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**Molecular Resolution of Zeolite Surfaces
as Imaged by Atomic Force Microscopy**

by

**J.E. MacDougall, S.D. Cox, G.D. Stucky, A.L. Welsenhorn
P.K. Hansma, and W.S. Wise**

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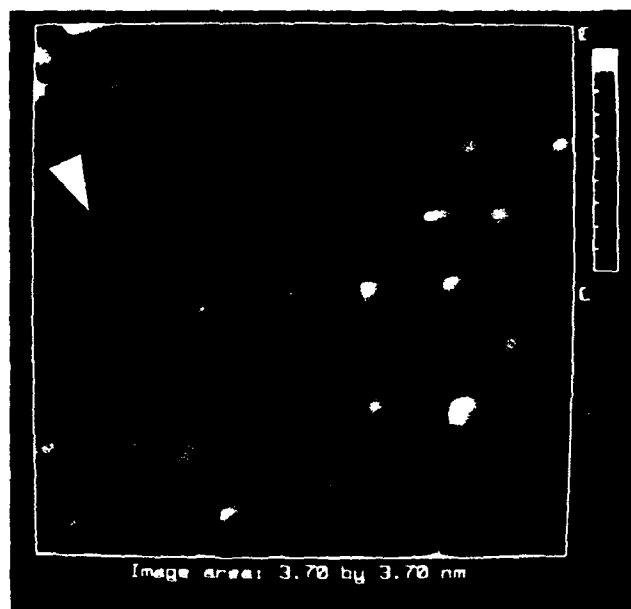
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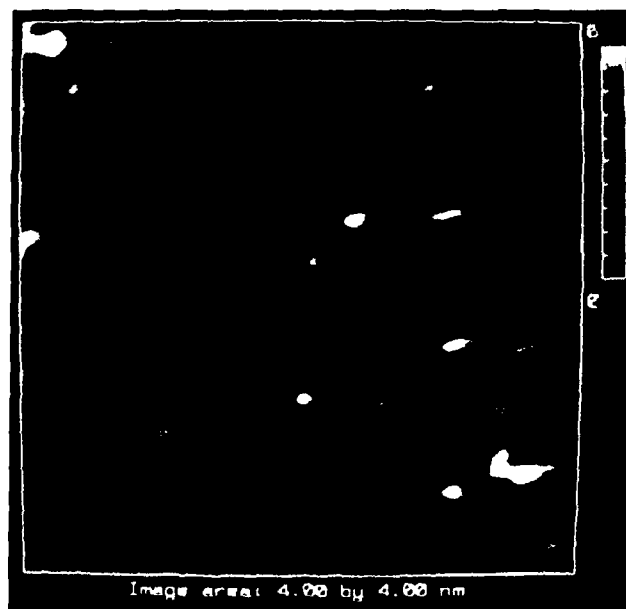
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Molecular resolution of zeolite surfaces as imaged by atomic force microscopy

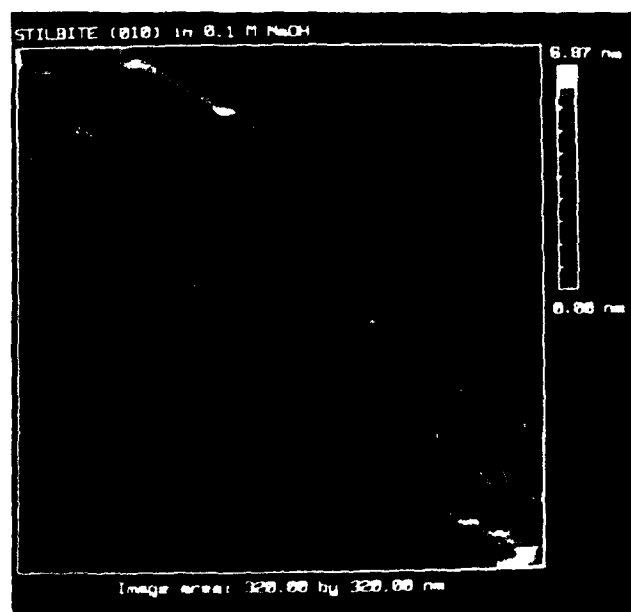
James E. MacDougall, Sherman D. Cox, Galen D. Stucky, Albrecht L. Weisenhorn, Paul K. Hansma, and William S. Wise



