The Adsorption of Alkyl Aldehydes on Cations Supported by Layer Silicate. Complex Formation Theory

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Abstract. Adsorption mechanism of alkyl aldehydes, acetaldehyde, acrolein, and crotonaldehyde on cations supported by layer silicates was studied by means of IR spectroscopy and X-ray. An analysis of four characteristic split bands in the region of 1720~1580 cm\(^{-1}\) was made. The carbonyl stretching band which shifted about 130 cm\(^{-1}\) to lower frequencies was observed only for Ni\(^{2+}\) and Al\(^{3+}\) but slightly with Ca\(^{2+}\) at high sample temperature and was attributed to >C=O···M complex formation. A sharp band which appeared as a shoulder at 1722 for acetaldehyde and 1690 for acrolein and crotonaldehyde was responsible for the interaction of carbonyl with surface hydroxyl. The second broad band which appeared at about 1710~1660 was responsible for hydrogen bonding between carbonyl oxygen and cationic hydroxyl group. The third band which appeared at about 1640~1660 was attributed to induced >C=C< double bond due to the strong carbonyl interaction. This was supported by the interlamellar spacings obtained by X-ray diffractometry.
Introduction

Silicas and silicates are used as catalyst supports in processes in which water is a product or a reactant along with organic compounds. There has been a wide interest in learning about the mechanism and dynamics of organic compound adsorption on a variety of silicate surfaces. The techniques of accurate analysis of the perturbed absorption bands of infrared spectra as one of the most useful tools employed in these studies have been intensively developed recently. The comparison of the isosteric heat of adsorption of several organic compounds including acetaldehyde allowed to contact silica with observed frequency shifts was made and the adsorbates used in the study were separated into two classes of compounds according to the electronic differences and hybrid orbital electrons. 1

The alkoxide type of physically adsorbed acetaldehyde on silica supported nickel was CH₃—CHM—OM found in its infrared absorption bands with the evidence of spectra from decarbonylation products, carbon monoxide, increased in intensity. A theory of the adsorption mechanism of alkyl ketones through the link formation of cationic hydroxyl groups supported by layer silicates was reported by these authors. The intensity of the —OH bands was analyzed and a resonance form of cationic hydroxyl was proposed as an adsorption site.

Other predominant active centers for water adsorption on partially hydrophobic silicas were reported to be the surface —OH groups, despite the presence of sodium and other foreign elements in these materials. 4

The frequency shifts observed during adsorption of organic compounds on the hydroxyl groups of several oxide surfaces have been measured and compared with the shifts observed when several alcohols are dissolved in the same solvents. 5 The comparison of these shifts with the pKa values for the various surface hydroxyl groups indicated a good correlation with Mulliken electronegativities of cations.

A thorough study about these three probable bonding natures: hydrogen bonding interactions between gaseous alkylaldehyde and cationic hydroxyl groups, hydrogen bonding between aldehyde carbonyl and surface hydroxyl groups and alkoxide type complex formation has not yet been made. As a subsequent work, a resolution of general problems which may lead to much definite knowledge about vibrational spectra and the bonding nature of substrates on cation supported layer silicates is intended.

Experiment

The Wyoming montmorillonite obtained from Archer Daniels Midland Co., Cleveland, Ohio and its self-supported film saturated by one of these cations, Li⁺, Na⁺, K⁺, Ca²⁺, Ni²⁺, Al³⁺, and Fe³⁺, were prepared as described in the preceding publication. 3

Alkyl aldehydes, acetaldehyde, acrolein and crotonaldehyde of extra pure grade as adsorbates were obtained from Sunzei Kagaku Co., Japan; Merck, Germany; and Tokeikasei Co., Japan, respectively. Pure acetaldehyde and crotonaldehyde were prepared by redistillation followed by treating the distillate with a molecular sieve to exclude trace amounts of water. Acrolein was also redistilled until the sample obtained in this way indicated that no amounts of hydroquinone inhibitor were involved in its infrared(IR) absorption spectra.

All the purified aldehydes were kept in a refrigerator at —15° to inhibit spontaneous polymerization and evaporation. Highly ordered self-supported films of the cation exchange
forms of the layer silicates were pretreated by means of evacuating up to $10^{-4}$ torr at about 200° for overnight in the specially designed gas cell.

