688 *Chem. Mater.* **1998,** *10,* 688−691

Surface Structure of Zeolite L Studied by High-Resolution Electron Microscopy

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*Received October 7, 1997
Revised Manuscript Received December 29, 1997*

Introduction

Zeolites are crystalline microporous alumino-silicate materials and have been used as molecular sieves, absorbents, and shape-selective catalysts for several decades. More recently, quantum size effects of small guest atom clusters confined in zeolite micropores have been investigated.[1,2] These applications take advantage of the micropores inside the zeolite crystals. On the other hand, periodic surface structures of zeolites might be available as substrates for keeping small atom clusters confined in two dimensions,[3] but the details of zeolite surface structures have not been thoroughly investigated except for a few cases.[4,5] It is important to reveal the surface structures not only for the applications to cluster science, but also for the understanding of the growth process of zeolite crystals.[5]

Transmission electron microscopy (TEM) is a powerful technique to study the fine structure of materials on the nanometer scale. Using high-resolution electron microscopy (HREM), one can observe crystal structures in real space with atomic resolution (less than 0.2 nm). Edge-on view HREM images, which are taken with the incident beam parallel to the crystal surface, can reveal surface structures, though the observed images are slightly distorted due to an effect caused by the electron lens. However, one can derive the actual structure by comparison of the observed images with simulated ones. Even though the edge-on view image is a one-dimensional structure by the projection of a two-dimensional surface structure, it is possible to reveal the two-dimensional surface structure by taking images with different incident beam directions and/or taking into account crystallographic symmetry.

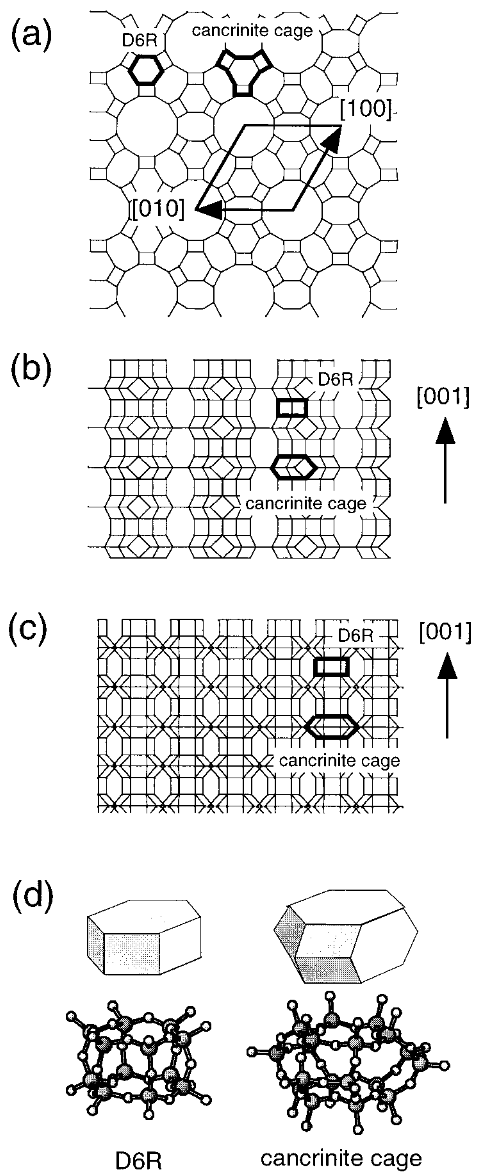

Figure 1. Schematic drawings of the framework structures of zeolite L, projected along the (a) [001], (b) [100], and (c) [1$\bar{1}$0] directions, respectively. Thick lines show D6R and cancrinite cages in these drawings. (d) Schematic diagrams of D6R and cancrinite cage. Large and small circles in lower diagrams show T-atoms (Si or Al) and oxygen atoms, respectively.

The framework structure of zeolites consists of SiO_4 and AlO_4 tetrahedra connected by sharing vertex O atoms. Since the distance between two T-atoms (Si or Al) is larger than 0.2 nm, it is possible to observe HREM images of the T-atom distributions in the zeolite framework structure. Although zeolites can quickly become amorphous under intense electron beam irradiation, it is still possible to obtain HREM image by using a low-intensity electron beam together with highly sensitive electron microscope films before the crystal structure is destroyed.

