VI-N Atoms and Molecules at Water-Zeolite Interfaces: Structure Determination based on AFM Observations

One of the striking capabilities of atomic force microscopy (AFM) is the direct observation of atoms and adsorbed molecules on a surface heretofore impossible, such as nonconductive materials like zeolite, under environments heretofore impossible, including underwater. The unprecedented resolution of AFM imaging enabled us to determine, for the first time, the positions of framework oxygen and extra-framework cation on a (010) surface of heulandite, a zeolite naturally occurring, and the array and the orientation structures of adsorbed molecules on its surface. Based on the *in situ* AFM observations, molecular simulations were performed to supplement the knowledge of aqueous phase adsorption processes.

VI-N-1 High-Resolution Imaging of Organic Monolayers Using Noncontact AFM

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Noncontact atomic force microscopy (AFM) provides useful technique for imaging organic molecules in high resolution. Here we present our recent advances in the noncontact AFM imaging of organic materials. (I) Molecular packing structures, defects and domain boundaries were clearly observed on adenine and thymine films. The noncontact AFM images revealed detailed features of the individual nucleic acid base molecules, thus allowing us to distinguish between adenine and thymine. (II) Both $(\sqrt{3}\times\sqrt{3})R30°$ structures and $c(4\times2)$ superlattice structures were resolved on alkanethiolate self-assembled monolayer (SAM) [CH_3-$(CH_2)_8SH$] (nonanethiol) on Au(111). We found that the $c(4\times2)$ superlattice structures changed into $(\sqrt{3}\times\sqrt{3})R30°$ structures when the tip-surface distance decreased.

VI-N-2 Study of Catalyst Preparation Processes by Atomic Force Microscopy (AFM): Adsorption of a Pt Complex on a Zeolite Surface

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Adsorption of a Pt complex commonly used for catalyst preparation onto a (010) surface of a natural zeolite heulandite was examined by *in situ* atomic force microscopy (AFM). The Pt complex appears to adsorb on the heulandite(010) surface at a three-times periodicity along the *c* axis, whereas along the *a* axis no specific periodicity was observed. Possible adsorption sites were also discussed.

VI-N-3 Recent Applications of Atomic Force Microscopy to the Study of Pyridine-Base Molecules Adsorbed on the (010) Surfaces of Heulandite and Stilbite Crystals

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Liquid-phase adsorption characteristics of pyridine-base molecules, pyridine and β-picoline, on (010) surfaces of two natural zeolites, heulandite and stilbite, were examined by atomic force microscopy (AFM). These adsorption systems formed well-ordered, two-dimensional (quasi-)hexagonal adsorbed layers, with their unit-cell dimensions ranging from 0.48 nm to 0.59 nm depending on the adsorbate-substrate combinations. Although there were near registries of the adsorbed phases with respect to the substrate (010) lattices, the molecular arrays were essentially incommensurate with the substrate atomic arrangements. Orientations of the molecules within the adsorbed layers were determined from the AFM images, which were compared favorably with semiempirical molecular orbital calculations.

VI-N-4 Atomic Force Microscopy Observations of Zeolite(010) Surface Atoms and Adsorbed Molecules

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Atomic force microscopy (AFM) is capable of directly observating surface atoms and adsorbed molecules on nonconductive materials such as zeolite, under various environments including vacuum, ambient and underwater. We have been successful in observing in situ atomic images of heulandite and stilbite (010) surfaces under aqueous environments, and molecular images of liquid-phase-adsorbed organics on these surfaces. The unprecedented resolution of the AFM imaging enabled us to determine, for the first time, the positions of framework oxygen and extra-framework cation, and the array and orientation structures of adsorbed molecules such as pyridine bases.