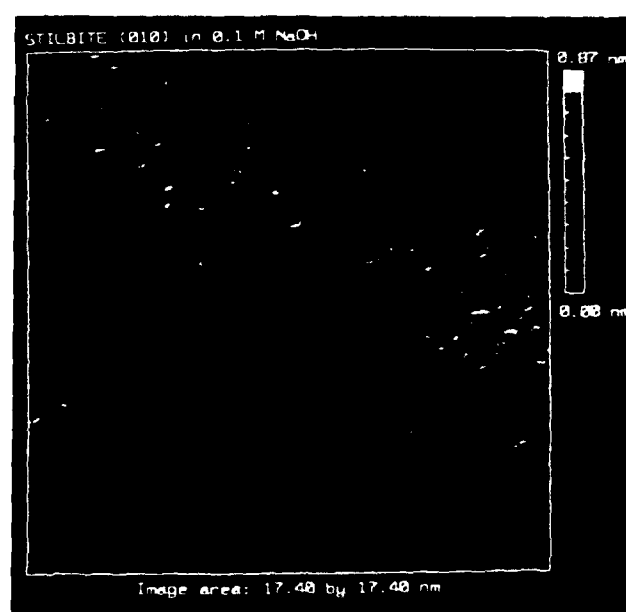
Color Plate 1 Scolecite (001) surface imaged in air. The image size is 37×37 Å. For the reader's convenience, a unit cell is outlined. The white arrow points to the six tetrahedra around a hole



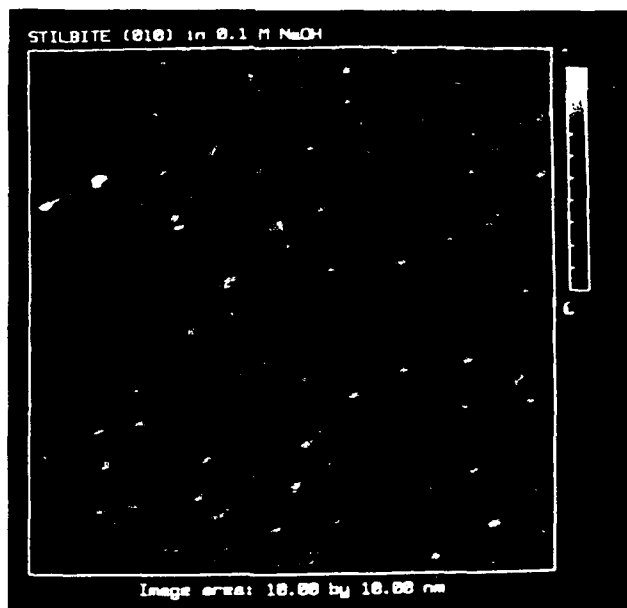
Color Plate 2 Twinning observed on the scolecite (001) surface in 0.1 M NaOH aqueous solution. The image size is 40×40 Å



