ADSORPTION AND TRANSFORMATION OF HCN ON THE SURFACE OF COPPER AND CALCIUM MONTMORILLONITE

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Abstract—Adsorption isotherms of HCN by Cu- and Ca-montmorillonites show that water present in the interlayer space decreases HCN adsorption.

For Ca-montmorillonite, i.r. spectra permit distinguishing between HCN interacting with the cations and molecules filling the interlayer space. Both types are removed upon outgassing. The residual water is not displaced by HCN.

On Cu-montmorillonite, species (presumably CN⁻ ions) strongly held by the cations are observed in addition to adsorbed HCN molecules. The residual hydroxyls retained in the interlayer space are removed by the adsorption of HCN. These hydroxyls, either OH⁻ or H₂O, are characterized by two well defined stretching bands.

Infra-red spectra of samples heated below 200°C show that adsorbed HCN is involved in chemical reactions. For both clays, bands appear in the region characteristic of carbonyl and carboxyl groups; the production of ammonium is detected for Cu-montmorillonite. The reactions and the observed spectral features could be accounted for by the formation of formamide.

INTRODUCTION

The adsorption of hydrogen cyanide (HCN) on inorganic surfaces has not yet received the attention that it should in view of the chemical reactivity of HCN and also of its possible connection with the synthesis of molecules of biological interest.

Kozirovski and Folman (1964, 1966) have studied by infrared spectroscopy the adsorption of HCN on some alkali halides (NaCl, NaI and CsCl) and on Vycor glass. On the silica surface, physical adsorption is followed by a polymerization process. This observation is peculiarly relevant to possible mechanisms of prebiotic synthesis, since it seems that in homogeneous as well as in heterogeneous systems, HCN may have played an important role in this respect.

It has also been suggested (Fripiat et al., 1972) that HCN was an important intermediate in the reaction of CO and NH₃ on the surface of molecular sieves, leading to the synthesis of purines and amino-acids.

It was, therefore, challenging to study the adsorption of HCN on cation exchanged montmorillonites and the possible interaction of HCN with residual water molecules. Hydrogen cyanide was expected to penetrate the interlamellar space since its dipole moment is 2.84 D.U. while that of H₂O is 1.85 D.U. Hydrogen cyanide and H₂O should compete to fill up the coordination sphere of exchangeable cations. By an adequate choice of the exchangeable cations, and especially of their electronic characters, some activation of the CN group could possibly be achieved.

For this purpose, the adsorption isotherms and the i.r. spectra of HCN adsorbed by Ca- and Cu-montmorillonites have been recorded at room temperature and at higher temperatures where reaction with residual water might be anticipated.

EXPERIMENTAL PROCEDURES

Adsorption isotherms were measured, with a conventional allglass instrument, for clays that had been outgassed either at room temperature for a short time (<1 hr) or at 90°C for periods longer than 2 hr.

Infra-red spectra of adsorbed HCN were recorded between 4000 and 1200 cm⁻¹ using films obtained by sedimentation of the <2 μm fractions of Ca- or Cu-montmorillonite.

A cell with an optical path of about 5 mm, permitted heating a self-supporting film up to 200°C in the presence or absence of the gas phase (cell A); the spectra
were recorded in transmittance with a Beckman IR 10 Spectrometer.

Another cell (B), with an optical path smaller than 1 mm, has been used for obtaining more quantitative data. The clay film, of about 20 mg for an area of the order of 5 cm², was deposited on a CaF₂ window and, in addition, about 200 mg of powdered clay was introduced in the cell. The amount of HCN adsorbed was measured volumetrically; before recording each spectrum, the sample was equilibrated with the vapor phase for a few hours. A Beckman IR4 was used with cell B.

**MATERIAL**

The clay used in this work was an oxidized Wyoming Bentonite and the chemical analysis of the Na, K₂O fraction gave the following results: Na₂O: 2.6%; K₂O: 0.48%; CaO: 0.42%; MgO: 2.28%; Fe₂O₃: 3.99%; Al₂O₃: 19.19%; SiO₂: 65.59%; loss on calcination: 5.6%.

