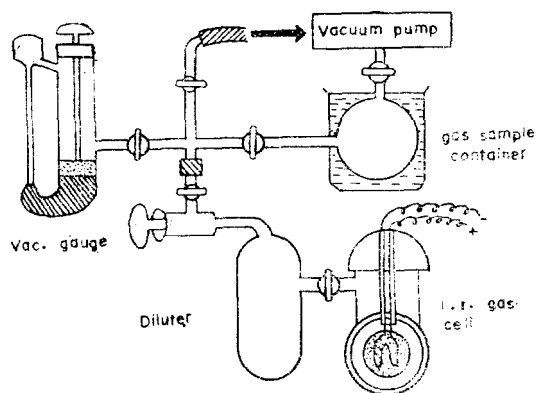


Fig. 1. The diagram of gas cell and sample injection unit.

in the specimen, the specimen was pretreated in the oven at 550 °C or lower followed by evacuation at 10^{-4} Torr for 4 hours within the i.r. gas cell. The resulting i.r. spectra were compared with those not pretreated. The i.r. spectrophotometer used was Hitachi model EPI-G 3 equipped with a 5X expansion unit. Since the variations of those film thicknesses were regarded as being as important as the intensity of absorption spectra, careful preparations were carried out on making uniform thickness and its intensity was calibrated by aid of reference peak intensity of polystyrene film occurred at 1803 cm^{-1} . To eliminate the mineral band itself from the i.r. spectra, the differential technique was used.

Result and Discussion

Bonding Through C=O. The most prominent i.r. band shift due to the adsorption was always observed in the range $1720\text{--}1680 \text{ cm}^{-1}$ as shown in Fig. 2. The resulting carbonyl

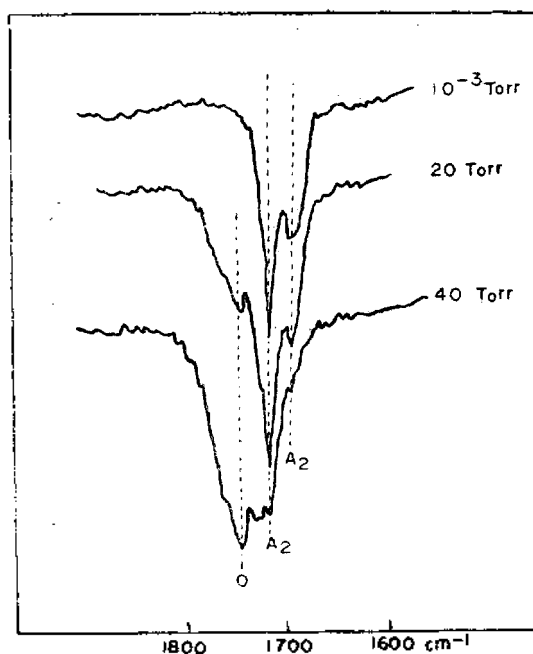


Fig. 2. i.r. spectra of carbonyl bands at 40 Torr and degassed to 20 and 10^{-3} Torr.

Table 1. i.r. Absorption frequencies (cm^{-1}) of hydroxyl and shifted carbonyl bands. (original carbonyl bands: ACT;1742, MEK; 1745, DEK;1742 cm^{-1})