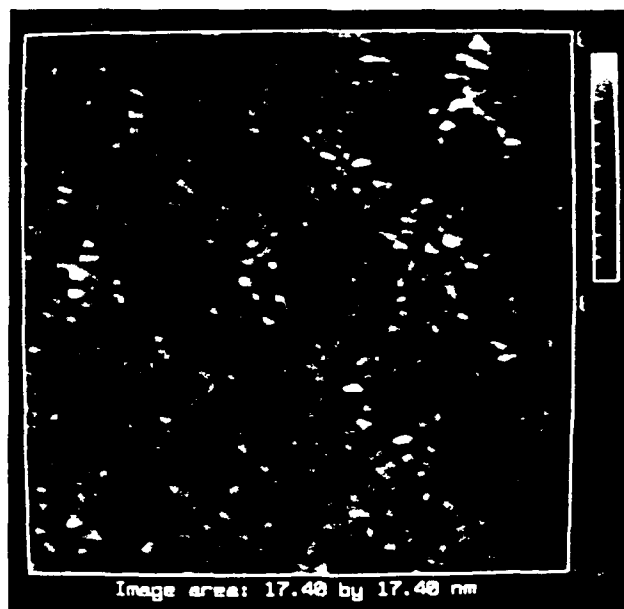
Color Plate 3 Large-scale image of stilbite (010) surface in 0.1 M NaOH aqueous solution. The image size is 3200×3200 Å; the height is about 70 Å. The step height (averaged over 12 steps) is 0.74 ± 0.06 nm



Color Plate 4 Molecular-scale image of stilbite (010) surface imaged in 0.1 M NaOH aqueous solution. The image size is 174×174 Å



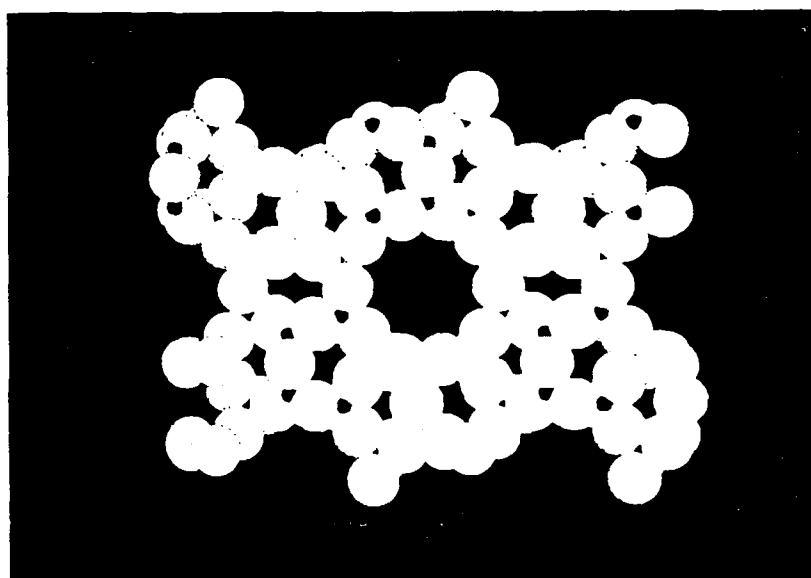
Color Plate 5 Molecular-scale image of stilbite (010) surface imaged in 0.1 M NaOH aqueous solution. The image size is 100×100 Å. Three unit cells are outlined



Color Plate 6 Faujasite (111) surface imaged in 0.1 M NaOH aqueous solution. The image size is 174×174 Å

Simulation of dynamic behaviors of benzene and toluene inside the pores of ZSM-5 zeolite

Tomoyuki Inui and Yoshiaki Nakazaki



Color Plate 1 Display of pore-opening structure of ZSM-5 crystal by computer graphics

Molecular resolution of zeolite surfaces as imaged by atomic force microscopy

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An atomic-force microscope (AFM) has been used to probe the surfaces of several natural zeolite crystals with known crystal structures. Scolecite, stilbite, and faujasite have been studied, and their AFM images have been compared with models based on their crystal structure data. In all cases, a particular Miller plane of the crystal was imaged with the AFM. Scolecite crystal was imaged in air along the (001) surface, and twinning, which had been confirmed by single-crystal X-ray diffraction, was observed on a molecular scale. Stilbite (010) was imaged in 0.1 M NaOH aqueous solution; both large- and molecular-scale images of the surface were obtained. The AFM image agreed well with the model of the (010) surface. Faujasite was imaged along the (111) surface and showed a rough surface consistent with cleavage through the four rings joining the sodalite unit. These observations demonstrate the utility of AFM for the characterization of zeolite surface structure and that it may lend itself to observing processes at the surfaces, such as surface reconstruction (manuscript in preparation) and ion exchange.

