POLYMERIZATION OF BENZENE AND ANILINE ON Cu(II)-EXCHANGED HECTORITE CLAY FILMS: A SCANNING FORCE MICROSCOPE STUDY

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Abstract—The technique of scanning force microscopy (SFM) was used to study the nanometer-scale structure of Cu(II)-exchanged hectorite thin films. Supporting data were also obtained from Electron Spin Resonance (ESR) and X-ray diffraction (XRD) techniques. The surfaces studied included pure Cu(II)-exchanged hectorite, Cu(II)-exchanged hectorite exposed to benzene and Cu(II)-exchanged hectorite exposed to aniline. SFM images of the unexposed Cu(II)-exchanged hectorite surface revealed a smooth surface composed of interlocking platelets. The lateral dimension of these platelets ranged from a few nm to about 1 μm. After exposure to refluxing benzene, the SFM showed that the platelets underwent vertical shifts in position. This is believed to have occurred from intercalated benzene that polymerized in the interlayer region. No SFM evidence was obtained for benzene polymerization on the surface of the hectorite. Hectorite films exposed to aniline at room temperature revealed a post-polymerization structure on the hectorite surface consisting of small polymer bundles. The diameter of these bundles was measured to be 300–3000 Å, similar to the structure seen on electropolymerized polyaniline films. Aniline polymerized on the surface of hectorite films at 180 °C revealed a structure similar to undoped n-methyl-pyrrolidinone (NMP) cast polyaniline films. In this case, the polymer bundles are only 300 Å in dimension on average. XRD and ESR data also indicated interlayer aniline polymerization in Cu(II) exchanged hectorite. Mechanistic considerations affecting these polymerization reactions are presented.

Key Words—Aniline, Benzene, Hectorite, Scanning Force Microscopy.

INTRODUCTION

Smectite clays such as hectorite or montmorillonite are 2:1 layer silicates containing interlayer galleries that result in many interesting and novel chemical properties. Aromatic organic compounds such as benzene readily polymerize in the interlayer region of smectite clays that contain exchangeable transition metal ions such as Cu^{2+} and Fe^{3+} (Mortland and Pinnavaia 1971; Rupert 1973; Pinnavaia et al. 1974; Eastman et al. 1984). These reactions are important in terms of 1) the formation of nanostructured materials; 2) the fate of aromatic compounds in the environment; and 3) unusual organic reaction mechanisms. In the case of benzene, interlayer polymerization apparently proceeds by a cationic mechanism; the reaction may be initiated by electron transfer from a benzene molecule to a transition metal. Eastman et al. (1984) used electron paramagnetic resonance (EPR) to investigate the reaction of benzene with Cu^{2+} and Fe^{3+} ions exchanged into the interlayer region of hectorite. It was demonstrated that the water content of the clay and the reaction time affected the nature of the products formed in the reaction. Other important features affecting the reaction outcome were 1) the orienting effect of the clay layers on the unreacted benzene molecules; and 2) the large electric fields in the interlayer region of the clay. Evidence to date suggests that liquid benzene has fluidity and order in the interlayer region. In these respects, the interlayer benzene behaves in a manner similar to a liquid crystalline material.

