Jpn. J. Appl. Phys. Vol. 35 (1996) pp. 3775–3777
Part 1, No. 6B, June 1996

# Atomic Force Microscopy Images of Liquid-Phase-Adsorbed Pyridine Molecules on Stilbite(010)

Masaharu KOMIYAMA and Minming GU
*Department of Chemistry, Yamanashi University, Takeda, Kofu 400, Japan*

(Received December 27, 1995; accepted for publication April 15, 1996)

For the first time molecular images of liquid-phase-adsorbed aromatics on a zeolite surface were obtained. Pyridine molecules adsorbed on a cleaved stilbite(010) surface from an aqueous solution were imaged by contact-mode atomic force microscopy. Adsorbed pyridine appears to form a 2-dimensional quasi-solid phase on the surface. The adsorbed layer exhibits an approximately hexagonal symmetry, with a unit cell dimension of 5.1 ± 0.3 Å. Molecular orientation within the adsorbed layer is also discussed.

KEYWORDS: atomic force microscopy, liquid phase adsorption, pyridine, stilbite, molecular arrangement, molecular orientation

## 1. Introduction

Atomic force microscopy (AFM) can be applied to nonconductive solid surfaces in various environments. Therefore, AFM can be used to determine the arrangement of molecules adsorbed on nonconductive solid surfaces, which is not possible using other existing surface analytical techniques. Atomic resolution with AFM was achieved only recently, however, and thus reports on adsorbed molecules observed by AFM are scarce, with the exception of those which deal with Langmuir-Blogett films.[1)]

Only a few papers on AFM observation of adsorbed molecules are known to the authors. One reported the molecular arrangement of *tert*-butanol adsorbed on a clinoptilolite(010) surface from its liquid phase,[2)] and another of 5-benzoyl-4-hydroxy-2-methoxybenzensulfonic acid on hydrotalcite(0001).[3)] In either work, the atomic arrangement within each molecule was not resolved, and each molecule appeared as a single mass in the AFM images.

We report the first observation of resolved molecular images of an aromatic species, pyridine, adsorbed on a cleaved (010) surface of a natural zeolite, stilbite. Zeolite is an industrially important material used as an adsorbent as well as a catalyst. Zeolites possess "surface acidity," which plays a key role in their catalysis. Measurement of surface acidity is often performed by pyridine adsorption, through which the amount and strength of surface acid is determined. Thus the knowledge on the detailed structure of adsorbed pyridine layer on a zeolite surface would be of interest.

## 2. Experimental

Stilbite from Ross Creek, Nova Scotia, Canada, was used as the adsorption substrate in the present study. This mineral is easy to cleave along its fault planes (010) and (020). AFM images of stilbite obtained under ambient conditions and their analysis have been reported elsewhere.[4)] Here, the zeolite sample was freshly cleaved under ambient conditions, and immediately placed in a sealed AFM liquid cell which was then filled with deionized and membrane-filtered water. The cantilevers employed were of a standard type, with a $Si_3N_4$ tip and a force constant of 0.38 kN/m. After AFM examination of the surface under water, the water was replaced with 1 vol% of aqueous pyridine solution, and the AFM examination was repeated. For the AFM observations a Nanoscope II contact-mode AFM (Digital Instruments) was employed. Imaging was performed in the repulsive force range, with a tip load of about 5 nN. The recorded images were presented with or without low-pass filtering for which 2-dimensional fast Fourier transform (FFT) was used.

## 3. Results and Discussion

### 3.1 *Stilbite(010) surface under water*

Figure 1 shows a wide area image of a cleaved stilbite surface observed under water. The cleaved surface is extremely flat, with terraces a few hundred nanometers wide, separated by steps whose height of about 1 nm corresponds to half the unit cell length along the *b* axis (1.82 nm).