Keywords: Atomic force microscopy; zeolite crystals; surfaces; stilbite; scolecite; faujasite

INTRODUCTION

The industrial importance of zeolites to areas of catalytic cracking of crude oil fractions and sieving of gases has led to a great interest in how molecules interact with the surfaces of zeolites and how diffusion on the external surface affects the interaction of a molecule with a particular zeolite surface. In a previous study,¹ we demonstrated that polar organic molecules are selectively aligned on the surface of polar molecular sieves (AlPO₄-11 or AlPO₄-5) before diffusion into the channels, with the onset of a second-order nonlinear optic effect (second harmonic generation) in the composite material. The phenomena of surface absorption of molecules may

also have importance in catalytic reactions and ion-exchange processes. The interest in these areas had led us to use an atomic-force microscope (AFM) to study both zeolite surfaces and surface adsorption of molecules.

Zeolites are crystalline aluminosilicates, made up of corner-sharing tetrahedra forming a three-dimensional 4-connected net.² Incorporation of Al atoms onto a silicate framework introduces a net negative charge, which must be compensated for with counteranions that coordinate loosely with the framework.* Naturally occurring zeolites can be found in the form of large single crystals (millimeters on a side) that are suitable for our AFM study. The techniques required to use AFM for synthetic crystals that are currently available (< 1 mm) are feasible and being developed.

Electron microscopy and electron diffraction have been used to image zeolite frameworks and obtain structural information about complex zeolite structure types.^{4–5†} These techniques require a high vacuum to work effectively, and the electron beam

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* For a comprehensive introduction to zeolites, see Ref. 3.

† For a recent review of this area, see Ref. 6.

can damage the material during data acquisition. The AFM allows the imaging of *insulating surfaces under ambient conditions with molecular resolution without destroying the surface*. We demonstrated the observation of real-time processes on the surface of a zeolite (clinoptilolite) single crystal by imaging with an AFM under water, salt solutions, and alcohols.⁷ Previously, AFMs have been used to nondestructively image other insulating surfaces with molecular resolution,⁹⁻¹² at 4 K¹³ or in vacuum.¹⁴ AFMs have imaged polymers,¹⁵ amino acids crystals,¹⁶ and magnetic domains.^{17,18} AFMs have also been used for atomic scale friction measurements^{19,20} and for the deposition and measurement of localized charges.²¹ Furthermore, AFMs are able to image soft surfaces such as Langmuir-Blodgett films²² and other biological samples²³⁻²⁵ in water, because they can image with nondestructive forces as small as 1 nN.²⁶

This report details the use of an AFM to image the surface structure of several different natural zeolites (scolecite, stilbite, and faujasite) under various conditions (i.e., air and aqueous solutions). We report on the twinning of a scolecite crystal observed at the molecular level, both large- and molecular-scale images of the surface of stilbite, and the surface roughness of faujasite. These observations demonstrate the suitability of AFMs for structural elucidation of complex systems. In addition, since the AFM can image under ambient conditions, this suggests its application to the study of processes important to zeolite chemistry, such as ion exchange or surface reconstruction.

