CLAY-ORGANIC MOLECULE INTERACTIONS: OXIDATION OF ACETALDEHYDE BY MONTMORILLONITE IN N₂ ATMOSPHERE AT ROOM TEMPERATURE

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Abstract—Oxidation of acetaldehyde molecules adsorbed on Na- and Mg-Wyoming montmorillonite at room temperature (20-25°C) and in N₂ atmosphere has been studied by I.R. spectroscopy. A comparison between clay–acetic acid complex and that prepared from acetaldehyde is given. The influence of the nature of the saturating cation as well as the clay pretreatment on this oxidation process are discussed and reaction pathways are proposed. Acetic acid directly adsorbed on the clay surface is almost removed at 110°C while that produced from the oxidation of the adsorbed acetaldehyde appears to be strongly held. Within a temperature range 180-230°C, the fixed acetic acid molecules dissociate to acetate form; then occurs an interaction of the acetate and the residual acid with the lattice OH of the clay at 200-300°C. This interaction involves the loss of the structural OH and deposition of carbon on the clay surfaces. The thermal decomposition of the residual complex is almost completed at 500-600°C.

Key Words—Acetaldehyde, Acetate, Adsorption, Montmorillonite, Oxidation.

INTRODUCTION

It is generally believed that crystalline aluminosilicates have very little intrinsic catalytic activity for oxidation reactions, and oxidation processes over zeolites invariably feature material containing transition metal ions (Leach, 1971). Oxidation processes over clay mineral surfaces have not been fully explored. Electron transfer reaction based on coloration of organic compounds on clay minerals were attributed to Al³⁺ at crystal edges, transition-metal ions and structural Fe³⁺ (Theng, 1971; Furukawa and Brindley, 1973). Recently, Eltantawy and Baverez (1975) showed that oxidation of acetaldehyde on Na- and Mg-montmorillonite (N₂ atmosphere) cannot be related to transition-metal cations which are absent, nor to structural Fe³⁺ (the region of OH librations in I.R. spectrum of the montmorillonites was not affected by adsorption and oxidation of acetaldehyde). The details of acetaldehyde oxidation with particular reference to the reaction pathways as well as to the thermal changes of the developed clay–organic complex are discussed in this report.

EXPERIMENTAL PROCEDURES

Na- and Mg-systems of Wyoming montmorillonite were prepared and their properties (CEC, surface area, DTMA. X-ray, etc.) were extensively studied by Eltantawy (1972). High-grade acetaldehyde (Fluka) was used and its purity was confirmed by I. R. and NMR methods. Infrared spectra index for a number of organic compounds was prepared to help in fingerprinting organic groups and in following any change which may occur upon adsorption or interaction of the organic substance on the clay surface.

A self-supporting film was prepared (5-20 mg, 15 mm in diameter) from the homoionic clay and placed in a sample-holder. The holder was inserted in the center of an I.R. cell, which was designed by G. Cornier and M. Baverez in 1970. This cell was made of stainless steel, fitted with water-cooled windows and a heating coil. Temperature was controlled by a thermocouple placed very close to the sample-holder and connected to a galvanometric regulator. The cell could be operated in a constant gas flow passing through the specimen (from inlet to outlet joints) or connected to a vacuum line.

Spectra were recorded on a Beckman I.R. 7 double beam spectrophotometer over the range 4000-600 cm⁻¹. As a routine procedure, the clay film was degassed by dry-N₂ (a constant flow of 100 cc/min) for 24 hr in the I.R. cell at room temperature and the spectrum was recorded. Following this, the cell was attached to an acetaldehyde container for 24 hr saturation (from its vapor pressure at 20–25°C), then sealed off and allowed to stand undisturbed for 112 hr. After this prolonged contact between the clay film and acetaldehyde vapor, the cell was degassed again by dry-N₂ at room and elevated temperatures (maintained 24–48 hr at each temperature) and the spectra were examined. Acetic acid–N₂ flow was used for preparing clay–acetic acid complex and D₂O–N₂ flow was sufficient for a mild D₂O
RESULTS AND DISCUSSION

The infrared spectra of Na-Wyoming montmorillonite before and after 112 hr contact with acetaldehyde vapor at room temperature (20–25°C), followed by N₂ degassing at 20 and 50°C are shown in Figure 1. The bands near 3200, 1600 and 1300 cm⁻¹ which appear on the spectra of the developed clay–organic complex, were absent from the spectra of acetaldehyde reported in the literature or filed in our organic index. Also, the aldehyde CH stretching vibrations (not shown) at 2720 and 2760 cm⁻¹ were absent in the spectra of the complex prepared from acetaldehyde. Acetate salts show broad absorption near 1600 cm⁻¹, which is assigned to asymmetrical vibration of the COO⁻ group of acetate ion.