The IR spectra of the films were taken by a Hitachi model EPI—G3 IR spectrophotometer at 20°, 50°, 80°, 110°, and 140° adjusted by a Hitachi model IRC—2 temperature controller. The gas cells used were similar to those used for the previous work except that the thermocouple tip was placed right on the center of the film so that measurement of the heating temperature would be more accurate.

Desired temperatures of the cell were achieved within 2° almost regardless of variation in the room temperature. An accurate mercury thermometer placed side by side with a thermocouple is adapted as a reference for the temperature correction.

Likewise, IR spectra of the adsorbates allowed to contact the film within the gas cell at 40 mm torr and degassed to $10^{-4}$ torr by a Welch high vacuum diffusion pump at each adjusted temperature were taken twice or three times, spending 5 times on the abscissa frequency scale. In order to compensate for the mineral absorption, identical film was positioned in the path of the reference beam.

To observe the moisture effect on the adsorption mechanism, the gas cell was connected to the dessicator which was equilibrated by 0.1, 4 and 18 mm vapour pressure adjusted by 80, 60 and 0% sulfuric acid solution at 20° respectively.

X-ray diffractograms of the film specimen used for IR measurement were taken by a Shimadzu model VD—1 X-ray diffractometer.

**Result and Discussion**

**>C=O···M Complex Formation.** The most significant perturbations in IR spectra due to the adsorption of alkyl aldehydes on the cation saturated layer silicates were always noticed in the broad range, 1700—1550 cm$^{-1}$. The complicated nature of the split bands within this range was characteristic and very different from those of alkyl ketones reported previously.

Our primary interest was to identify active centers for the aldehyde adsorption and specific adsorption sites of alkyl aldehyde molecules. The shift of carbonyl stretching frequency due to the adsorption proved that the adsorption took place through carbonyl oxygen instead of other sites of molecules. The formal charge of each atom of alkyl aldehydes calculated by means of the two-center Hückel method shows the possibility of forming bonds through carbonyl oxygen.

However, theoretical questions about several split bands as shown in Fig. 1 and 2 indicate the existence of many different adsorption sites on the adsorbent. Careful study of the bands leads us to make separate these adsorption sites correlated with the extent of carbonyl band shifts into two classes; those on which the carbonyl bands shifted about 30—50 cm$^{-1}$ and those on which negative shift exceeded 120 cm$^{-1}$.

The 1st group occurred predominantly with Li$^+$, Na$^+$, and K$^+$, whereas the second group, as shown in Fig. 2, prevailed for the adsorption of alkyl aldehydes on Ni$^{2+}$ and Al$^{3+}$ saturated layer silicates and both of the groups seemed to act equally with Ca$^{2+}$. One of the most prominent pieces of evidence that
Layer Silicates의 지지에 네온장에서의 알킬알데히드의 吸着機構

shows the 2nd group to be naked cations on which $\text{C} = \text{O} \cdots \text{M}$ type complex formation likely takes place is the deep blue color observed with Ni$^{3+}$ and Al$^{3+}$ montmorillonite. This was supported by the fact that the intensity of the perturbed carbonyl D band in Fig. 2 and 3

**Fig. 1.** IR spectra of carbonyl bands of crotonaldehyde adsorbed on Na$^+$-mont. at 40 torr and degassed to 20 and 10$^{-3}$ torr

**Fig. 2.** IR shifted carbonyl bands of crotonaldehyde adsorbed on cations supported by layer silicates at 40 torr and degassed to 10$^{-3}$ torr

**Fig. 3.** IR carbonyl bands of crotonaldehyde adsorbed at different temperatures

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increased systematically with increasing temperature of pretreatment, by which direct contact of the substrate with cations should be promoted. This was well supported by fade-out of the D band by water interaction at higher vapour pressure as shown in Fig. 4.