The Ca and Cu forms were obtained by repeated contacts with 1 N CaCl₂ and CuCl₂ solutions, followed by repeated washings by centrifugation.

The exchangeable Na⁺ and Ca²⁺ were 0.84 and 0.90 m-equiv/g respectively, while surprisingly 0.98 g atom Cu/g were measured. This seems to indicate the presence of Cu⁺ or CuOH⁺ instead of Cu²⁺ on the surface. A reduction could have been produced by Fe²⁺ in the lattice in agreement with recent results by Banin (1973). However, even by assuming that the whole iron content is present as Fe²⁺, the amount present in the lattice is too low to explain the amount of copper I on the surface. It should nevertheless be mentioned that an attempt to obtain a Hg²⁺ exchanged clay failed because of the reduction of Hg²⁺ into Hg⁺ and perhaps metallic Hg, as suggested by a gray deposit observed in the clay suspension.

The use of a vacuum chamber in conjunction with a X-ray diffraction goniometer permitting measuring the first basal reflection of clay films outgassed at increasing temperatures. The results reported in Table 1 correspond to treatments of about half an hour at each temperature under a vacuum of the order of 10⁻¹ Torr.

**ADSORPTION PROCESS**

**Isotherms**

Discussed first are the results obtained under conditions where chemical transformation of the adsorbed species is not likely.

Figure 1 shows the HCN adsorption isotherms obtained at 21°C after outgassing the clay at 90°C. At this temperature the first basal reflection is close to 10 Å (Table 1), indicating there is no longer a continuous layer of adsorbed water. The BET linear transform indicates for Ca-montmorillonite a monomolecular layer content nₐ = 3.4 x 10⁻³ mole g⁻¹ of air-dried clay. Since the molecular packing of HCN is at least larger than that usually accepted for N₂, i.e. 160 Å² molecule⁻¹, the surface area corresponding to this nₐ is higher than 327 m² g⁻¹. This result indicates clearly that the adsorption of HCN occurs in the interlamellar space.

The BET transform for Cu-montmorillonite is linear only for P/Po < 0.16. Regardless of its physical significance the corresponding nₐ is 1.6 x 10⁻³ mole g⁻¹. The discrepancy with Ca-montmorillonite would suggest either that only a fraction of the internal surface area is available to adsorbed HCN, perhaps because the Cu system retained more water or because HCN interacts with the copper cation in some peculiar manner.

![Fig. 1. Adsorption (O) and desorption (●) isotherms of HCN at 21°C: (a) Cu-montmorillonite outgassed for less than 1 hr at room temperature; (b) Cu-montmorillonite outgassed overnight at 90°C; (c) Ca-montmorillonite outgassed for less than 1 hr at room temperature; (d) Ca-montmorillonite outgassed overnight at room temperature.](image-url)
Adsorption and transformation of HCN

Table 2. Infra-red spectra of HCN adsorbed at 20°C as compared to that of solid HCN

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>Solid*</th>
<th>NaCl†</th>
<th>Silica‡</th>
<th>Cu-mont.</th>
<th>Ca-mont.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (cm$^{-1}$)</td>
<td>2089</td>
<td>2101</td>
<td>2095</td>
<td>2105</td>
<td>2100-2120</td>
<td>2100</td>
</tr>
<tr>
<td>$v_3$ (cm$^{-1}$)</td>
<td>3312</td>
<td>3128</td>
<td>3145</td>
<td>3040</td>
<td>3267</td>
<td>3240</td>
</tr>
</tbody>
</table>

$v_1 =$ CN stretching; $v_3 =$ CH stretching.

* Krause et al. (1972).
† Kozirowsky et al. (1966).
‡ Kozirowsky et al. (1964).
Presumably cyanide ion.