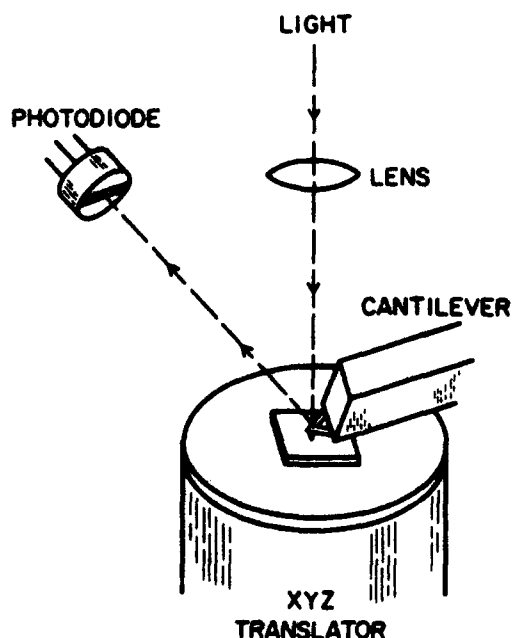


Figure 1 AFM schematic. The AFM detects the vertical motion of the tip by sensing the displacement of the reflected beam with a two-segment photodiode. A feedback loop keeps the vertical deflection of the tip, and therefore the force that the tip applies on the surface, constant by moving the surface up and down with the xyz translator.

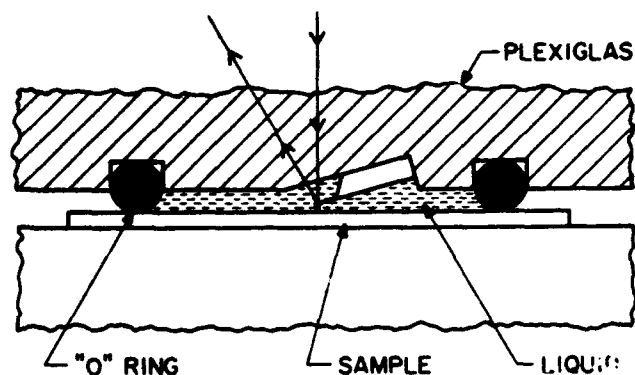


Figure 2 The imaging under liquids was performed with a sealed cell that is made of Plexiglas and sealed with an O-ring. For more details, see Ref. 32.

EXPERIMENTAL

Scolecite,[‡] stilbite,[§] and faujasite^{||} natural crystals were used initially without any chemical modification. The surfaces studied were determined from both crystal morphologies and cleavage planes common to the particular zeolite.²⁷ The scolecite crystal was found to be twinned by a single-crystal X-ray diffraction. Computer simulations of the structure were carried out on a DEC Micro-Vax II computer running either Chem-X* or Struplot²⁸ and using published crystallographic parameters.**

Each crystal was imaged either in air or 0.1 M NaOH aqueous solution. The images were collected with Nanoscope II electronics and associated software.^{††} Each image required 2.5–10 s for acquisition. The crystal was mounted in a particular orientation onto a stainless-steel plate with a small amount of 2 ton epoxy (Devcon 2 ton), and the plate was placed in the sample holder of the AFM (Figure 1). Imaging in liquids was performed with a sealed cell shown in Figure 2. Several reproducible scans were made for each sample, to insure that the applied force in each experiment was nondestructive. Images were slightly

** Structural references for each are as follows: scolecite, Ref. 29; stilbite, Ref. 30; faujasite, Ref. 31.

‡ A scolecite crystal was kindly supplied by Mark Davis of Virginia Polytechnic Institute and R.B. Higgins (Mobil). The crystal had been identified by X-ray diffraction.

§ The stilbite crystal (Oxbow Dam, Oregon) was identified by powder X-ray diffraction on some smaller crystals with the same habit as the one used in this study. The crystals were kindly provided by Norman Herron of Central Research and Development department, E.I. duPont de Nemours & Co.

|| The faujasite crystals used in this study were kindly provided by the UCSB Geology Department. The crystals were identified by X-ray diffraction and electron microprobe data.

* Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.

†† Digital Instruments, Inc., 6780 Cortona Drive, Santa Barbara, CA 93117.