pretr.	ACT			MEK			DEK			
	νOH	A_1	A_2	νOH	A_1	A_2	νOH	A_1	A_2	
Li ⁺ -	(25 °C)	3630	1714	1687	3627	1710	—	3630	1698	—
	(350 °C)	3630	1714	1687	3633	1710	—	3630	1705	—
	(550 °C)	3630	1714	1687	3638	1710	—	3630	1711	—
Na ⁺ -	(25 °C)	3627	1716	1693	3620	1713	1684	3625	1711	1687
	(350 °C)	3627	1716	1693	3638	1713	1684	3633	1711	1687
	(550 °C)	3635	1716	1693	3638	1713	1684	3636	1711	1687
K ⁺ -	(25 °C)	3625	1716	1698	3625	1714	1692	3625	1711	1690
	(350 °C)	3630	1716	1698	3633	1714	1692	3633	1711	1690
	(550 °C)	3630	1716	1698	3637	1714	1692	3635	1711	1690
Ca ²⁺ -	(25 °C)	3625	—	1701	3622	—	1693	3625	—	1693
	(350 °C)	3640	—	1701	3631	—	1693	3632	—	1693
	(550 °C)	3642	1740	—	3640	—	1693	3640	—	1693
Ni ²⁺ -	(25 °C)	3633	—	1698	3622	—	1693	3625	—	1692
	(350 °C)	3638	—	1701	3633	—	1693	3635	—	1692
	(550 °C)	3641	1712	—	3645	—	1693	3640	—	1692
Al ³⁺ -	(25 °C)	3628	—	1700	3625	—	1688	3625	—	1688
	(350 °C)	3643	—	1703	3633	—	1688	3635	—	1688
	(550 °C)	3648	1714	1703	3640	—	1688	3645	—	1688
Fe ³⁺ -	(25 °C)	3629	—	1701	3622	—	1689	3625	—	1686
	(350 °C)	3635	—	1701	3630	—	1689	3633	—	1686
	(550 °C)	3640	1710	—	3640	—	1689	3642	—	1686

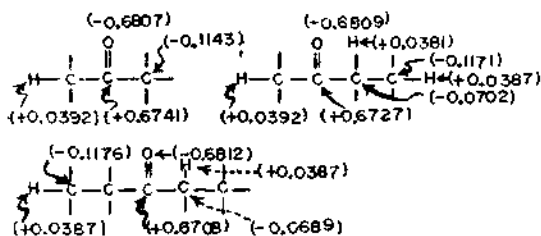
frequency shift varied from 26 to 60 cm^{-1} depending on the cation as well as the alkyl ketone.

The bands, A_1 and A_2 in the Table 1 as well as in the Fig. 2, persisted after evacuation at 10^{-3} Torr and 25 °C for 20 minutes and attributed to the chemical adsorption of ketones rather than physical adsorption. Blyholder and Neff¹ made an i.r. study of aldehydes adsorbed on silicate supported Ni and assigned the bands found in the range from 1725 to 1600 cm^{-1} to acyl formation. They denied the surface structure of formaldehyde held to the surface by a coordinate bond donating a lone pair of oxygen's electron to a nickel atom and believed that this type of coordinate bonding was too weak to produce stable surface species. How-

ever, we failed to find any evidence to support this theory such as the existence of carbon monoxide or other decomposed compounds.

We have calculated the formal charge of each atom of alkyl ketones by means of the two-center Hückel method¹⁵ to provide information to estimate the possibility of bond formation. The large negative charge calculated on an oxygen atom definitely shows a high possibility of bond formation through carbonyl oxygen.

On the other hand, a fairly large positive charge on the carbonyl carbon atom possibly prohibits the approach to the surface cation supported by silicate but allows the approach to surface oxygen to form surface carboxylate species weakening the carbonyl double bond



character. However, it was noticed that the weak bands near 1585 and 1430 cm^{-1} occurred only with some instance of Al^{3+} - and Fe^{3+} -montmorillonite to prove insignificant surface carboxylate formation and not with the rest of the adsorbents.

The fact that the higher the temperature of thermal pretreatment the more significant were the complex bands implies carbonyl interaction with surface oxygen which is uncovered by dehydration. Considering that such a low intensity in these bands occurred on the complexes with Al^{3+} - and Fe^{3+} -montmorillonite and acetone which have relatively larger formal charge, the carboxylate species formed must be very small in proportion to the bonding through carbonyl oxygen. The complex formation of carbonyl oxygen with cation might utterly depend upon the electron donating power of carbonyl oxygen as well as electron accepting tendency of cation. As a matter of fact, carbonyl band shifts found near 1690 cm^{-1} and equivalent changes in bond force constant calculated indicate good correlation with the negative formal charge of ketones in increasing order of $\text{ACT} < \text{MEK} < \text{DEK}$. Thus we do not agree with Young and Sheppard's alternate theory⁷ of σ -complexed species or π -complexed species through carbonyl carbon forming a double bond directly bonded to a metal atom or cation at this case but coordinate bonding through carbonyl oxygen.