In Fig. 1 are also given isotherms obtained after evacuating the sample for a short time at room temperature (basal spacing of about 12 Å). Comparison with those obtained after outgassing at 90°C shows that for both clays the presence of residual water tends to decrease the adsorption of HCN. Thus, water prevails in the competition for covering the surface or interacting with exchangeable cations. Moreover collapsing the clay by a moderate heat treatment appears to be more favorable to the adsorption of HCN than does leaving an appreciable amount of H$_2$O molecules. It is interesting to note the presence of a well marked hysteresis loop in the isotherms of Fig. 1. Perhaps this hysteresis arises from a specific interaction between a fraction of the adsorbed HCN and the cations.

Adsorption isotherms were also obtained at 50°C for both clays outgassed at 90°C. The isosteric heat of adsorption calculated for Ca-montmorillonite is $9.1 \pm 0.6$ kcal mole$^{-1}$, while the heat of vaporization of liquid HCN is 7.34 kcal mole$^{-1}$. The low reproducibility of the isotherms obtained for the Cu-clay precluded the computation of reliable heats of adsorption.

Infra-red study of Ca-montmorillonite

The frequencies of the i.r. bands observed for HCN in various systems (gas, solid, NaCl surface, silica surface) are listed in Table 2. As expected, hydrogen bonding decreased the frequency of CH stretching band ($v_3$), which shifted from 3312 cm$^{-1}$ in the gas to 3128 cm$^{-1}$ in the solid phase. Still larger shifts are observed when the molecule is adsorbed on alkali halides (Kozirovski and Folman, 1966) or forms solid complexes with dimethyl ether (Seel and Sheppard, 1969). The CH bending band ($v_2$) which appears at 712 cm$^{-1}$ in the gas phase will not be used here because of the overlapping with bands of the silicate network. The CN stretching band ($v_1$) has a very low intensity in the gas phase because of the quasi-isoelectronic properties of the HC and N fragments of the molecule (Herzberg, 1963). The intensity is appreciably increased by the asymmetry resulting from interactions

(Kozirovski and Folman, 1966; Krause and Friedrich, 1972) but the frequency does not deviate appreciably from 2090 to 2100 cm$^{-1}$, even when the H bonding is strong enough to provoke a large shift of the CH stretching band (Caldow and Thompson, 1960; Seel and Sheppard, 1969).

The spectra given in Fig. 2 are representative for HCN adsorbed on Ca-montmorillonite at room temperature; the use of cell B permitted estimation of the amount adsorbed. Series A was obtained with a sample outgassed at room temperature. The same sample was then outgassed again and hydrated under 5-5 Torr H$_2$O vapor; the subsequent adsorption runs provided spectra of series B.

It may first be noted that outgassing at room temperature leads to the complete desorption of HCN.
Table 3. Adsorption of HCN at room temperature on dehydrated and hydrated Ca–montmorillonite: adsorption data, intensity of the i.r. bands and estimation of the respective amounts of the species responsible for the 2120 and 2100 cm\(^{-1}\) CN bands

<table>
<thead>
<tr>
<th>Pretreatment (room temperature)</th>
<th>(P_{\text{r}}) (Torr)</th>
<th>(n) (mmoles g(^{-1}))</th>
<th>Area of CH band (arb. units)</th>
<th>Absorbance of CN bands (%): 2120 cm(^{-1}), 2100 cm(^{-1})</th>
<th>Calculated amount of HCN (mmole g(^{-1})): (n_{2120}), (n_{2100})</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outgassed</td>
<td>89</td>
<td>2.27</td>
<td>4.6</td>
<td>15</td>
<td>5.5</td>
<td>1.75, 1.04, 2.79</td>
</tr>
<tr>
<td></td>
<td>242</td>
<td>4.07</td>
<td>7.7</td>
<td>20.5</td>
<td>10.5</td>
<td>2.40, 1.98, 4.38</td>
</tr>
<tr>
<td></td>
<td>367</td>
<td>5.03</td>
<td>10.0</td>
<td>21.5</td>
<td>12.5</td>
<td>2.51, 2.36, 4.87</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>5.82</td>
<td>9.5</td>
<td>23</td>
<td>14</td>
<td>2.69, 2.65, 5.34</td>
</tr>
<tr>
<td>Sample used above, outgassed again and rehydrated under 5.5 Torr H(_2)O</td>
<td>133</td>
<td>1.5</td>
<td>2.4</td>
<td>1</td>
<td>8</td>
<td>0.12, 1.51, 1.63</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>2.5</td>
<td>4.3</td>
<td>3.5</td>
<td>13</td>
<td>0.41, 2.46, 2.87</td>
</tr>
<tr>
<td></td>
<td>281</td>
<td>2.7</td>
<td>4.15</td>
<td>3.5</td>
<td>13.5</td>
<td>0.41, 2.55, 2.96</td>
</tr>
<tr>
<td></td>
<td>383</td>
<td>3.8</td>
<td>4.8</td>
<td>4.5</td>
<td>15</td>
<td>0.53, 2.83, 3.36</td>
</tr>
</tbody>
</table>