Polymerization of conductive polymer species follows in a similar manner. Mehrotra and Giannelis (1992) described the polymerization of both aniline and pyrrole in Cu^{2+} ion exchanged fluorohectorite galleries. It was proposed that the gallery cations act as a catalyst, providing reactive oligomers which subsequently polymerize. In addition, the metal cations may act to oxidize this resulting polymer. Polyaniline wires have also been prepared in the channels of mesoporous aluminosilicate hosts (Wu and Bein 1994a), as well as in "track-etch" and porous alumina membranes (Martin 1995). Finally, Wu and Bein (1994b) formed graphite-like carbon wires in the 3-nm wide hexagonal channels of MCM-41. One of the primary goals of these various projects has been to study the effect of nm-scale environments and constraints on the synthesis of various materials. In this study, we used the technique of scanning force microscopy (SFM) to investigate the polymerization of benzene and aniline on thin films of Cu^{2+} exchanged hectorite. SFM instruments can provide local, nm-resolved images on the surface of both conducting and nonconducting materials. Newer generation SFM instruments may also operate in noncontact modes as well as in the traditional contact imaging mode. The noncontact mode allows for nondestructive surface imaging of softer samples.
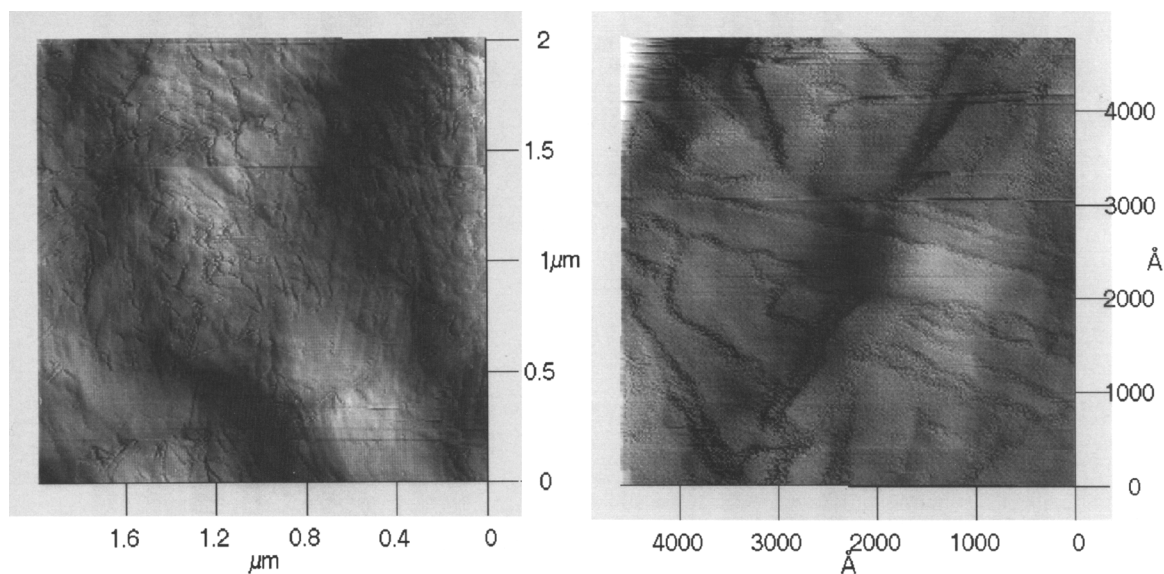
Figure 1. a) 2.0 × 2.0 μm SFM image of unexposed hectorite surface. The Z-range in this image is 300 Å. b) 4500 × 4500 Å SFM scan on unexposed hectorite surface. The film surface is nearly flat, composed of interlocking platelets. The largest of these platelets has dimensions on the order of 1 μm.

EXPERIMENTAL

Spray-dried hectorite was obtained from NL Industries. The cation-exchange capacity of this clay is 100 meq/100 g. The exchanged clay was washed with deionized water and stirred in a solution of 1.0 M $CuCl_2$ for 24 h. These samples were then washed with distilled water and centrifuged until a negative Ag^+ test for Cl^- was obtained. The treated hectorite was resuspended in deionized water and air-dried to form thin films.

