ABSTRACT: The adsorption of acrylonitrile (AN) monomer vapour in the interlamellar space of smectites exchanged with different cations (Na or Y or hexylammonium) was monitored and used to yield macromolecular layers. Polymerization in the presence or absence of a free-radical initiator was obtained by heating at 100°C for 72 h. Cyclization can already be obtained at this stage, and is completed by heating the polyacrylonitrile (PAN)-complexes at 220°C for 48 h.

Clay-organic systems have attracted the attention of researchers from various fields because of their technological importance in agriculture and industry (Theng, 1974). More particularly, the adsorption of acrylonitrile (AN) monomer and its polymerization in the interlamellar space have been intensively studied since 1961 by Blumstein (1961, 1965), Blumstein et al. (1974).

Recently, Sugahara et al. (1984) reported on the synthesis of oxynitride ceramics by carbothermal reduction of AN-montmorillonite precursors prepared by impregnation of the clay by liquid AN. In an attempt to have better control of the precursor composition and structure, we have tried to intercalate AN (as carbon source) in clays and obtained polymerization-cyclization of the adsorbed molecules in the interlamellar space of the smectite, hoping that the better contact between the two materials (carbon and silicoalumininate) would favour the formation of the ceramic material. The present work reports the results obtained with AN and montmorillonite or hectorite, after exchange with a number of cations (Na, Y, hexylammonium (C6)). The adsorption was followed by a combination of techniques: adsorption isotherms, infrared (IR) spectroscopy, and X-ray diffraction (XRD). The successive polymerization and cyclization steps were followed by IR spectroscopy.

MATERIALS AND METHODS

Wyoming montmorillonite (Mt) was first purified and Na-exchanged by classical treatment with NaCl solution, followed by dialysis to eliminate the remaining chloride anion, then freeze-dried. Yttrium- (or C6+) samples were prepared from Na-exchanged montmorillonite by treatment with Y(NO3)3 or hexyl-ammonium chloride solutions, respectively, prior to dialysis and freeze-drying. Chemical analysis showed that 90% of the Na+ ions were successfully replaced by the equivalent amount of Y3+ ions.

Hectorite (Ht, from Hector, California) was first purified by removal of carbonates (HCl treatment of the clay suspended in water), followed by ion exchange in the solution brought to pH 7 by addition of NaOH. The subsequent treatments were the same as those for the three cationic montmorillonites.

Powder samples were used for adsorption isotherms, and thin self-supporting films of the
modified montmorillonite and hectorite, prepared by millipore (0-1 μm) filtration under vacuum, for IR spectroscopy or XRD.

During the adsorption, the AN monomer vapour was held at room temperature and the cell containing liquid of AN was covered by Al paper to avoid polymerization of the monomer by light.

In the experiments aiming at polymerizing the intercalated AN with an initiator, the clay was first impregnated with a solution of 2,2'-bisazoisobutyronitrile (NC(CH3)2-CN=NC(CH3)2-CN) in hexane. The solvent was evaporated, yielding a loading of 1 wt%.

Adsorption isotherms were obtained by a gravimetric method: samples of the three cation-exchanged montmorillonites or hectorites were degassed at 100°C for 15 h under 10^{-2} Pa, then equilibrated with AN vapour for 2 h. At each equilibrium pressure, the weight (±0.1 mg) of adsorbed AN was obtained by weighing.

The basal spacing was determined by XRD using Siemens equipment and oriented films in a camera equipped with beryllium windows.

IR spectra of the oriented films were recorded in the 4000–400 cm^{-1} range in an evacuatable stainless steel cell with NaCl windows (Perkin-Elmer, type 180 IR spectrometer).

RESULTS AND DISCUSSION

Adsorption isotherms

Fig. 1 shows adsorption isotherms of AN on Na-, Y- and C6-clays. From the projected area of the molecule of monomeric AN (0.27 nm²) and the specific area of the smectite (780 m²/g), it was found that 0.25 g of AN will form a bilayer sandwiched between clay sheets. For montmorillonite, the value 0.25 g AN/g clay was only obtained with Y-Mt (Fig. 1b) at AN relative vapour pressure of 0.98. For hectorite, this value is obtained with Y-Ht and Na-Ht (Fig. 1c,d) at a relative vapour pressure of AN >0.90. As the isotherms show an inflection point at half this value, it may be concluded that a monolayer is formed first, followed by the intercalation of a second AN layer.

The other samples, Na-Mt, C6-Mt, and C6-Ht (Figs. 1a,c,f) do not reach this value, the maximum amount adsorbed being 0.17 g AN/g clay for Na-Mt. These results agree with those of Blumstein et al. (1974) for Na-montmorillonite. It can therefore be assumed that the filling of the interlamellar space is intermediate between single and double layer coverage.