The other hand, according to the intensity of the bending and stretching bands characteristic of H\(_2\)O, the adsorbed water is not significantly removed by HCN. The CH stretching frequency at about 3216 cm\(^{-1}\) indicates that HCN is interacting through moderate H bonds, similar to those formed in organic solvents (Caldow and Thompson, 1960). The CN stretching band has two components at ca. 2100 and 2120 cm\(^{-1}\), the relative intensity of which depends strongly on the degree of hydration. The 2120 cm\(^{-1}\) is stronger when the clay has a low water content while it appears as a weak shoulder when the surface is hydrated.

In Table 3 are listed the intensities of the CH and CN bands of Fig. 2 and of additional spectra corresponding to intermediate adsorbed amounts. Plots of \(n\) or of the sum of the absorbances of the two CN bands as a function of the CH band area are essentially linear and intersect the axes at the origin. A good fit is observed between the data obtained for the outgassed and the hydrated clays. On the other hand a plot of the absorbance of either single CN band as a function of the CH band area shows a segregation of the two sets of data and a non-zero intercept. This shows clearly that both bands are due to HCN species and not to CN\(^{-}\) ions. As the CH band does not show any splitting it is concluded that the two species detected do not differ by the strength of hydrogen bonding. In view of their relative intensities in the presence or absence of water the 2120 cm\(^{-1}\) band must be assigned to HCN interacting with a Ca\(^{2+}\) ion, while the 2100 cm\(^{-1}\) band would be due to molecules filling the interlayer space. It is also concluded that HCN does not remove H\(_2\)O from the coordination sphere of Ca\(^{2+}\) ions.

Since spectroscopic data and adsorption isotherms are available for the same clay sample (Table 3), the quantity of adsorbed HCN may be tentatively related to the CN band absorbance by the following relationship:

\[ n = k_{2120} A_{2120} + k_{2100} A_{2100}. \]

The \(k\) factors are proportional to the inverse of the respective absorption coefficients; they contain also an experimental factor related to the thickness of the clay film and to the additional amount of powder present in the cell. Data of Table 3 permitted computation of the following regression equation, where the number of adsorbed molecules is in \(10^{-3}\) mole g\(^{-1}\) units and the absorbance in per cent.

\[ n = 0.117 A_{2120} + 0.189 A_{2100}. \]

The numbers of HCN molecules in the cationic coordination shell (\(k_{2120} A_{2120}\)) and filling the surface (\(k_{2100} A_{2100}\)) are shown in Table 3. Because of the limited number and the low accuracy of experimental data, these results should be considered as rough approximations. There is indeed rather poor agreement between the experimental \(n\) and the calculated values given in the last column of Table 3. Such a calculation provides an estimate of the two types of HCN present on the surface but it would not be useful to discuss further the relative value of the adsorption coefficients of the two species.