ACS spectrophotometric grade benzene was obtained from Aldrich Chemical and used as received. An approximately 1 cm^2 sample of the air-dried hectorite film was placed in 50 mL of benzene; the system was heated until the benzene started to reflux. After approximately 1 h of refluxing, the color of the film had changed from blue to dark brown. The film was then air-dried and mounted on the SFM instrument. The aniline polymerization reaction was carried out both at room temperature and at higher temperatures using Baker Analyzed Reagent grade aniline. In the high-temperature reaction, a sample of the hectorite film was suspended in a condenser attached to a round-bottomed flask containing refluxing aniline. This technique was employed to minimize the possibility that any polyaniline or aniline oligomers dissolved in the liquid in the round-bottomed flask would be adsorbed onto the hectorite. In the low-temperature reaction, a beaker containing the liquid aniline was placed in a vacuum desiccator with a sample of the film. The desiccator was evacuated and the aniline allowed to diffuse onto the film. Typically, the film was

exposed to the aniline vapor for a period of days. In both cases, the films were a dark blue-violet color.

All SFM scans were performed using an AutoProbe CP in noncontact mode from Park Scientific. Scans were taken in true noncontact mode, thus preventing any surface modification during scanning. A pyrex and quartz apparatus that allowed a clay sample to be studied by ESR in a controlled atmosphere was designed and built. With this apparatus, a sample of the clay film could be studied in the air-dried state or under vacuum. Samples under vacuum could be subsequently exposed to organic vapor under well-controlled conditions. XRD measurements were performed using a Siemens (Model D-500) powder diffractometer.

RESULTS AND DISCUSSION

ESR spectra of the Cu^{2+} exchanged hectorite films showed that the exchange sites within the film were strongly ordered (Eastman et al. 1984). Figure 1a shows a 2 μm × 2 μm SFM scan on the unexposed hectorite surface. Over the scan range of 2 μm, the surface is flat to within 300 Å. All of the hectorite clays prepared in this fashion contained large flat surface regions such as that shown, interspersed with smaller regions of greater roughness (>300 Å). In Figure 1b, an image of dimensions 4500 Å × 4500 Å is shown for the same film surface. At this higher resolution, the surface is seen to be composed of a system of interlocking platelets. The film surface is generally flat, with the platelets simply butting up adjacent to one another. In some areas, some overlap is observed.
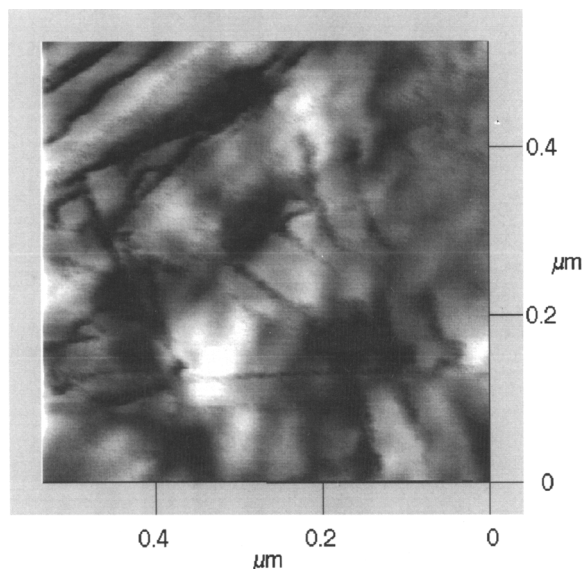
Figure 2. Hectorite surface after refluxing with benzene. The Z-range is 90 Å. The once level platelets are now shifted vertically with respect to one another. The vertical steps between plates ranges from 7–10 ± 2 Å to over 80 Å.

The surface exposed area of the platelets varies in size, with the smallest exposed areas having dimensions on the order of 100 Å and the largest approaching 1 μm in size. Hectorite is a trioctahedral smectite clay having an average dispersed particle size of 0.8 μm × 0.8 μm × 0.001 μm. The largest measured platelet sizes thus correspond reasonably well with the dispersed particle size. The smaller platelets are most likely due to fractures in the larger particles.