Figure 2 shows a low-pass-filtered narrow-area AFM scan of the cleaved surface.In the image the surface unit cell expected for a bulk-terminated (010) surface is su-

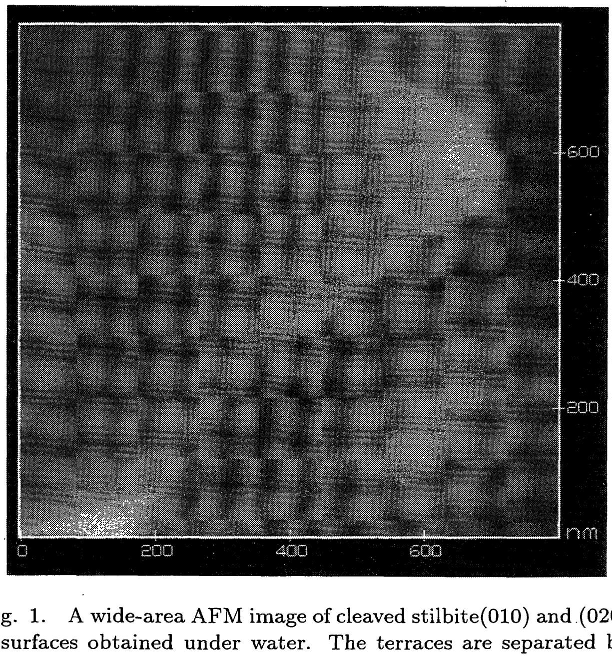

Fig. 1. A wide-area AFM image of cleaved stilbite(010) and (020) surfaces obtained under water. The terraces are separated by steps whose height of about 1 nm corresponds to half of the *b* axis unit cell length. The gray scale is 6 nm full scale.

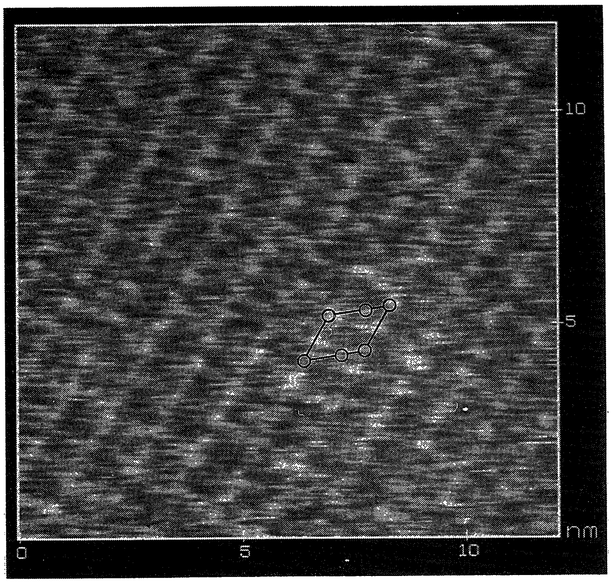

Fig. 2. A low-pass-filtered AFM image of a cleaved stilbite surface obtained under water. The surface unit cell expected for a bulk-terminated (010) face is superposed. The open circles in the unit cell indicate the positions of top-layer oxygen atoms. The gray scale is 2 Å full scale.

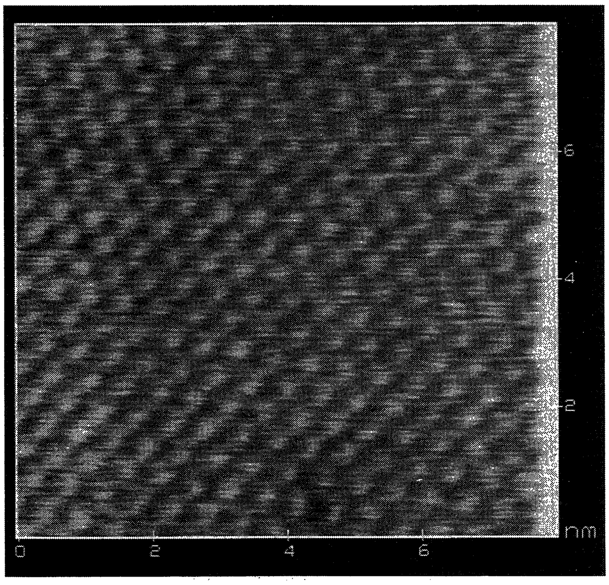

Fig. 3. A low-pass-filtered AFM image of a stilbite(010) surface in an aqueous pyridine solution. The gray scale is 4 Å full scale.