Y-Ht (Fig. 1e) behaves as Y-Mt (Fig. 1b) and adsorbs 0.25 g AN/g clay at an AN relative vapour pressure of 0.92. The behaviour of Na-Ht (Fig. 1d) is similar to that of Y-Ht (Fig. 1e) but not to that of Na-Mt (Fig. 1a), while C6-Ht (Fig. 1f) adsorbs smaller quantities than the other two samples. We note that the AN absorption on hectorite is not associated with highly polarized exchangeable cations, as suggested by Yamanaka et al. (1974) for montmorillonite. It is suggested that the role of the host clay is also important in AN adsorption.

The isotherms of adsorbed AN expressed in number of molecules/cation (Figs. 2 and 3) can be obtained from the measured isotherms of AN (in g of AN/g of clay) and the known CEC of the smectites (92 mEq/100 g for Mt, and 76 mEq/100 g for Ht). They show that
about three molecules are adsorbed per Na⁺ or C₆⁺ cation; this is compatible with a steric configuration in which some of the acrylonitrile monomers surround the cations, in direct interaction with them. However, the number of Y³⁺ ions in Y-clays corresponds to 1/3 of the number of Na⁺ ions in Na-clays, though there are still 15–18 molecules of AN per Y³⁺ cation. It must be remembered that these data relate to statistical distributions of molecules and cations, implying that there are only 3 to 4 molecules in direct contact with the cation. The remaining molecules must, therefore, be located either in the interlamellar space but not in direct interaction with the cations, or out of the interlamellar space. This has been demonstrated previously for adsorbed molecules of alcohols (Annabi-Bergaya et al., 1981).
X-ray diffraction

The 001 basal reflections measured under a 95% relative vapour pressure equilibrium after 48 h are presented in Table 1. For Y-clays, the basal spacings confirm that there is a bilayer of intercalated AN molecules: assuming that the interlamellar distance $d_{001}$ between the two sheets when the clay is collapsed is 0.96 nm, there is an increase of 0.90 nm for Y-Ht and 0.73 nm for Y-Mt, sufficient to accept two superposed AN molecules between the sheets. These values are close to those reported by Yamanaka et al. (1975) for Ca-, Mg-, Ni- and Co-montmorillonites (in fact, the $d_{001}$ spacing of degassed Y-Mt and Y-Ht is more than 0.96 nm, probably due to the presence of residual water molecules).

The increase in basal spacing of the hexylammonium clays lies between 0.38 nm and 0.43 nm which probably implies monolayer intercalation. We note that the volume of the hexylammonium cation itself is important, and that it does not permit the collapse of the

<table>
<thead>
<tr>
<th>Clays</th>
<th>$d_{001}$ at room temperature (nm)</th>
<th>$d_{001}$ under vacuum (nm)</th>
<th>$d_{001}$ after adsorption of AN (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>1.27</td>
<td>0.96</td>
<td>1.35</td>
</tr>
<tr>
<td>Y-Mt</td>
<td>1.49</td>
<td>1.08</td>
<td>1.68</td>
</tr>
<tr>
<td>C_{6}-Mt</td>
<td>1.33</td>
<td>1.29</td>
<td>1.34</td>
</tr>
<tr>
<td>Na-Ht</td>
<td>1.26</td>
<td>0.96</td>
<td>1.46</td>
</tr>
<tr>
<td>Y-Ht</td>
<td>1.54</td>
<td>1.18</td>
<td>1.86</td>
</tr>
<tr>
<td>C_{6}-Ht</td>
<td>1.38</td>
<td>1.35</td>
<td>1.39</td>
</tr>
</tbody>
</table>
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TABLE 2. Infrared C≡N stretching frequency of adsorbed AN, and the polarizing power of the interlayer cation.

<table>
<thead>
<tr>
<th>Interlayer cation</th>
<th>C≡N frequency (cm⁻¹)</th>
<th>Ionic radius (R) Å</th>
<th>Polarizing cation (charge/ionic radius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>2235</td>
<td>0.95*</td>
<td>1.05</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>2256</td>
<td>0.92*</td>
<td>3.26</td>
</tr>
<tr>
<td>C₆⁺</td>
<td>2228</td>
<td>8.20**</td>
<td>0.12</td>
</tr>
</tbody>
</table>

** Calculated by ionic radius from Handbook of Chemistry and Physics assuming that the cation is ellipsoidal.

interlamellar space after degassing. This explains the small variation in basal spacing after intercalation of the monomer.

The basal spacing of the Na-clays is intermediate between those of the C₆- and Y-clays. In Na-Mt, the basal spacing is compatible with a single intercalated layer confirming the results of the adsorption isotherm. For Na-Ht, the basal spacing is larger than that expected for an intercalated monolayer, but smaller than that for two intercalated layers, even although two layers are indicated by the adsorption isotherms. The presence of an interstratified structure with single and double layers, respectively, is therefore likely.