In Figure 2, an image of the hectorite film surface after refluxing in benzene is shown. The dimensions of this image are 0.5 μm × 0.5 μm. The surface is no longer flat, but is instead composed of many smaller flat regions with step-like transitions between them. Using the SFM instrument, these vertical steps can be measured accurately. The step heights fall into groups, with the smallest being 7–10 ± 2 Å. The next group of steps has vertical heights in the range 13–20 ± 2 Å. This continues until the largest group, in which the step sizes are 78–83 ± 2 Å in height. Benzene appears to polymerize only in the interlayer region of the hectorite where electric field and orientation effects would be most pronounced. The intercalative polymerization "raises" many of the clay platelets from the plane of the unreacted clay. The "width" of a benzene molecule is approximately 7 Å (dimension parallel to the molecular plane), while the "thickness" (measured perpendicular to the molecular plane) is about 3.5 Å (Goddard et al. 1995). This suggests that the polymer in the interlayer region is formed from benzene molecules oriented perpendicular to the surface of the film, or in double layers oriented parallel to the film

surface. The ESR spectral parameters from the organic radicals in the clay films also indicate ordering of the polymer (Eastman et al. 1984).

The hectorite films were also exposed to aniline at room temperature and at approximately 180 °C in order to study the polymer microstructure as a function of polymerization conditions. The dark blue-violet color of these films indicates that the polymer on the surface is in the conducting, emeraldine oxidation state (Langer 1990). The violet tint may be indicative of fairly low conjugation lengths along the chains. Figure 3a shows a 4 μm × 4 μm SFM image of the low-temperature-exposed surface, while in Figure 3b an image of the high-temperature-exposed surface is presented. In both images, it is apparent that a great deal of polymerization of the aniline has taken place on the film surface, as opposed to the case with benzene, in which little or no surface polymerization can be seen. The low-temperature film (Figure 3a) is composed of polymer bundles or micrograins. The dimensions of these micrograins range from 300 to over 3000 Å. This nm-scale polymer bundle structure has been previously observed by SFM (Porter et al. 1994) in electro-polymerized polyaniline thin films on Pt substrates. The micrograin sizes in the present study correspond well with the range of sizes reported in this earlier study. The nm-scale structure of the high-temperature aniline exposed films is not clearly resolved in Figure 3b. In Figure 4, a higher resolution scan of dimensions 1.5 μm × 1.5 μm is shown. In this image, we can see that the polymerized surface is composed of small, nearly spherical micrograins. These micrograins also appear to be grouped together into larger clusters. This structure corresponds more closely to that seen for chemically prepared, NMP-cast, free-standing polyaniline thin films (Porter et al. 1995). SFM data were also obtained from aniline exposed hectorite films with no Cu(II) treatment (Na-hectorite). These films showed no indication of surface polymerization upon exposure to either benzene or aniline. No SFM evidence in the form of polyaniline "bundles" was observed, nor was there the characteristic color change (to dark violet) due to the presence of conjugated surface polymer.