The band near 1300 cm⁻¹ (assigned to the coupled C=O stretching and OH deformation vibrations of the carboxyl groups) becomes stronger and shifts (10 cm⁻¹) to the high frequency side by D₂O treatment and appears stronger on the spectrum of the complex prepared from acetaldehyde (Figures 3, 4). This may indicate the similarity of both bands which can be ascribed to OH stretching vibration of the bonded carboxyl groups (our organic index, Bellamy, 1962; Little, 1966; Farmer, 1974 were used for band assignments throughout the text). The band near 1600 cm⁻¹ is not affected by D₂O treatment and appears stronger on the spectrum of the complex prepared from acetaldehyde. The spectra of 10% acetic acid in D₂O (capillary film) improves the spectra in this region and the as-
Oxidation of acetaldehyde by montmorillonite

Fig. 3. I.R. spectra of Na-montmorillonite: (a) in dry N₂ at 20-25°C, (b) in contact with acetaldehyde vapor 112 hr, then degassed by N₂ at 20-25°C, (c) in D₂O-N₂ flow 24 hr at 20-25°C, then degassed by N₂ following treatment (b).

Fig. 4. I.R. spectra of Na-montmorillonite: (a) in N₂-acetic acid flow 112 hr, then degassed by N₂ at 20-25°C, (b) D₂O-N₂ flow 5 min at 20-25°C, then N₂ at the same temperature, (c) as treatment (b) for 24 hr.

Fig. 5. I.R. spectra of Mg-montmorillonite: (a), (b), (c) as in Figure 1.

Figures 1-4 indicate an interaction between the clay surface and some of the carboxyl groups. This interaction seems to be stronger than that occurring between the molecules of the dimer. The CH deformation frequencies of CH₃ groups near 2950 and 2860 becomes possible. The C=O stretching vibrations at 1770 and 1720 cm⁻¹ corresponding to the monomer and the dimer were observed for 2.5% acetic acid in CCl₄. The broad C=O stretching band which moved towards lower frequency (Figures 1-4) indicates an interaction between the clay surface and some of the carboxyl groups. This interaction seems to be stronger than that occurring between the molecules of the dimer. The CH deformation frequencies of CH₃ groups near 1450 and 1380 cm⁻¹ and the symmetrical vibration of the carboxyl groups (near 1420 cm⁻¹) together show broad band on this region due to overlapping. When some of the adsorbed acid is removed either by replacement with D₂O or by N₂ degassing at 110°C, the band near 1380 cm⁻¹ is separated (weak bands mainly of academic interest are not discussed).

Adsorption of acetaldehyde and acetic acid appears to have similar effects on the clay surface. The lattice OH stretching (3640 cm⁻¹) of the clay appears to be perturbed. Thus, a band near 3520 cm⁻¹, not shifted by the mild D₂O treatment may arise from the perturbed lattice OH. Although the main lattice OH band appeared less intense, confirming this interaction, there was no change to be seen in the region of OH librations. Similar perturbation of lattice OH by H⁺ was reported by Russell and Fraser (1971). The absence of OH stretching near 3400 cm⁻¹ and H–OH deformation near 1640 cm⁻¹ indicates that adsorbed H₂O on the clay surface almost disappears during the adsorption of both organic compounds.

It is obvious from the I.R. work that strongly held organic products developed from acetaldehyde adsorption on a montmorillonite surface are mainly acetic acid (molecular and ionic form). It should be pointed out that acetaldehyde vapor is stable in the I.R. cell (N₂-purged) in the absence of the clay and this has been already discussed in detail in the preliminary report (Eltantawy and Baverez, 1975). Examining the I.R. spectra after acetaldehyde contact with the clay and before N₂ degassing for weakly adsorbed products, showed that the starting substance (acetaldehyde) and the produced acetic acid are the only organic compounds that can be detected, and CO₂ formation did not occur in this reaction.
Table 1. The effect of the clay pretreatment (vac., O₂, H₂ and H₂ followed by O₂ at 200°C) in the total acidity yields of 50% aqueous acetaldehyde.

<table>
<thead>
<tr>
<th>Acidity meq/g clay (110°C bases)</th>
</tr>
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<tbody>
<tr>
<td>Vacuum</td>
</tr>
<tr>
<td>2.4</td>
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**FACTORS AFFECTING THE OXIDATION PROCESS**

The type of the exchangeable cation may have no effect on the oxidation of acetaldehyde on the clay surface. The complex obtained from Mg-system (Figure 5) is similar to that of Na-system. When the clay film was O₂ degassed at room temperature before and after acetaldehyde contact, the I.R. spectra obtained were similar to that obtained using N₂. It was concluded that the clay surface has its limit for acetic acid retention and any increase in the amount of acid produced in O₂ treatment may be removed by degassing. The stability of the spectra observed for the complex in N₂ flow changed to O₂ flow confirms the absence of strongly adsorbed acetaldehyde molecules (nonoxidized). Such molecules would have been susceptible even to direct oxidation by oxygen (cause spectral change) if the clay surface had fixed them in nonoxidized form.