Previously, we published a HREM study which revealed that nanometer-sized platinum clusters dispersed on zeolite L crystals sit at special positions on the surface of the crystals and briefly reported the framework termination structure of zeolite L on the (001) surface.[3] In this report, we present the determi-

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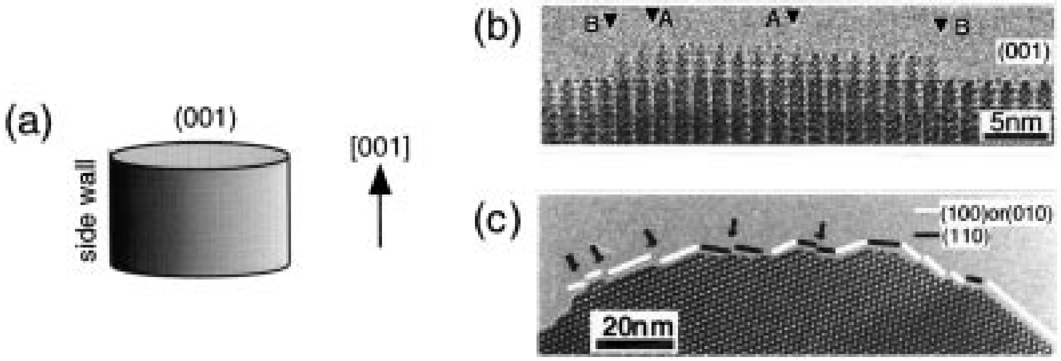

Figure 2. (a) A schematic drawing of the typical crystal morphology of zeolite L crystallites. (b) A HREM image of the zeolite L taken with the incident beam parallel to the [100] direction at 400 kV. Arrows indicate positions of surface steps. (c) A HREM image of the zeolite L taken with the incident beam parallel to the [001] direction at 400kV.