It is interesting that the aniline polymerizes on the surface of the clay while the benzene apparently does not. Benzene does not readily react in the presence of Cu salts; the reactivity in the clay systems probably arises from the large electric fields in the interlayer of the clay. The separation of charge in the interlayer galleries (in the form of parallel sheets of positive and negative charge, to a first approximation) may result in fields not unlike that found within a parallel-plate capacitor. The small "plate" separation with respect to the charge distribution, and the dielectric effect of the interlayer water molecules will result in strong local deviations from the simple capacitor model. In ei-
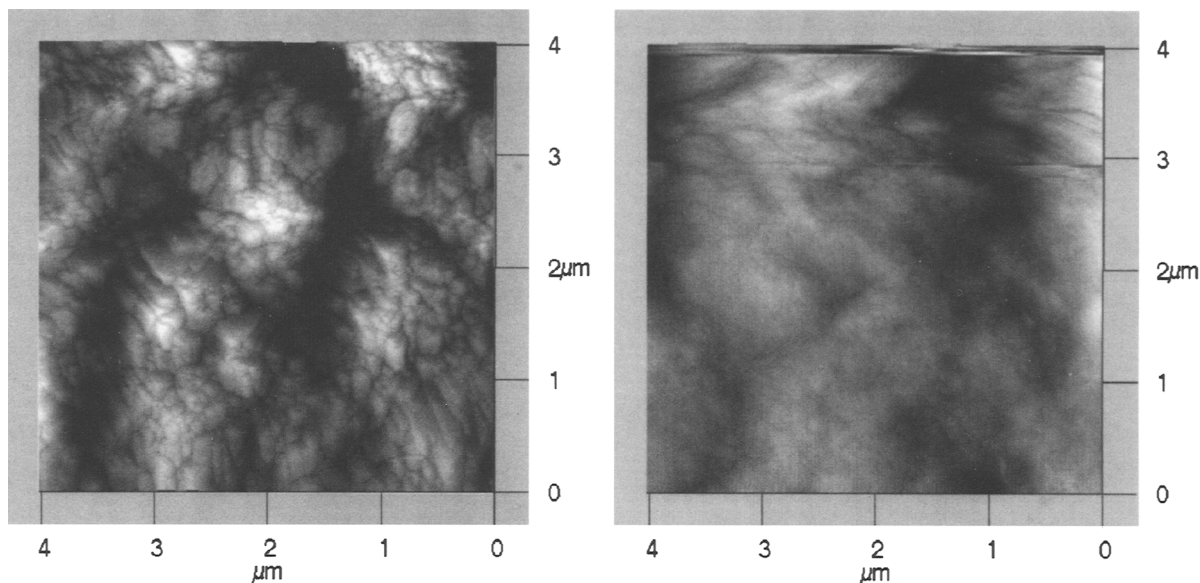
Figure 3.   a) Film surface after low-temperature aniline exposure. The Z-range in these images is 0.5 μm. The aniline has polymerized readily on the hectorite surface. The polyaniline microstructure is composed of small, nm-scale grains or bundles. b) Hectorite surface after high-temperature (180 °C) aniline exposure. The surface is completely coated with polyaniline; however, the polymer microstructure is not resolved in this image.

ther case, it is clear that these fields will be considerably stronger than that found on the surface of the clay (on which there is no such charge separation). These fields facilitate electron transfer from the benzene to the Cu^{2+}; indeed, the production of free radicals in these systems increases as the concentration of

Figure 4.   1.5 × 1.5 μm SFM scan on the high-temperature aniline exposed film. The vertical range in this image is 3000 Å. The polyaniline on this surface is composed of small, nearly spherical grains. Many of these grains are grouped together in larger clumps.

Cu^{2+} decreases (Eastman 1984). The production of a polymer, perhaps polyphenylene as suggested by Soma et al. (1983), with a portion of the aromatic groups existing as cations, would lead to a lowering of free energy in the hectorite/benzene system. There are no large fields on the surface of the clay and, as a consequence, the benzene behaves in a fashion similar to that of the bulk phase (that is, with no polymerization). Aniline is much more easily oxidized than benzene and readily undergoes polymerization in an oxidizing environment. In the clay systems, aniline may oxidize at sites accessible from the surface of the clay. Here the electric fields in the interlayer region are not necessary for the polymer to propagate.