The oxidation of acetaldehyde to form RCOO⁻ initiated by dissociative adsorption of some acetaldehyde molecules on the metal surface are reported as responsible for two strong bands, 1580 and 1430 cm⁻¹. However, the shifted band D which appeared at 1580 cm⁻¹ for Ni²⁺ and Al³⁺, was not accompanied by an arising strong band at about 1430 cm⁻¹ to deny RCOO⁻···M type complex formation.

Blyholder and Neff reported infrared results from the chemisorption of acetaldehyde on nickel and iron and concluded that the surface species on iron was alkoxy type CH₃CHOM. However, alkoxy type adsorption did not
seem to take place in our case, since there was no evidence of carbon monoxide produced and theoretical calculation of the average distance between the neighbouring cations turned out to be nearly \(10^4\) \(A\) order for this layer silicate, whose cation exchange capacity and specific surface areas were 68 meq/100 g and 400 m\(^2\)/g respectively.

\(>\text{C}=\text{O} \cdots \text{HO} \cdots \text{Hydroxyl Bridges.}\) Carbonyl frequencies which lie in the range 1685~1625 cm\(^{-1}\) have been reported as metal acyl type complexes in solution.\(^6\)\(^\text{-}\)\(^1\) However, several split bands of comparable intensity in the 1690~1640 cm\(^{-1}\) region raise the question whether these cannot be attributed to water involvement in the gaseous adsorption process on cations ascribed in the previous report.\(^1\) The carbonyl bands, \(A\) and \(B\), in the Fig. 5, show a consistent increase in intensity with increasing vapour pressure of water. If the acyl formation truly occurs, it is expected that the intensity of the bands in this region should diminish by competitive inhibition of water around the cation.

The relatively constant negative shift, as much as 27 cm\(^{-1}\) for the \(A\) band, a broad \(B\) band at about 40 cm\(^{-1}\) negative shift and the \(C\) bands which appeared at about 1660 cm\(^{-1}\) for acetaldehyde and about 1643 cm\(^{-1}\) for the rest are in contradiction to the case of cation-acyl complex formation in which a single band would vary in the broad range according to the different charge densities of cations.

Accurate analysis of these three perturbed bands indicated the following distinct characteristics. The \(A\) band always appeared as a sharp independent band or as a high frequency shoulder at 1722 cm\(^{-1}\) for acetaldehyde and 1690 cm\(^{-1}\) for the rest with \(\pm 1\) cm\(^{-1}\) variation. The \(B\) band appeared as a relatively broad intense band covering the range of shifts from 34 to 50 cm\(^{-1}\) and showed appreciable variation in its frequency and shape according to the cations as well as adsorbates. The broadness of the band, nevertheless, increased by shifting the maximum point of peak to a lower frequency as the amount of moisture increased. The magnitude of the shifts for dryish cations such as Ca\(^{2+}\) and Al\(^{3+}\) is always larger than that of easily dry cations such as K\(^+\), Li\(^+\) (Table 1).

The relatively weak sharp \(C\) band showed little variation in the frequency appearing at 1642 cm\(^{-1}\) for acrolein and crotonaldehyde and at 1666 cm\(^{-1}\) for acetaldehyde according to the cations.

All the moisture tests raised relative intensities of the \(A\) and \(B\) bands but not the \(C\) band with an increasing amount of moisture as shown in Fig. 4 and 5.

The careful analysis of the IR spectra correlated with moisture amount made us attribute each band to the different type of bonding as follows:

- \(A\) band, \(>\text{C}=\text{O} \cdots \text{HO} \cdots \text{Si(surface hydroxyl)}\)
- \(B\) band, \(>\text{C}=\text{O} \cdots (\text{HO})_{\text{m}} \cdots \text{M(cationic hydroxyl)}\)
- \(C\) band, \(>\text{C}=\text{C} \cdots \) (double bond)

The intermediate hydroxyl group, somewhat between a water molecule and a hydroxyl group expressed as resonance form whose hydrogen is partly deprotonated by the interaction with a silicate surface, is responsible for the \(B\) band. The perturbed band observed at a low frequency side of the \(B\) band is deduced by the stronger adsorption of carbonyl on the hydroxyl group.

