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High-Resolution Electron Microscopic Studies of Some Y- and A-Zeolites

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Application of high-resolution electron microscopy to structural studies of Y- and A-type zeolites is described. The structure images of channels and some crystallographic imperfections in the samples, such as incoherent twinning boundaries, dislocations, metastable elastic distortion, and coin-like domains, were observed. The radiation damage processes were also recorded *in situ*.

INTRODUCTION

The direct imaging of structure by high-resolution electron microscopy (HREM) is increasingly used as a technique for the study of zeolites. The great merit of HREM is that it can give structural information, in real space and at the atomic level, about materials that are not amenable to structure determination by X-ray crystallographic and other conventional techniques (*1*).

Zeolites are microporous, crystalline aluminosilicates of general formula $M_{x/n}$ $[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$. They may be regarded as open structures of silica, SiO_2, in which aluminum has substituted silicon in a fraction $x/(x+y)$ of the tetrahedral sites. The net negative charge of the aluminosilicate framework is neutralized by exchangeable cations, M, of valence n, and the void space, which may be more than 50% of the crystal volume, is occupied by m molecules of water per unit cell. Depending on the particular structure of the zeolites, the porosity may consist of one-, two-, or three-dimensional networks of interconnected channels (*2*).

Zeolites are of considerable importance not only as absorbents but also as catalysts. In particular, the role of synthetic shape-selective zeolites in the conversion of methanol into hydrocarbons in particularly promising. In principle, electron microscpy is well suited for probing the microstructure of such materials but, until recently, its application to zeolites has been limited by the sensitivity of aluminosilicate framework structures to electron beam irradiation. However, techniques have now been developed which, in favorable circumstances, have made possible the direct imaging of zeolitic crystals at the subnanometer level (*3–6*).

EXPERIMENTAL

The specimens of industrial zeolites of Y- and A-types for HREM observations were prepared by the following two methods (*7*). (1) The zeolites were ground in an agate mortar and dispersed in methanol and the thin fragments were then collected on a carbon film (specially made, extremely thin) supported on a copper grid. (2) The zeolites were embedded in methyl methacrylate and butyl methacrylate (1 : 1) at 45–60°C for 24 h, and then sliced into thin foils of a thickness of ca. 5–10 nm, at random in certain edge regions, using an ultramicrotome, and

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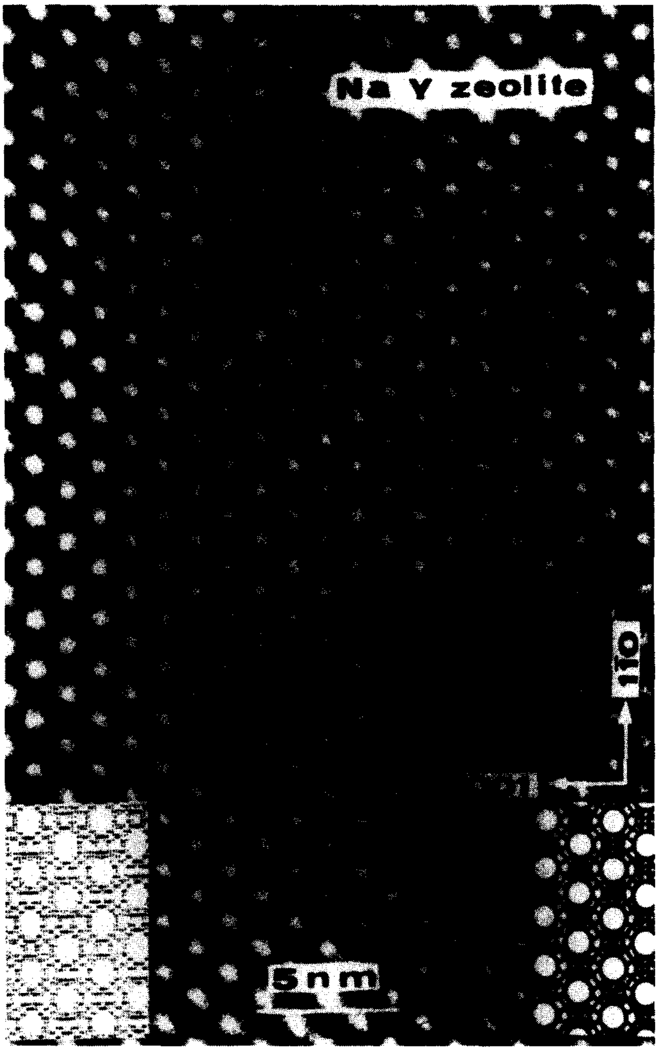