**Infra-red study of Cu–montmorillonite**

Figure 3 illustrates the main spectral features observed for Cu–montmorillonite and adsorbed HCN. In addition to the constitutional OH stretching band, the clay outgassed at room temperature shows two rather sharp bands at about 3473 and 3390 cm\(^{-1}\), which might be assigned to interlayer Cu OH\(^{+}\) or to strongly coordinated H\(_2\)O. These species must be
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strongly adsorbed as they are not removed completely by outgassing for 45 min at 100°C or overnight at room temperature. The basal spacings reported in Table 1 confirm that the Cu-clay collapses at higher temperature than the Ca-material. Such a doublet has also been observed for montmorillonites saturated by other divalent cations, but no clear assignment can be proposed so far. It might possibly be related to the existence of OH− ions coordinated to the exchangeable cations; the presence of CuOH+ would explain the high Cu content of the clay.

For very small amounts of adsorbed HCN, two CN stretching bands are observed around 2223 and 2160 cm⁻¹. When adsorption increases they are no longer distinct but a very clear absorption occurs at 2170 cm⁻¹. Proceeding further leads to the growth of another band around 2100–2120 cm⁻¹. The development of the CH band, around 3240 cm⁻¹, is clearly delayed with respect to that of the band at 2170 cm⁻¹. Outgassing the sample does not affect significantly the intensity of the latter; however, it removes the 2120 cm⁻¹ band and reduces strongly the CH band. The OH stretching bands at 3473 and 3390 cm⁻¹ disappear progressively as adsorption proceeds and they are not restored by outgassing the sample.

These observations indicate that an important fraction of HCN adsorbed by Cu-montmorillonite has been transformed into other species, strongly held on the surface and responsible for the absorption around 2170 cm⁻¹. The band at 2100–2120 cm⁻¹ would be due to molecules adsorbed in a way very similar to that observed for Ca-montmorillonite.

The frequency of 2170 cm⁻¹ is indeed much higher than those observed for HCN species in various systems (Table 2; Caldw and Thompson, 1960; Seel and Sheppard, 1969). According to data collected by Nakamoto (1963), the CN⁻ ions which may presumably be responsible for this band must interact strongly with the exchangeable cations Cu²⁺ or Cu⁺. It is interesting to note that the CN band of solid AgCN and CuCN appears between 2170 and 2180 cm⁻¹; however this does not imply necessarily that CuCN species are formed on the surface, because the CN frequency depends on several factors. Another possibility would be the formation of CuCN⁺ species by reaction of HCN with CuOH⁺ present in the original product.

**REACTIVITY OF ADSORBED HCN**

In order to study the reactivity of adsorbed HCN, i.r. spectra were recorded for samples treated at in-
Fig. 4. Infra-red spectra of Cu-montmorillonite having adsorbed about 0.9 mmole HCN g\(^{-1}\) and treated successively as follows: (A) outgassed overnight and left 3 days at room temperature; (B) equilibrated under 7.2 Torr \(\text{H}_2\text{O}\) at room temperature; (C) equilibrated under 14 Torr \(\text{H}_2\text{O}\) and heated for 15 min at 96\(^\circ\)C; (D) heated for 10 min at 162\(^\circ\)C; (E) heated for 15 min at 200\(^\circ\)C.

Increasing temperature. The thermal treatment was sometimes carried out in the presence of gaseous HCN and/or \(\text{H}_2\text{O}\) vapor in order to prevent desorption to some extent.

In Fig. 4, an example of this is shown for Cu-montmorillonite, heated in the presence of 14 Torr \(\text{H}_2\text{O}\) up to ca. 200\(^\circ\)C.

The spectrum observed for the unheated sample shows features in the 1300–1700 cm\(^{-1}\) region which were not observed in Fig. 3. The \(\text{H}_2\text{O}\) bending band appearing at 1625 cm\(^{-1}\) for the outgassed clay is replaced by two bands at 1638 and 1690 cm\(^{-1}\) while another band appears at 1430 cm\(^{-1}\). Complementary experiments show that these spectral changes do not always follow the development of the CN band at 2170 cm\(^{-1}\); their appearance seems to depend on the amount of water present and on the time of contact.