Resonance in Hydrated Water. The intensity of the OH stretching bands between 3600

and 3700 cm^{-1} decreased as the predrying temperature increased from 150 to 550°C . These results are similar to those obtained by Bhasin and his coworker¹⁶. Canwelaert¹⁰ claimed the two different types of surface hydroxyl distribution, paired and unpaired hydroxyls and their relative proportions on the silicate surface, are deeply related to the reactivity of the surface towards adsorbates. It is known that the dehydroxylation of surface hydroxyl begins to take place at 350°C whereas dehydration of adsorbed water is almost completed at this temperature. The extent of dehydroxylation indicated by i. r. band intensity in Table 2 is prominent after higher temperature thermal pretreatment for alkali metal but even more prominent after lower temperature treatment for the other cations at which only dehydration of adsorbed water might have taken place. The dehydration at lower temperatures and the difference of absolute amounts of hydroxyl groups due to the cation as

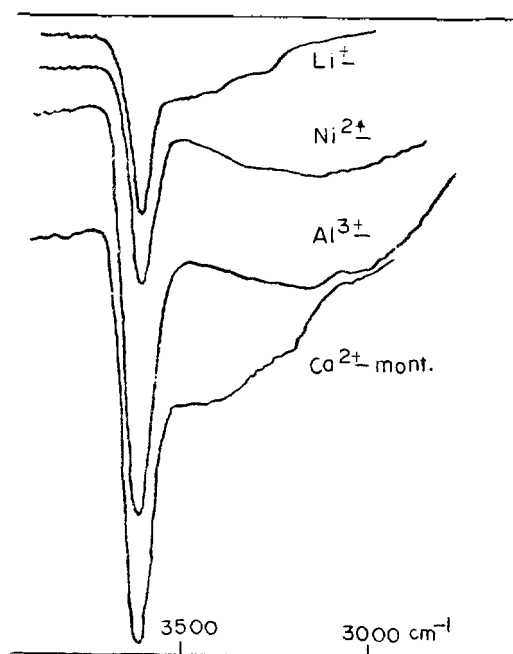


Fig. 3. i. r. spectra of νOH of specimens air-dried at room temperature.

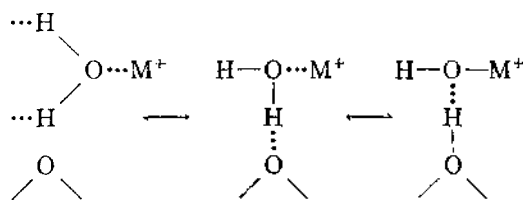
Table 2. The relative intensities of surface hydroxyl band (near 3630 cm^{-1}) pretreated at different temperatures in transparent %.

pretr. temp. ($^{\circ}\text{C}$)	Li^{+} —	Na^{+} —	K^{+} —	Ca^{2+} —	Ni^{2+} —	Al^{3+} —	Fe^{3+} —
25	24	39	37	47	31	46	49
300	21	28	34	38	26	37	38
550	18	23	28	35	23	33	21

indicated in Table 2 and Fig. 3 provide evidence to support the hydroxylation theory of adsorbed water at the spheres of cation through an interchange between a hydroxyl group and water.

Farmer and Russel¹⁷ referred to the adsorbed water, which is highly structured, with the water in the outer spheres of coordination forming dielectric links via hydrogen bonding between the cation and the negatively charged silicate structure.