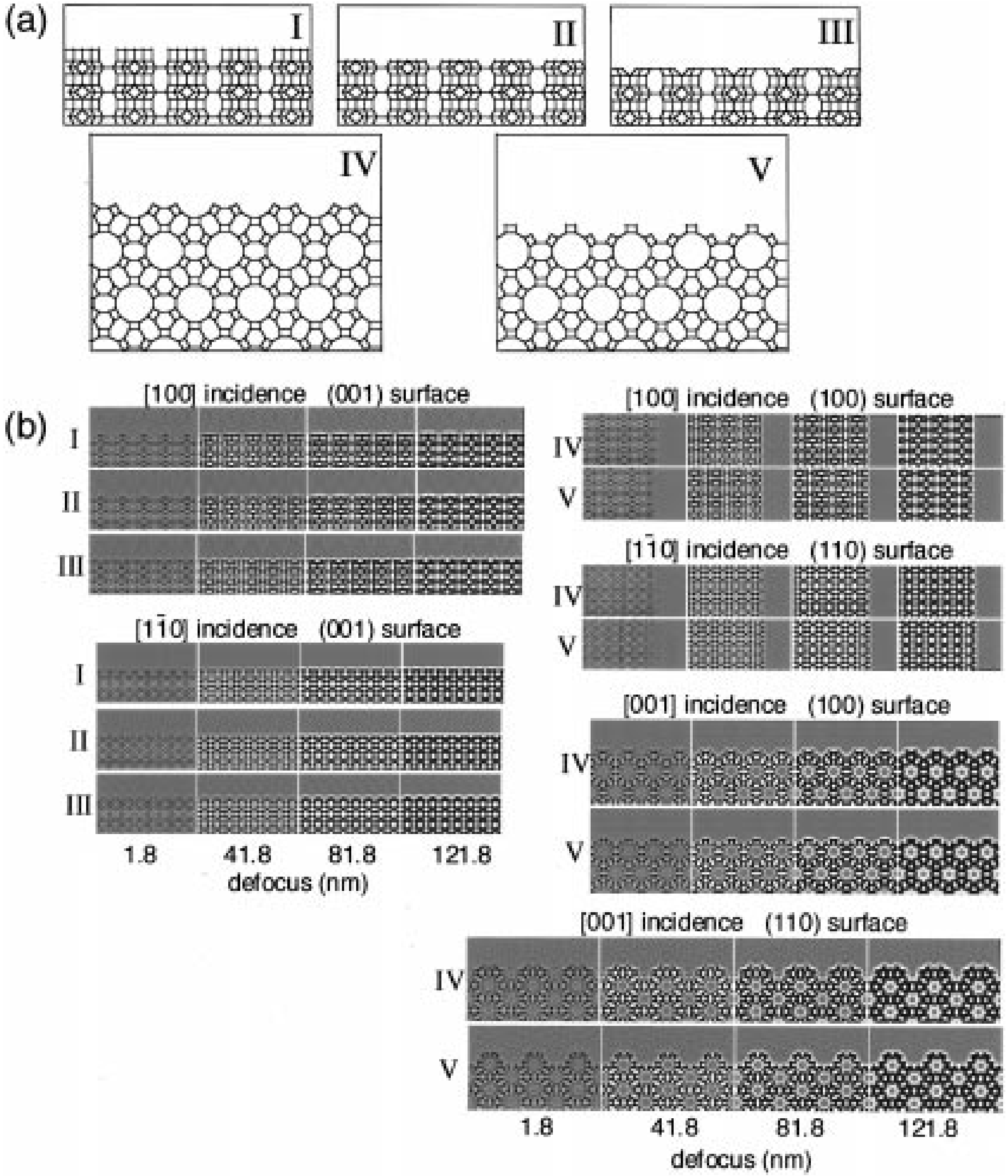

Figure 3. (a) Schematic diagrams of three different (001) surface structural models projected along the [100] direction and two models on the side wall projected along the [001] direction. (b) Calculated HREM images of the (001) surface and the side wall by the multislice method for the five models with the three different incident directions. Crystal thickness is 10 nm.