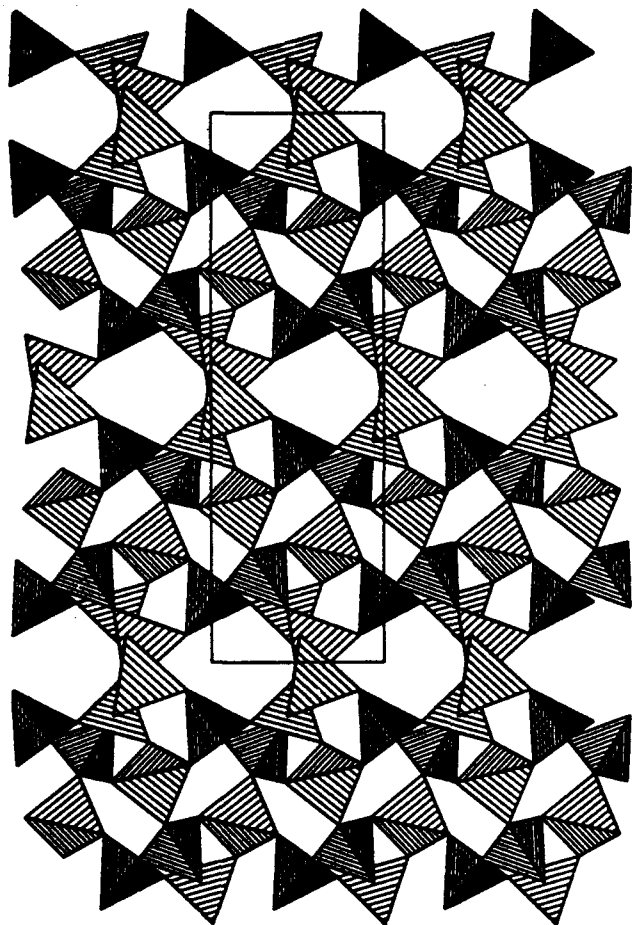


Figure 3 Structural representation of the scolecite (001) surface showing interconnected aluminate and silicate tetrahedra ($a = 6.52 \text{ \AA}$, $b = 18.96 \text{ \AA}$, $\beta = 108.86^\circ$). A unit cell is outlined

processed using a low-pass filter. All features described were apparent in the unprocessed data. The height information from the molecular resolution images is a convolution of the surface structure with the tip shape and does therefore reveal only relative and not absolute height information. No roughness calculation was done for this reason either.

DISCUSSION

By comparing the AFM images with the crystal structure simulation, agreement within 10% of the distances and angles in the image and crystal face structure was found for each.

The scolecite (001) surface was cut with a scalpel and then imaged in air. The resolution obtained is remarkable (*Color Plate 1*): Measured repeating distances of $5.3 \pm 0.6 \text{ \AA}$ in the $116 \pm 3^\circ$ direction (angles of these directions are measured from the positive x -axis counterclockwise; the distances and angles were determined by Fourier transformation), $6.6 \pm 0.6 \text{ \AA}$ in the $60 \pm 3^\circ$ direction, and $5.7 \pm 0.6 \text{ \AA}$ in the $10 \pm 3^\circ$ direction are observed. The corresponding values from crystal structure data for the (001) surface are 5.0, 6.6, and $6.2 \text{ \AA}$. The measured (and

crystal structure data) angles between two directions are 50° (46°), 74° (72°), and 56° (62°). These distances and angles correspond to the arrangement of the 8-ring centers in the structure. The repeating distances of the AFM image (*Color Plate 1*) agrees well with the computer simulation of the structure (*Figure 3*), considering that the (001) surface is not readily cleavable and was cut with scalpel and hammer. The resolution enables one to clearly see the 8-ring pores of the structure. Furthermore, six individual tetrahedra (white points) around a hole can be seen in the AFM image (see white arrow in *Color Plate 1*; the hole is at about the distance of the length of the arrow from the tip of the arrow in the pointing direction of the arrow).

Apparent twinning is also observed on a different section of the surface of the crystal as shown in *Color Plate 2*. Comparing *Color Plate 2* with the computer-simulated structure in *Figure 3*, one notices that the pattern rather abruptly changes as one moves from the upper right-hand corner to the lower left-hand corner, although the twin boundary is not clearly delineated. This is most apparent in the inversion of the dark and light spots on the image. Since the periodicity remains the same in both directions, it would appear that the crystal began growing in two different spatial directions but with the same crystallographic symmetry. The repeating distances are analogous to those observed in the other section of the crystal.