Upon heating, the band at 2170 cm\(^{-1}\) decreases in intensity; accordingly a broad band develops at 3300 cm\(^{-1}\). In the bending region the bands at 1638 and 1690 cm\(^{-1}\) vanish progressively while the band at 1430 cm\(^{-1}\) increases in intensity. The latter and the band at 3300 cm\(^{-1}\) could be accounted for by the formation of \(\text{NH}_4^+\) and would then be assigned to the

Fig. 5. Infra-red spectra of Ca-montmorillonite treated successively as follows: (A) outgassed for 15 min at room temperature; (B) equilibrated under 55 Torr HCN at room temperature \((n = \text{1-2 mmole/g})\); (C, D, E) heated for 15 min under 75 Torr HCN, at 75, 170 and 195\(^\circ\)C respectively.
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NH₄⁺ deformation and NH stretching respectively. The formation of NH₄⁺ could be explained by the hydrolysis of nitrile residues. It is interesting also to observe that at the end of this treatment the color of the clay film is dark violet.

In the case of Ca-montmorillonite it was necessary to carry out the heat treatment in presence of HCN (Pₐ = 60 Torr). Even so as shown in Fig. 5, the v₁ and v₃ bands assigned to adsorbed HCN disappear at 85°C. Simultaneously very interesting transformations are observed in the bending region (Fig. 5). The H₂O bending band at 1635 cm⁻¹ disappears completely at 170°C while new bands appear at 1717 (very strong), 1600, 1435 and 1380 cm⁻¹. The development of the 1717 cm⁻¹ band is preceded by that of a band at 1695 cm⁻¹. This experiment has been repeated several times and it may be claimed that the reaction leading to these transformations occurs in the absence of gaseous O₂. It must be also pointed out that some white-gray powder appears on the wall of cell (A) at the place where the clay film is allowed to cool before being introduced into the i.r. beam.

The nature of the transformation products is difficult to determine on the sole basis of the i.r. data. For both clays, two bands develop in the spectral region of the carbonyl or of the carboxyl groups. On the other hand, the acidity of residual water or protons liberated by the formation of cyanide would play an important role in hydrolysis processes. If formamide were one of the products formed

\[
\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H} - \text{C} = \text{O} \rightarrow \text{NH}_3 + \text{CO}
\]

it could be transformed into NH₃ and CO at increasing temperature,

\[
\text{H} - \text{C} = \text{NH}_3 + \text{CO}
\]

while NH₃ would combine with the acidic residual water to form NH₄⁺.

Some of the bands reported by Tahoun and Mortland (1965) for acetamide adsorbed by H₃montmorillonite are similar with those shown in Fig. 5. For instance, in the acetamide cation, the C=N stretching is at 1718 cm⁻¹, while the amide I band in the neutral form appears at 1680 cm⁻¹. The NH deformation is at 1664 cm⁻¹ in the cation while it shifts at 1610 cm⁻¹ in the neutral form. On the calcium clay after heating for a short time at 170°C, similar spectral features are observed indicating that a mixture of protonated and neutral amide could be present (Fig. 5).

Of course reactions much more complex than those shown above are possible, especially if, as has been suggested for silica (Koziorowski et al., 1964) HCN would polymerize on the surface. Sanchez et al. (1972) have observed that chloroacetanitride and trichloroacetanitride, but not acrylonitrite, hydrolyze in the adsorbed state on montmorillonite and that amide I, II and IV bands appear at room temperature after a few days.

CONCLUSIONS

The adsorption isotherms show that Ca-montmorillonite adsorbs more HCN than Cu-montmorillonite. Comparison of isotherms obtained after various pre-treatments indicates that a preliminary collapse of the interlamellar spacing is more favorable to the subsequent adsorption of HCN than an appreciable amount of residual water between the layers.

The adsorption by Ca-montmorillonite gives rise to two types of adsorbed species, the respective amount of which depends on the amount of surface water. The molecules interacting with the exchangeable cations have a CN stretching band at 2120 cm⁻¹, while a band at 2100 cm⁻¹ is assigned to molecules filling the interlamellar space. Both species are removed by outgassing at room temperature and do not displace the residual water.