perposed with open circles which indicate the positions of the topmost oxygen atoms. The bulk unit cell has $a$ and $c$ dimensions of 13.6 Å and 11.3 Å, respectively, at an angle of 128°. Within one unit cell along the $a$ axis there are two oxygen atoms, the distances between them being 5.3 Å and 8.3 Å. The observed image has a periodicity corresponding to that of the bulk-terminated unit cell, whereas within a unit cell the positions of the topmost oxygen atoms are not clear. Similar AFM images have been reported by MacDougall *et al.*[5] for underwater examinations of stilbite(010) surfaces.

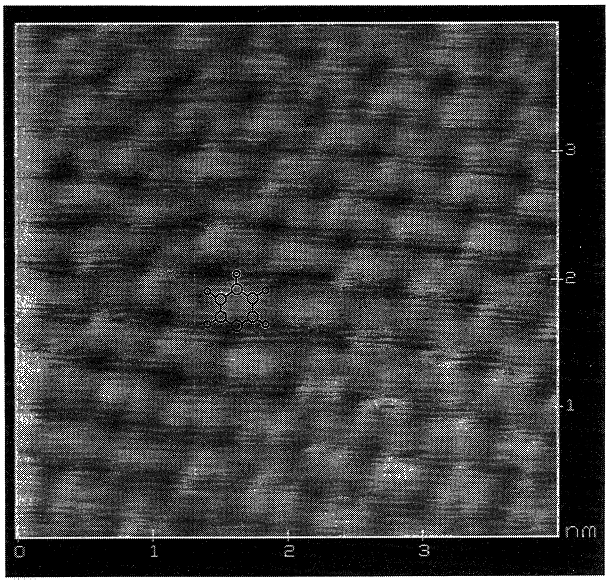

Fig. 4. A low-pass-filtered narrow-area image of a pyridine-adsorbed surface showing an array structure of pyridine rings. A ball-and-stick model of a pyridine molecule is superposed on one ring. The gray scale is 4 Å full scale.

### 3.2 *Pyridine adsorbed on stilbite(010)*

After surface imaging under water (Figs. 1 and 2), the fluid content of the liquid cell is substituted with aqueous pyridine solution. Allowing some time after the substitution for adsorption to reach equilibrium, AFM scanning of the surface was initiated. The first few scans showed an ordered surface structure that was not identifiable as either the adsorbed phase (see later) or the clean substrate surface. Then a stable ordered structure started to appear, an example of which is shown in Fig. 3. In this low-pass-filtered image an array structure totally different from that of the clean surface is observed. The array structure in this particular image exhibits approximately hexagonal symmetry, with lattice spacings of 4.8, 5.1 and 5.4 Å along the three axes, which are at the angles of 115°, 121° and 124°. These lattice constants show small fluctuations depending on the position. In some cases, perfect hexagonal symmetry with 5.0 Å lattice spacing and 120° axis angles is observed, and in other cases a rhombic structure with 4.9 and 5.4 Å lattice spacings and 120° axis angles is observed. Overall, we consider this structure to be approximately hexagonal, with a unit cell dimension of 5.1 ± 0.3 Å.

When scanning was confined to a smaller region, images such as that shown in Fig. 4 were obtained. The surface appears to be covered with a well-ordered array of rings, although only half of each ring is clearly visible. In the image, a ball-and-stick model of pyridine is superposed on one ring structure. The size of the observed ring appears to be well matched with the molecular model, supporting the notion that the observed image is that of adsorbed pyridine molecules.