Thus we propose an intermediate surface species related to the equilibrium between the adsorbed water and hydroxyl formation in this reasonably dehydrated condition.



This type of resonance will be more prominent when the interactions of polyvalent cations with adsorbed water are allowed and thus more stabilized than the water simply adsorbed around the cation. Such a hydroxylation mechanism probably is promoted by deprotonation activity of adjacent surface oxygen. The size of the cation and orientation of water around the cation, controlled by coordinating power of the cation and the space around it should also be an important factor. This could be a favorable interpretation for Ca^{2+} —montmorillonite to hold more water. An ionic radius of about

1 \AA for mono and divalent cations seems most favorable as shown by the cases of Na^+ , K^+ , and Ca^{2+} .

Thus the resonance theory is reasonable and has supporting evidences, i. e. the tendency of dehydroxylation and dehydration at lower temperature than $350\text{ }^{\circ}\text{C}$, the intensities and shapes of $\nu\text{ OH}$ band found in the region of $3200\sim 3640\text{ cm}^{-1}$. The cations which indicated strong water adsorption by the broad band occurred at $3200\sim 3600\text{ cm}^{-1}$ also show intense absorption at 3620 cm^{-1} to support hydroxylation of hydrated water. The position and the broadness of the hydroxyl band observed in the region of $3600\sim 3700\text{ cm}^{-1}$ was different from those of surface hydroxyl group indicated by 3747 cm^{-1} observed by Canwelaert.¹⁰ The portion of lower frequency near 3620 cm^{-1} always disappeared as the intensities of the band diminished and appeared as a sharper band near 3650 cm^{-1} which is assigned to hydrogen bonded OH by other. Similar disappearing of 3625 cm^{-1} , cationic hydroxyl band, when the specimens are adsorbed by ketones imply the interaction of cationic hydroxyl with carbonyl group of ketones.

Bonding Through OH. Although the tendency of the carbonyl band shift of alkyl ketones were essentially the same, the main difference between the alkali metal complexes and the complexes with the rest of the cations was the positioning of the carbonyl band shift as well as a rise of the doublet or singlet. We observed a doublet with maxima at about 1713 and 1690 cm^{-1} in the spectra of alkyl ketones adso-

Table 3. Average weight % of water dehydrated (relative to wt. of montmorillonite) by thermal pretreatment for 2 hours.

	Li ⁺ -	Na ⁺ -	K ⁺ -	Ca ²⁺ -	Ni ²⁺ -	Al ³⁺ -	Fe ³⁺ -*
150°C	21.4	22.6	14.2	19.1	17.4	14.8	17.8
300°C	0.5	1.5	0.3	3.4	2.0	3.0	0.3

*Samples at room temperature were equilibrated by moisture of 15.5mm Hg.

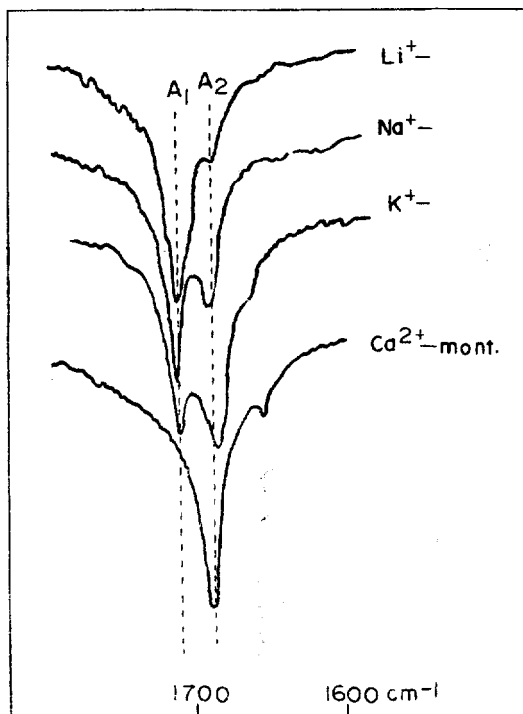


Fig. 4. i. r. spectra of carbonyl band of acetone adsorbed on Li⁺-, Na⁺-, K⁺- and Ca²⁺-montmorillonite.