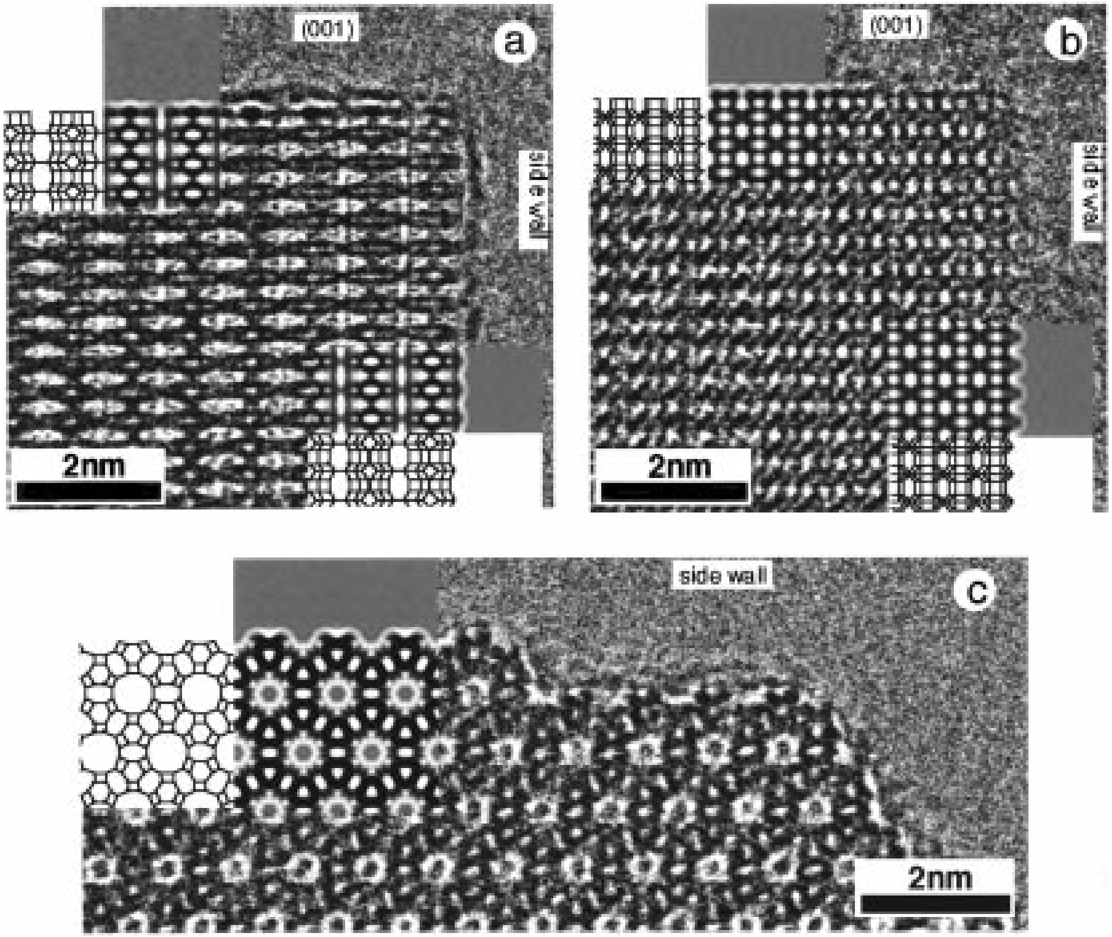

Figure 4. HREM images of the zeolite L, taken with the incident beam parallel to the (a) [100], (b) $[1\bar{1}0]$, and (c) [001] directions at 1250 kV. Simulated images and corresponding schematic diagrams of the framework structure are inserted. Parameters of the simulation: thickness = 10 nm, defocus = (a) 10.18 nm, (b and c) 12.18 nm.

nation of the surface structure of ideal models on various surfaces of zeolite L by HREM.

Experimental Section

Potassium zeolite L crystals (Si/Al = 3) were kindly supplied from Tosoh Corp. A 1250kV high voltage TEM (JEM-ARM1250, Cs = 1.7 mm, point resolution = 0.102 nm) and a 400 kV TEM (JEM-4000EX, Cs = 1.0 mm, point resolution = 0.17 nm) were used to take HREM images. The zeolite L crystallites were dispersed by sonication in acetone and dropped on a holey carbon film. Highly sensitive films (MEM) were used to record HREM images with an extended developing time. HREM simulations were performed by the multislice method using the MacTempas program.

Results and Discussions

The crystal structure of zeolite L has a hexagonal lattice of the space group $P6/mmm$ with lattice constants of $a = 1.84$ nm and $c = 0.75$ nm.[6] The crystal has a one-dimensional channel of 12-membered rings with channel openings of 0.71 nm in diameter. Projected framework structures of the zeolite L along the [001], [100], and $[1\bar{1}0]$ directions are schematically shown in parts a, b, and c of Figure 1 respectively, where three indices are taken to represent directions or planes of the hexagonal lattice. The intersection of lines in these schematic drawings correspond to the positions of T-atoms, and oxygen positions are located near the middles of the lines. One can see that the framework includes cancrinite cages and double six-membered rings (D6R), which are shown in Figure 1d. The zeolite L crystallites used for HREM observations have a cylindrical shape with typical dimensions of about 300 nm in diameter and 200 nm in height (top and bottom surfaces are parallel to the (001) plane (Figure 2 a)). Hereafter, the top and bottom surfaces are denoted as a (001) surface and the remaining surfaces are called a side wall. There are some steps and overgrowth crystallites on the surfaces of the zeolite L crystallites. The nature of the overgrowth has been revealed by a previous HREM study.[7] The height of all steps on the (001) surface is integer multiples of the lattice constant of c ($n \times 0.75$ nm where n is an integer). A HREM image including the (001) surface (Figure 2b) shows examples of the steps; that is, the step A is c in height and the step B is $3c$. This result indicates that growth units having the minimum step height ($= c$) must exist in the process of crystal growth. A low-magnification HREM image taken with the incident beam parallel to the [001] direction is shown in Figure 2c. By tracing an arrangement of bright dots, which correspond to the channel positions, in the image, it is clear that the surface of the side wall consists of the (100) and (110)

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[6] Barrer, R. M.; Villiger, H. Z. *Kristallogr. Board* **1969**, *128*, 352.