The (010) face of stilbite was cleaved and then imaged in 0.1 M NaOH solution, and a low magnification image is given in *Color Plate 3*. The "sheaflike" structure of the (010) surface manifests as steps between terraces in this image. These are common in natural stilbite crystals as noted by Gottardi and Galli.³³ At a higher magnification and using a high-pass filter (second-order filter, 12 dB/octave),³² the terraces above and below one step that are at different height levels separated by the step height appear to be at the same height level (*Color Plate 4*). The step between these terraces shows the framework very distorted, because the slope is very large at the position of the actual step. At an even higher magnification of the stilbite surface, only one terrace was imaged (*Color Plate 5*). The observed repeat distances between cavities were $6.5 \pm 0.6 \text{ \AA}$ in the $51 \pm 5^\circ$ direction and $5.3 \pm 0.5 \text{ \AA}$ in the $173 \pm 2^\circ$ direction, which agrees well with the known spacings and angles ($1/2a = 6.8 \text{ \AA}$, $1/2c = 5.6 \text{ \AA}$, $b = 128^\circ$) (*Figure 4*).

The faujasite crystal was imaged as is along the (111) surface in 0.1 M NaOH (*Color Plate 6*). This image shows an extremely rough surface compared to the other zeolites in this study. Furthermore, steps across the image make the surface even rougher. A

³² This high-pass filter has here a cutoff period of $8 \text{ \AA}$. Periodic structure of less than $8 \text{ \AA}$ is not attenuated in height. Every doubling of the periodic structure, starting at $8 \text{ \AA}$, attenuates the height by a factor of 4 (1.6 nm : attenuation $1/4$; 3.2 nm : attenuation $1/16$; etc).

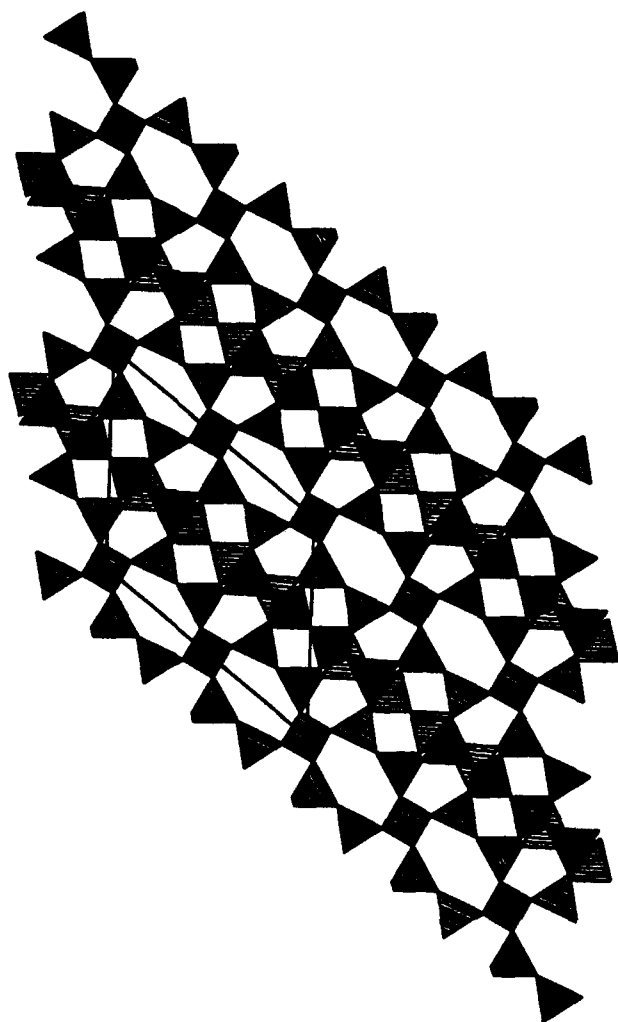


Figure 4 Structural representation of stilbite (010) surface showing interconnected aluminates and silicates tetrahedra ($a = 13.64 \text{ \AA}$, $c = 11.27 \text{ \AA}$, $\beta = 128.0^\circ$). A unit cell is outlined