rbred on alkali-montmorillonite. These two types of shift designated as A₁ and A₂ in Fig. 4 definitely indicate the formation of two different surface species. The carbonyl band A₁ obtained after different temperature pretreatment was shown to have a relatively identical position $1713 \pm 3 \text{ cm}^{-1}$. And the correlation of this band with the cation seems so low that we assigned this band to carbonyl adsorbed by surface hydroxyl $\text{R}_2\text{CO} \cdots \text{HOSi}$. Young and Sheppard⁷ rou-

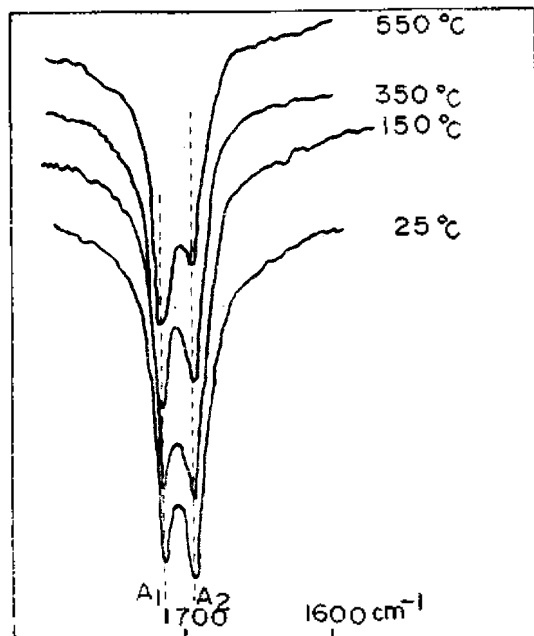


Fig. 5. i. r. spectra of MEK adsorbed on K⁺-mont. pretreated at different temperatures for 2 hours.

ghly assigned the νCO band near 1690 cm^{-1} to "some species present on nickel" and a band of less intensity appeared between 1710 and 1700 cm^{-1} on silica after standing overnight to a band occurred probably due to acetone physically adsorbed to silica through hydroxyl group. This was supported by the intensity study of the A₁ bands which diminished more than 30 % by heating at 350°C prior to the adsorption whereas only about 10 % after 150°C pretreatment for 2 hours. Natural montmorillonite as a hydrophilic product of a weathering process could be expected to possess hydrated surfaces in a moderately air dried condition. Drying at

Table 4. i. r. bands assignment of ketones.

(ACT)	(MEK)	(DEK)		
3015, 2972	2993	2990 ν CH ₃	E
—	2970, 2958	— ν CH ₂	B ₁
2950	2948	2950 ν CH ₃	A ₁
—	2923	2916 ν CH ₃	A ₁
1432	1462	1462 δ CH ₃	E
—	1434, 1416	1414 δ CH ₂	A ₁ bend.
1366	1379	1379 δ CH ₃	A ₁
—	1367	1365 δ CH ₂	B ₂ wagg.

or below 150 °C preferentially removes the outer sphere water which is highly structured on the silicate surface and around cations and free some of the silicate surface for the adsorption of organic molecules.

The extent of the carbonyl band shift A_2 was significantly different according to the cations in the order of $\text{Li}^+ \text{---} \langle \text{Na}^+ \text{---} \langle \text{K}^+ \text{---}$ to illustrate their close correlation with cation as indicated in Table 1. This order is consistent with the tendency of hydroxylation at the surface of correspondng cation.