Infrared spectra

Adsorption. The absorption of the C≡N vibration generally appears in the 2230–2290 cm⁻¹ region. In liquid AN, the strong band at 2230 cm⁻¹ is assigned to ν₄ (C≡N stretching), and the shoulder at 2280 cm⁻¹ is attributed to the bending vibration of CH₂ (ν₆) associated with the stretching vibration of C=C (ν₁₁) (Halverson et al., 1948). As the clays do not absorb in this region, it is easy to follow the adsorption of the AN molecules by IR spectroscopy.

It is well known (Nakamoto, 1978) that two modes of coordination are possible between the AN and a transition metal ion: (i) through the N atom of the CN group, in which case the absorption bands of C≡N undergo a shift to higher frequencies; or (ii) through the π electron of the C=C double bond, in which case the C=C band disappears and the C≡N bands shift to lower frequencies. The first type of coordination for the AN molecules is found (Table 2) in the different samples of cation-exchanged montmorillonite or hectorite, as clearly shown by the presence of the C≡C band at 1605–1610 cm⁻¹ (Figs. 4 and 6) even after adsorption of AN, and by the shift of the C≡N vibration to higher frequencies. The exact frequency of the C≡N vibration of the adsorbed AN depends on the nature of the cation present. This shift increases with the polarizing power of the exchangeable cations (Table 2), in agreement with the results of Serratosa (1968) with benzonitrile, and with those of Yamanaka et al. (1974) with AN adsorbed by M⁺⁺-montmorillonite. Moreover, the absorption band at 1630 cm⁻¹ of the residual water of the clay does not change after AN adsorption, from which it can be concluded that water does not act as a ligand for the cation and the AN molecules; there is direct coordination of the CN groups polarized by the electrostatic field of the cations.
Polymerization and cyclization. Polymerization of the adsorbed AN is not spontaneous in the absence of light, but occurs after heating the adsorbed AN complexes at 100°C for 72 h, or when initiated by 2,2′-bisazoisobutyronitrile. The IR spectra of the AN-clay complexes during heating are shown in Fig. 4 with initiator, and in Fig. 6 without initiator.

When the temperature increases, the intensity of the absorption at 2256–2230 cm⁻¹ decreases, and that of the band at 1660 cm⁻¹ increases. This is compatible with the scheme of polymerization and cyclization of the monomeric AN (Fig. 5) in which the C-N group (absorbing at 2256 cm⁻¹) disappears, and a C=N bond, expected to absorb at 1690–1660 cm⁻¹ (Bellamy, 1966) is formed and seen at 1660 cm⁻¹.

When the temperature reaches 220°C, the band at 1660 cm⁻¹ increases and that at 2256 cm⁻¹ disappears. It is difficult to attribute this band to a conjugated cyclic C=N (expected in the 1660–1480 cm⁻¹ region), as a higher temperature would probably be needed to obtain complete dehydrogenation of the cyclic polymer (Gibson, 1984). Heating the adsorbed polymer at 400–600°C leads to a black solid which is opaque to infrared, this colour probably being due to extensive conjugation of the polymeric structure.

The same results, without an initiator of polymerization, were obtained for the two clays in the same conditions. Fig. 6 clearly shows the appearance of the band at 1660 cm⁻¹ in the third spectrum, the appearance of several bands in the 1660–1480 cm⁻¹ region in the second (as expected for the conjugated cyclic C=N) and the complete disappearance of the C=N...
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![Chemical structure]

Fig. 5. The evolution of polyacrylonitrile (PAN) with temperature.

band. We can conclude that complete cyclization occurred without an initiator, contrary to the statements of Blumstein (1961, 1974) that gamma irradiation or a radical initiation would be necessary to obtain polymerization and cyclization of AN.

Impregnation of clays by liquid AN

The intercalation of smectites by impregnation with liquid AN (with or without initiator) does not occur. This result agrees with that of Blumstein (1961), indicating the non-reproducibility of liquid AN intercalation for montmorillonite. Attempts at intercalating liquid AN in kaolinite (from Charentes) were not successful even after expansion with hydrazine. Simultaneously with the end of our work, Sugahara et al. (1989) obtained the intercalation of AN in kaolinite after expansion by ammonium acetate instead of hydrazine.

CONCLUSIONS

The effect of the host clays in the intercalation of AN vapour is important: Na-montmorillonite and Na-hectorite do not have the same behaviour; for montmorillonite, the effect of the polarizing power of the cations seems to determine the amount of AN adsorbed, as reported by other authors, but not for hectorite. In both cases, however, cyclization-polymerization of AN occurs in the interlamellar space, even without an initiator, and under extremely mild thermal treatment.
FIG. 6. IR absorption spectra of a Y Hectorite film: (a) under vacuum; (b) after AN intercalation; (c) heated at 100°C for 72 h; (d) heated at 220°C for 48 h.

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REFERENCES


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