[7] Terasaki, O.; Thomas, J. M.; Millward, G. R. *Proc. R. Soc. London* **1984**, *A395*, 153.

planes with some steps indicated by arrows in the figure. The above result shows that the zeolite L crystallites have three different types of external surfaces, which are parallel to the (001), (100), and (110) planes. Therefore, we chose the incident directions parallel to the [100], [1$\bar{1}$0], and [001] directions to observe HREM images.

We should consider five ideal models shown in Figure 3 to calculate the multislice simulation. Figure 3a shows a schematic diagram of the three models (I, II, and III) for the termination structure of the framework on the (001) surface, projected along the [100] direction, and that of the two models (IV and V) on the side wall, projected along the [001] direction. Model I shows that the framework is terminated with D6R on the (001) surface, model II shows six-membered ring termination, and model III terminates with four-membered rings. On the side wall, models IV and V correspond to the termination structures with the cancrinite cages and with only four-membered rings, respectively. Computed images by the multislice simulation using structural parameters of those five models with three incident directions are shown in Figure 3b. Normally, Si atoms on the surface might be terminated with OH, but H atoms were omitted in this simulation because its electron-scattering power is very small. Also, cation atoms were omitted because the atoms are moving in the crystal under high-density electron beam irradiation and so the cations do not make a large contrast in HREM images.[8] The simulation was performed with parameters of an accelerated voltage = 1250 kV, Cs = 1.7 mm, depth of focus = 9.3 nm, semiangle of beam convergence = 0.6 mrad, and various crystal thicknesses and defocus values (only part of the simulated images of each model is shown in Figure 3b). From these simulations, the differences in the contrast around the surfaces between those models can be readily seen. By comparison of these simulated images with observed HREM images, we can obtain an indication of the surface structure.

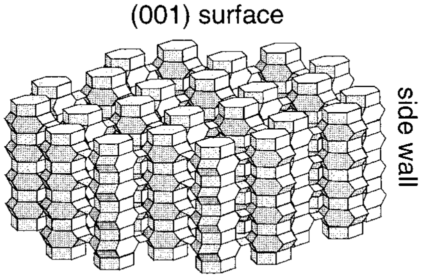

Figure 5. A proposed ideal framework structure model on the surfaces of the zeolite L.

Figure 4a,b,c shows HREM images taken with the incident beam parallel to the [100], [1$\bar{1}$0], and [001] directions, respectively. Simulated images, which are in a good agreement with the contrast around the (001) surface and the side wall in those HREM images, and schematic diagrams of the framework structure corresponding to the simulated image are inserted in each HREM image. The model type inserted is model I for the (001) surface in Figure 4a,b and model IV for the side wall in Figure 4a–c. The slight difference between the observed HREM image and the simulated one in Figure 4a, that is, a dark line nearby the surface, is caused by the incident direction slightly inclined from the [100] direction. These results show clearly that the framework of the most suitable model is terminated with the D6R on the (001) surface and with the cancrinite cage on the side wall (Figure 5).

We have also performed simulations for various mixture models of the two or three models on the (001) surface. That result shows that the structure of model I is the majority (more than 80%) of the (001) surface structure of the zeolite L.[9]

Acknowledgment. The authors greatly acknowledge CREST, Japan Science and Technology Corporation, for financial support. O.T. also thanks the Grant-in-Aid for Scientific Research in Priority Areas, the Ministry of Education, Science, Sport and Culture of Japan for the support.

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[8] In compositional analysis of zeolite by using EDS method, we can often see that the result of the analysis, especially cation composition, depends on density and probe size of incident electron beam. It means that the cations are moving in the crystallite under high-density electron beam irradiation.

[9] Ohsuna, T.; Horikawa, Y.; Hiraga, K.; Terasaki, O. Manuscript in preparation.