FIG. 1. Channel image of Na-Y zeolite in the [110] direction. The lower right inset is the structure model projection. The lower left inset is the computer-simulated image.

the foils were then supported on a copper grid. From a comparison of the two methods, the second one is better as regards results but has greater difficulties on account of the microtome cutting. Since the untreated zeolites are very beam-sensitive, the specimens were placed in a vacuum chamber at 10^{-5} Torr for several days before the EM examination in order to remove moisture and improve the stability under electron beam irradiation (*8*). Minimum exposure techniques were used to minimize the radiation damage. In addition, it was advantageous to use an image intensifier for image recording at a rather weak illumination and a low dose of electron irradiation. Furthermore, continuous observation of phase transitions as well as radiation damage process were recorded *in situ*.

HREM observations were carried out at 200 kV using a JEM-200 CX electron microscope equipped with a high-resolution top entry goniometer stage. Usually, the structure images were recorded at 3.8×10^5

times, using an objective aperture corresponding to a radius of 0.55 $Å^{-1}$ in the diffraction pattern.

Computer-simulated images of the zeolites were calculated by using the multislice method with a program written by Ishizuka (*9*). The parameters used were as follows: spherical aberration coefficient, 1.2 mm; the focus spread due to chromatic aberration, 3 mm; incident beam convergence, 0.4 mrad; the number of diffracted beam included in the dynamic diffraction calculation, 964; the value of defocus, −60 nm (~the Scherzer defocus).

RESULTS AND DISCUSSION

HREM examinations were made on a series of Y- and A-type zeolites. Figure 1 shows the channel structure images of an industrial Na-Y zeolite. The lower right inset is the atomic projection along the [110] direction of the structure model and the lower left one is the computer-simulated image along the [110] projection with the Scherzer defocus of −60 nm. All of them are in good agreement. Twins were observed in Na-Y zeolite and some other cation-exchanged Y zeolites. Figure 2 shows the twinning structure with an inset of the corresponding SAED pattern in Pd-Y zeolite. It should be noticed that both coherent and incoherent twin boundaries exist. Such a kind of incoherent twin boundaries have also been seen frequently in rare-earth REY zeolite (chemical formula: $Re_2O_3 \cdot Na_2O \cdot Al_2O_3 \cdot 4.7SiO_2$) and HY zeolite (chemical formula: $H \cdot Na_2O \cdot Al_2O_3 \cdot 4.7SiO_2$). Figure 3 shows the typical incoherent twin boundary observed in HY zeolite. The inset corresponds to the structure model projection of a coherent boundary. The twin boundary changes its direction from one atomic row to the neighboring row at the places indicated by arrows. If every β-cage can be treated as a lattice point, this incoherent twin boundary can be seen as a series of dislocations at the arrowed places. The microtome process is known to cause fractures in the materials and may be responsible for a slight change of orientation leading to the disappearance of one set of (111) planes. It seems that the incoherent twin boundaries are apt to occur when Na is substituted by other cations, such as Pd, H, and rare-earth elements. Radiation damage in the zeolites is common and the processes have been recorded by a video system. At the beginning, only a few

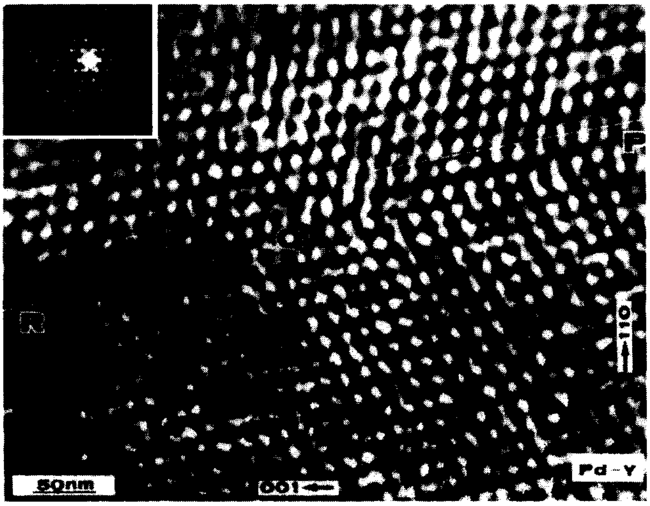

FIG. 2. Coherent twin boundaries (at P and R) and incoherent twin boundary (at Q) in Pd-Y zeolite. The inset is the corresponding SAED pattern.