While the pyridine molecules appear to form a well-ordered structure on the surface, giving a nearly perfect hexagonal 2D lattice, comparison of the structure of the adsorbed surface with that of the bare surface indicates that the arrangement of adsorbed molecules does not exactly correspond to the expected arrangement of the topmost oxygen atoms. This excludes the possibility that the observed image is due to one pyridine molecule adsorbed on the tip apex, thus indicating that the observed AFM image is not a reflection of the tip apex structure in the surface atoms of the sample. On the other hand, this arrangement of adsorbed pyridine molecules, which is independent of the substrate surface structure, indicates that the molecules are not adsorbed on specific sites on the surface, but are arranged in a manner similar to that known as self assembly.

In order to explain this arrangement of pyridine molecules, we consider the formation of a 2-dimensional solid phase on the surface based on the the following observations. First, as discussed above, the array structure appears to be independent of the substrate surface atomic arrangement and the substrate surface unit cell. Second, the ordered structure appears only after several surface scans, although it is assumed that the pyridine adsorption on the surface is complete before the scanning. The scanning may cause a phase transformation from the 2-D liquid (adsorbed) phase to the 2-D solid (adsorbed) phase, the driving force being the high local pressure in the tip apex-sample surface vicinity. With an applied force of 5 nN and an assumed affected surface area of 10 to 100 nm$^2$, the local force exerted is 500 to 50 MPa, which may be sufficient to cause mechanochemical effects such as phase transformation on the surface. Third, the AFM image resolution is unexpectedly stable for a system of simple adsorbed molecules, with no signs of molecular rotation or movement. The formation of a 2-D pseudo-solid phase would explain the high resolution and the stability of the AFM images.

### 3.3 *Molecular orientation and arrangements within the adsorbed phase*

Despite the above statement that the molecular arrangement of the adsorbed pyridine appears to be independent of the atomic arrangement on the substrate surface, we note some correspondence between them. The substrate surface unit cell dimensions ($a = 13.6$ Å and $c = 11.3$ Å) are within 10% of integer multiples of the dimensions of the adsorbed layer unit cell ($5.1 \pm 0.3$ Å). The angle of the substrate unit cell (128°) is also similar to that of the adsorbed layer (about 120°). These facts indicate that, despite the apparent self arrangement of pyridine molecules on the surface, there may be an interaction between the adsorbed molecules and the substrate surface, which may have some influence on the structure of the adsorbed phase.

Also, the pyridine molecules appear to be adsorbed on the surface with their molecular axes tilted away from the surface parallel. This is inferred from the observation that the images show only half of each ring clearly, which indicates that the rings are tilted away from surface parallel so that the lower part is not visible with the AFM tip. This inference is further supported by the fact that it is not geometrically possible to arrange pyridine molecules parallel to the surface with the spacings observed by AFM. Detailed analysis of the orientation of the adsorbed molecules will be published elsewhere.6)

1) J. Frommer: Angew. Chem. Int. Ed. Engl. **31** (1992) 1265.
2) A. L. Weisenhorn, J. E. MacDougall, S. A. C. Gould, S. D. Cox, W. S. Wise, J. Massie, P. Maivald, V. B. Elings, G. D. Stucky and P. K. Hansma: Science **247** (1990) 1330.
3) H. Cai, A. C. Hillier, K. R. Franklin, C. C. Nunn, M. D. Ward: Science **266** (1994) 1551.
4) M. Komiyama and T. Yashima: Jpn. J. Appl. Phys. **33** (1994) 3761.
5) J. E. MacDougall, S. D. Cox, G. D. Stucky, A. L. Weisenhorn, P. K. Hansma and W. S. Wise: Zeolites **11** (1990) 429.
6) M. Komiyama, T. Shimaguchi, T. Koyama and M. Gu: to be published in J. Phys. Chem.