simulation of the faujasite structure is shown in *Figure 5*. This simulation depicts the tetrahedral atoms of the framework only for clarity. If one views the structure as sodalite units (60 atom truncated octahedra, $\text{Si}_{12}\text{Al}_{12}\text{O}_{36}$) arranged in a tetrahedral fashion through the bridging oxygen atoms of "double" 6-rings³⁸ to form supercages, the idea that the surface should be rough becomes clear. As one looks into a supercage down a threefold axis, there are 6 sodalite units that surround the 12-ring opening. Each sodalite is connected to the next through a double 6-ring, and 4 sodalite units are arranged in a tetrahedral manner around any central one. These sodalite units then must alternate up and down around the 12-ring window, which appears to be deeper due to the larger pore size. Therefore, these units and 12-ring windows are not coplanar. Flatter crystal surfaces, naturally occurring or chemically

³⁸ The nomenclature 6-ring, etc., corresponds to the number of tetrahedral atoms in the opening of a zeolite. For an introduction to zeolites, see Ref. 3

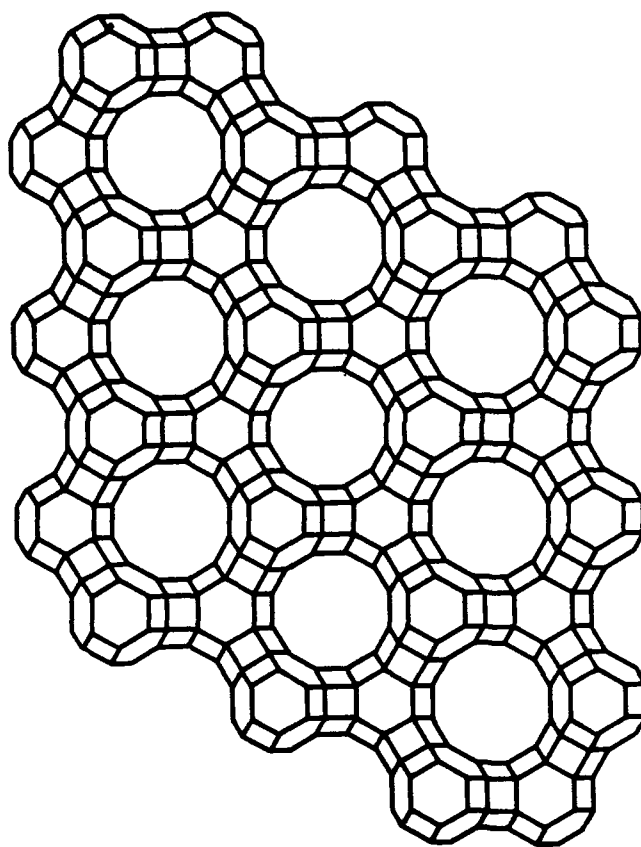


Figure 5 Structural representation of the faujasite (111) surface. Only tetrahedral atoms are shown for clarity. The distance between the centers of two 6-rings or between 6-rings and 12-rings is $10 \text{ \AA}$ projected onto the (111) surface

synthesized and modified, might increase the resolution of the faujasite (111) surface when imaged with an AFM.

CONCLUSION

This study demonstrates the utility and versatility of an AFM for examining the surface structure of zeolite surfaces under conditions of interest, i.e., in aqueous solutions or in air. We have observed twinning of scolecite (001) on the molecular scale, both large-scale and molecular images of stilbite's (010) surface, and the (111) surface of faujasite. Since the AFM can image under ambient conditions, surface processes (e.g., ion exchange or external surface adsorption) that are significant to science and technology can be studied. The ability to observe the surface of faujasite is extremely important due to the commercial applications of its isostructural analogs: zeolites X and Y.

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