Clay samples heated in N₂ or O₂ flow at 500°C (6 hr) appeared completely dehydroxylated and both showed similar effect in acetaldehyde oxidation. This effect will be considered elsewhere. Although the total acidity determination may not serve as an absolute value for the amount of acetic acid produced (Eltantawy and Baverez, 1975), it can be used for comparison of acidity yields in various pretreatments. Acidity values of Na-montmorillonite treated by O₂, H₂ or H₂ followed by O₂ at 200°C (to keep the expansion property of the clay) and that heated in vacuum at the same temperature before contact with 50% aqueous acetaldehyde solution, for 10 days, are given in Table 1. The acidity yield was greatly reduced by H₂ pretreatment of the clay. This effect seems to be irreversible (see H₂/O₂ pretreatment). Values obtained for untreated clay (air dried) and those pretreated in O₂ and vacuum (200°C) were very close.

**PROPOSED REACTION PATHWAYS**

Preliminary results for oxidation of aqueous acetaldehyde on the clay surface at room temperature and in the presence of oxygen showed that acidity developed was about 10 times that developed in its absence. Oxidation by dissolved O₂ may proceed as follows:

(I) \( H₂O + \frac{1}{2} O₂ \rightarrow 2(OH) + CH₃ - CHO \rightarrow CH₃ - COOH + H₂O \)

(II) \( H₂O + CH₃ - CHO \rightarrow CH₃ - CH(OH)₂ + \frac{1}{2} O₂ \rightarrow CH₃ - COOH + H₂O \)

Reactions I and II involve the addition of OH or H₂O followed by the loss of H atoms to form water by reaction with OH or oxygen. Such reactions may not only take place in aqueous solution but also in N₂-degassed clay saturated with acetaldehyde vapor as long as strongly adsorbed water and oxygen are present. H₂ pretreatment of the clay is expected to suppress this reaction.

**THERMAL CHANGES**

The thermal changes of clay–acetic acid complex and clay–acetic acid prepared from acetaldehyde were followed by I.R. within a temperature range of 110–600°C, in N₂ flow and the spectra are shown in Figures 6 and 7. Acetic acid molecules appear to be mostly vaporized at 110°C (indicated by the diminishing of all frequencies except that near 1600 cm⁻¹, compare Figure 2c and 6a) in the case of the complex prepared directly from acetic acid, in contrast to that prepared from acetaldehyde which retains a considerable amount of acid at the same temperature.

Within a temperature range of 180–230°C the C=O stretching vibration which indicates nonionized carboxyl groups becomes very weak, while the band near 1600 cm⁻¹ (indicating ionized carboxyl groups) becomes sharper. This change is known to be due to ionization of the carboxyl groups and hence acetic acid molecules are ionized to acetate form on the clay surface at this stage and the reaction may proceed as follows:

\[ M^+ + CH₃ - COOH \rightleftharpoons H^+ + CH₃ - COOM \]

(The apparent gain of the 1600 cm⁻¹ peak relative to the 1700 cm⁻¹ peak could also be due to preferential loss.
of acetic acid relative to acetate at higher temperature, as pointed out by a referee.)

In this case the clay is converted to H-system and the ionization process is limited to the number of the exchangeable cation (1 meq/g). This reaction seems to be very weak at room temperature as indicated by the weak band near 1600 cm\(^{-1}\) for the complex prepared directly from acetic acid at room temperature. Perturbation of the lattice OH (Na- and Mg-system) by the presence of acid even before thermal treatment (discussed earlier) may be due to H\(^+\) on the exchange sites (Figure 7b presents this stage and the start of the following reaction).

The lattice OH stretching vibration (3640) as well as OH librations (not shown) gradually disappeared (between 200 and 300°C) in the spectrum of the complex prepared from acetaldehyde (Na- and Mg-system). Such disappearance did not occur on the spectra of the complex prepared directly from acetic acid or untreated clay, which show normal dehydroxylation at 500°C. The loss of lattice OH was accompanied by the removal of residual acetic acid molecules and some of the acetate form and by deposition of carbon on the clay surface. Heating in O\(_2\) instead of N\(_2\) showed similar effect, which may be attributed to direct interaction between the lattice OH and the organic species in what appeared to be a strong dehydrogenation process. Although the nature of this dehydrogenation reaction has not yet been understood, it seems to be highly dependent on the type and the amount of the organic compounds fixed on the clay surface. Chi Chou and McAtee (1969) proposed an oxidation reaction involving carbon and the evolved structural water of the clay in normal dehydroxylation process (500–700°C), whilst interaction between the constitution hydroxyls of montmorillonite and ND\(_2\) above 200°C was reported by Mortland et al. (1963). However, strong interaction between the adsorbate and lattice OH, leading to complete dehydroxylation of the clay surface is not known. Indeed, in some cases this chemical dehydroxylation was almost completed at 200°C. The final thermal change within the range of 400–600°C appeared to be a decomposition of the residual complex. Analysis of the evolved products is needed in order to understand the role of the clay surface as well as the organic residues in such high temperature reactions.

These observations may improve the understanding of clay–organic molecule interactions and may have great implications in the field of catalysis. It may also indicate the importance of the clay surface in turnover of organic compounds in soil.

**REFERENCES**