The question of interlayer aniline polymerization in hectorite was also studied using XRD and ESR. XRD spectra for Cu(II) exchanged hectorite and Cu(II) exchanged hectorite-aniline films were obtained. The (001) spacings were determined by averaging (001) through (008) reflections for these patterns exhibiting a rational sequence of reflections. Constant humidity was maintained for all samples. Unexposed films showed a d-spacing of 12.6 Å, in good agreement with the results of McBride et al. (1975). An increase in the d-spacing for the (001) reflection from 12.6 Å in the inorganic host to 15.1 Å in the inorganic-organic host-guest hybrid was observed, indicating possible inclusion of the aniline in the interlayer regions. For the ESR studies, samples of air-dried Cu(II)-exchanged hectorite films were placed in the apparatus designed for controlled atmospheric studies. ESR of the air-
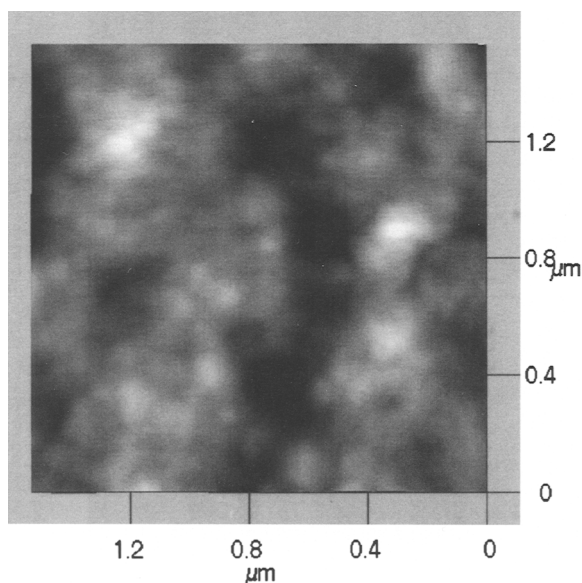
dried film showed that the Cu^{2+} ions are in an axial field characterized by ESR parameters of $g\| = 2.353$, $g\perp = 2.076$ and $A\| = 151$ Gauss. It was not possible to resolve $A\perp$ values in the 100% exchanged sample, owing to dipolar broadening. Removing water from the sample, by exposing the sample to vacuum, broadened the resonances observed for both orientations. The immediate effect of exposing the dehydrated sample to aniline was a reemergence of a well characterized ESR signal for the Cu^{2+} ions ($g\| = 2.369$, $g = 2.076$, and $A\| = 144$ Gauss). The film darkened slightly upon exposure to aniline, but still retained the blue color characteristic of Cu^{2+} ions. Within 24 h the film had turned dark purple and the ESR from the Cu^{2+} ions had essentially disappeared (residual $Cu^{2+} < 5\%$ of the original concentration). A free radical signal, similar to that produced by the reaction of benzene with Cu^{2+} ions in hectorite, was observed. This signal was characterized by a g value of 2.003 and a linewidth of 13 Gauss when the film was oriented with the plane of the film perpendicular to the applied field. Rotating the sample by 90° increased the linewidth to 23 Gauss but did not noticeably change the g value. These results show that evacuating the sample removes water around the Cu^{2+} ions, and that aniline vapor rapidly penetrates the interlayer region of the desiccated sample to complex the Cu^{2+} ions. The polymerization reaction does not occur immediately at room temperature, but is essentially complete after 24 h under the conditions described. Clearly, the Cu^{2+} ions throughout the sample react. This observation plus the change in spacing observed from XRD data provide strong evidence that the polymerization occurs in the interlayer region. The anisotropy in the linewidth for the free radical signal in the "24-h" sample also indicates orientation of the polyaniline in the interlayer region. It seems reasonable to believe that the interlayer polyaniline has a different structure than the polymer on the clay surface; this difference would arise from the orienting effect of the interlayer region and the interlayer fields. In the case of benzene, it may be that polyphenylene forms in the interlayer region. However, the available experimental information does not preclude other possibilities, and the conditions under which the reaction occurs may well lead to unusual reaction mechanisms and reaction products.

CONCLUSIONS

The technique of SFM has been used to study the structure of clean hectorite thin films and hectorite films exposed to benzene and aniline. The unexposed films consisted of a structure of submicron-sized interlocking platelets. Exposure to refluxing benzene resulted in polymerization in the film interlayer regions, but not on the surface. Aniline exposure resulted in both surface and interlayer polymerization. This difference could be explained in terms of the electric-field-assisted oxidative polymerization of benzene in the interlayer regions, while aniline readily polymerized without assistance in the presence of the Cu salts.

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