Among the two probable surface species, the complexed directly to cation and the complexed indirectly through hydrogen bonding, it is apparent that pretreatment at a higher temperature would promote the direct complex formation uncovering the silicate surface and may eventually increase the band intensity. However, the relative intensity observed in this region decreased markedly after pretreatment at a higher temperature gives evidence to support certain hydroxyl involvement instead of direct complex formation. Competition in proportion to two active adsorption sites, surface hydroxyl and cationic hydroxyl, seems sensitive to montmorillonite supported monovalant ions depending on thermal treatment. Greater decrease in intensity of A_2 band for $\text{K}^+ \text{---}$ montmorillonite at the lower pretreatment indicate looser but abundant interaction of cation with hydrated water molecules

than $\text{Na}^+ \text{---}$ or $\text{Li}^+ \text{---}$ montmorillonite. The singlet nature of carbonyl absorption near 1700 cm^{-1} for divalent and trivalent cations could be attributed to the increased probability of complex formation with cationic hydroxyl group.

C-H...O Bonding. Nolin and Jones¹⁸ made assignment of the 2977 , 2936 and 2883 cm^{-1} band of diethyl ketone which correspond to B, C and E in Fig. 6 to methyl stretching vibration and 2902 cm^{-1} , D band in Fig. 6 to methylene stretching vibration after careful study of deuterium substitution products. They also assigned 1461 and 1379 cm^{-1} band to methyl deformation* vibration and 1414 and 1355 cm^{-1} bands to methylene deformation frequencies corresponding to K, M and L, N in the Fig. 6 respectively.

Schumann and Aston¹⁹ assigned the 2950 , 1432 and 1340 cm^{-1} band of acetone to methyl stretching, methyl asymmetric deformation and symmetric deformation respectively. The frequencies of three gaseous ketones can be assigned as follow by analogy with those assignments of DEK and ACT illustrated above and by others.²⁰⁻²² The slight displacement of band B and C of diethyl ketone adsorbed on $\text{Na}^+ \text{---}$ montmorillonite to lower frequency was accompanied by the positive displacement of the K band in the Fig. 6 providing information for hydrogen bonding through the methyl hydrogen probably with oxygen of surface or hydroxyl group. Similar tendency of the band shifts

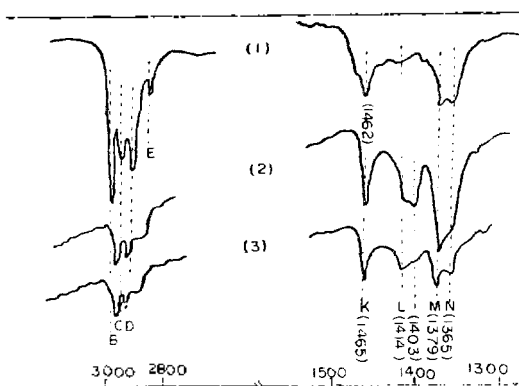
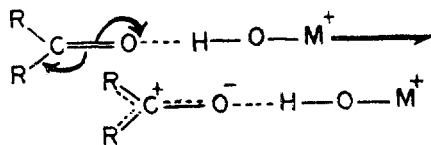


Fig. 6 i.r. absorption spectra of diethyl ketone adsorbed on Na⁺-montmorillonite.

- 1) only DEK,
- 2) adsorbed after pretreated at 150°C for two hours,
- 3) adsorbed after pretreated at 350 °C.

was observed always with other ketones but more significant with the adsorbents pretreated at lower temperature. Both of the C-H stretching frequency of the methylene group and its deformation band L and N shifted significantly to lower frequency. This is attributed to the weakening effect of the methylene C-H bond due to the increase of double bond character of the adjacent C-C bond which is induced by lowering of C=O bond order. This also supports the supposition that the ketones preferentially bond through the carbonyl oxygen instead of through carbonyl carbon. The possibility of a hydrogen bond formation through the methyl



hydrogen was supported by calculated positive formal charges on methyl hydrogen by means of two-center Hückel method. The new bands which appeared at 1230~1265 cm⁻¹ probably are related to the increased skeletal bond order which has not been confirmed by other means.

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