The consistent increase in intensity of the \(C\) band along with the intensity of the \(D\) band, as the case of Ni\(^{2+}\) and Al\(^{3+}\), indicates a good agreement with the conclusions reached above. This was also supported by the fact that the weakest \(C\) band occurred in the IR
spectra of acetaldehyde which could have weakly induced C=C double bond and weak for acrolein adsorbed.

The thickness of the covering around cations could be measured by X-ray study. The general consequences of interlamellar spacing illustrated in Table 2 are understandable in principle.

It seems Ca and Al cations persist in holding water molecules even by thermal treatment at 150° for three hours while cationic water of Na⁺ and Ni²⁺ is likely, hydroxylated or dehydrated, to be trapped into hexagonal cavities. Air dried Na-montmorillonite holds a water network³ around the cation while Ca²⁺—, Al³⁺— may hold a double layer of water in the air dried state.

An attempt to represent a schematic diagram of the hydroxylation and dehydration process of cationic water was made in view of results obtained by Mortland and his coworker. They investigated the stereochemistry of the hydrated cation in the interlamellar surface of layer silicate by ESR and proposed an inclined octahedral arrangement of water for the double layer and a planar arrangement for the single layer of water.

However, this did not lead to much definite knowledge about hydroxylated or dehydrated

Table 1. Carbonyl infrared absorption band frequencies of alkyl aldehydes adsorbed on cation saturated layer silicates, treated vapour pressure about 40 mmHg

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Ni²⁺</th>
<th>Al³⁺</th>
<th>Fe³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde (1749)</td>
<td>1722</td>
<td>1722</td>
<td>1724</td>
<td>1722</td>
<td>1722</td>
<td>1721</td>
<td>1722</td>
</tr>
<tr>
<td>Acrolein (1717)</td>
<td>1691</td>
<td>1669</td>
<td>1680</td>
<td>1691</td>
<td>1690</td>
<td>1689</td>
<td>1689</td>
</tr>
<tr>
<td>Crotonaldehyde (1717)</td>
<td>1689</td>
<td>1690</td>
<td>1690</td>
<td>1690</td>
<td>1689</td>
<td>1688</td>
<td>1688</td>
</tr>
</tbody>
</table>

Table 2. Interlamellar spacings of cation saturated layer silicates with or without alkylaldehydes (Å).

<table>
<thead>
<tr>
<th>Layer silicate only</th>
<th>Acetaldehyde</th>
<th>Acrolein</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°</td>
<td>150°</td>
<td>20°</td>
</tr>
<tr>
<td>Li⁺</td>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.8</td>
<td>1.4</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Ca⁴⁺</td>
<td>5.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>5.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>3.2</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*Calculated assuming a non-expanded interlayer spacing of 9.6 Å
states; those scarcely allow interlamellar spacing for a mono-layer or double layer of water.

Heating Li\(^+\), Na\(^+\) and K\(^+\) silicates up to 150\(^\circ\)C with evacuation diminished interlamellar spacing to about 1.4 \(\text{Å}\) to show that hydroxylation of cationic water is obvious due to the hydrogen interaction with surface oxygen (Fig. 6). Hertl and Hertl indicated that the freely vibrating hydroxyl groups are strong adsorption sites particularly with lone pair adsorbates, although the effect of adsorbed water on the enhanced adsorption of other molecules as a bridge is significant\(^\text{14}\).

Likewise, formation of a monolayer of hydrated water around Ca\(^{2+}\) and Al\(^{3+}\) and hydroxylation of water around Ni\(^{2+}\) in course of the dehydration process at 150\(^\circ\)C seems understandable. A monolayer thickness of interlamellar spacings for Ca\(^{2+}\) and Al\(^{3+}\) at a high sample temperature does not mean hydroxylation may not take place but it may be masked by a thicker molecule.

There is no doubt that such dehydrated states eventually provide adsorption sites for direct complex formation with alkyl aldehyde and increase the interlamellar spacing up to an inclined double layer thickness of water.

This is consistent with the IR spectra designated as the \(D\) band in the previous section. A systematic analysis of the OH vibration of the hydroxyl-containing system which moves to lower frequencies due to the H-bonding interaction between the hydroxyl group and alkyl aldehydes will be discussed in a subsequent paper.

References

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