For Cu-montmorillonite, the real state of the copper ions before any adsorption is not clear. Both the oxidation state and the structure of the coordination shell should be investigated further.

The adsorption of HCN produces species strongly held by the copper cations; they show a CN band at 2170 cm⁻¹ and are thought to be CN⁻ ions. The residual OH groups, wither OH⁻ or H₂O retained in the interlayer space are removed. A HCN species similar to that filling the Ca-montmorillonite surface is also observed (CN band at 2100 cm⁻¹).

The adsorbed hydrogen cyanide reacts upon heating and in some cases, even at room temperature. For both clays, bands appear in the region characteristic of carbonyl and carboxyl groups; on the other hand the production of ammonium is detected for Cu-montmorillonite. These observations might be accounted for by the formation of molecules like formamide which would decompose at higher temperature.

REFERENCES

Banin, A. (1973) Personal communication.


Résumé—Les isothermes d’adsorption de HCN par les montmorillonites Cu et Ca montrent que l’eau présente dans les espaces interfeuillets diminue l’adsorption de HCN.

Dans le cas de la montmorillonite Ca, les spectres infrarouges permettent de faire la distinction entre HCN interréagissant avec les cations et les molécules remplissant l’espace interfeuillet. Ces deux types de molécules sont éliminés par dégazage. L’eau résiduelle n’est pas déplacée par HCN.

Dans le cas de la montmorillonite Cu, des espèces (probablement des ions CN⁻) fortement retenues par les cations sont observées en plus des molécules HCN adsorbées. Les hydroxyles résiduels retenus dans l’espace interfeuillet sont éliminés lors de l’adsorption de HCN. Ces hydroxyles, soit OH⁻ soit H₂O, sont caractérisés par deux bandes de stretching bien définies.

Les spectres infrarouges d’échantillons chauffés en dessous de 200°C montrent que HCN adsorbé participe à des réactions chimiques. Pour les deux argiles étudiées, des bandes apparaissent dans la région caractéristique des groupes carbonyle et carboxyle; la production d’ammonium est détectée avec la montmorillonite Cu.

Ces réactions et les caractéristiques des spectres observés pourraient être interprétées par la formation de formamide.

Kurzreferat—Adsorptionsisothermen von HCN an Cu- und Ca-Montmorilloniten zeigen, daß in den Zwischenschichten befindliches Wasser die HCN-Adsorption herabsetzt.


In Cu-Montmorilloniten sind zusätzlich zu den adsorbierten HCN-Molekülen lonenartigen (vermutlich CN⁻) zu beobachten, die von den Kationen stark gebunden werden. Die restlichen Hydroxylionen, die im Zwischenschichtraum zurückgehalten werden, werden durch Adsorption von HCN entfernt. Diese Hydroxylenwasser OH⁻ oder H₂O-sind durch zwei wohldefinierte Streckschwingungsbanden gekennzeichnet.

Резюме — Изотермы адсорбции (HCN), шианистого водорода, медными (Cu) и кальциевыми (Ca)-монтморillonитами показывает, что количество воды в пространстве между слоями уменьшает адсорбцию HCN.

В случае Ca-монтомориллонита инфракрасным спектром можно различить взаимодействие HCN с катионами и молекулами, наполняющими междууслоеевое пространство. Оба типа уничтожаются льготацией. Остаточная вода не смешается HCN.

В случае Cu-монтомориллонита наблюдаются, кроме адсорбированных молекул HCN, частицы (поядимому CN- ионы), крепко удерживаемые катионами. Держанные в пространстве между слоями остаточные гидроксиды уничтожаются адсорбцией HCN. Эти гидроксидные группы, OH- или H2O, характеризуются двумя определенными расширяющимися полосами.

Инфракрасные спектры образцов, нагретых ниже 200С, показывают, что адсорбированный HCN участвует в химических реакциях. Для обоих видов глин, полосы появляются в районе характеризующимся карбонильными или карбоксильными группами; в случае Сu-монтомориллонита наблюдается образование аммония. Эти реакции и наблюдаемые спектральные черты могут объясняться образованием формамидов.