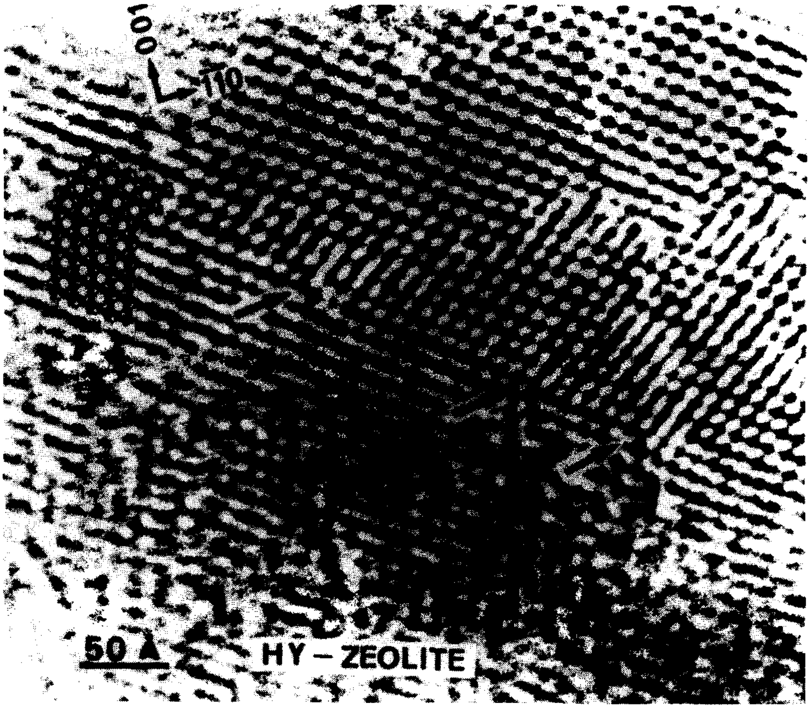

FIG. 3. Incoherent twin boundary and dislocations (arrowed) in HY zeolite. The inset is the twinning structure model projection along the [110] direction.

image spots disappeared; the amorphous regions gradually grew as separated islands and finally merged together, the whole field becoming amorphous. Moreover, if the exchanged cations are in excess, they may form separated clusters as shown in Pd-Y zeolite with excess Pd atoms (see Fig. 4).

A-Type zeolites have a simple cubic structure in which every lattice point can represent a β-cage. The tunnel image was

FIG. 4. Clusters (dark spots) of Pd atoms in Pd-Y zeolite. The white spots are the channel images.

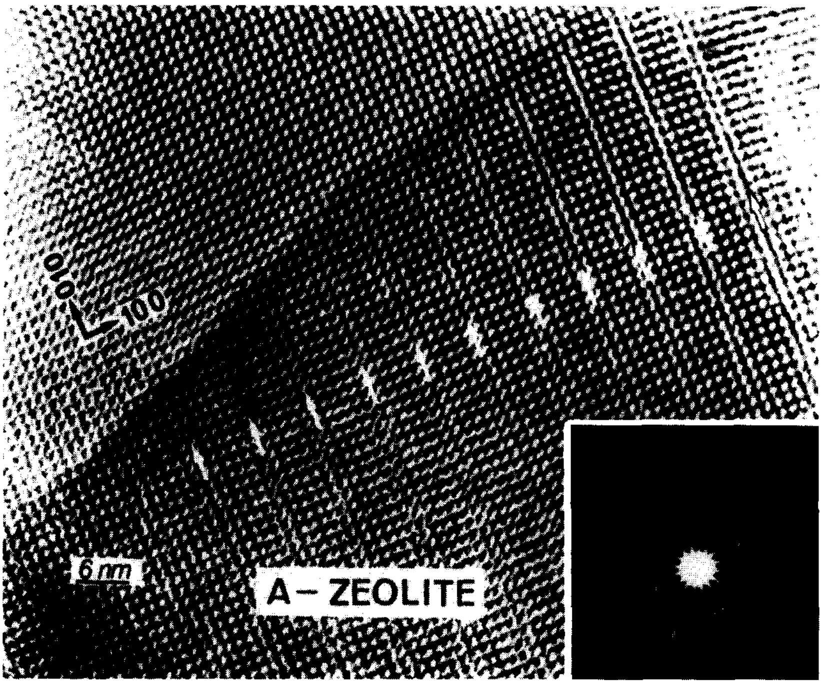

FIG. 5. HREM images of a metastable structure in 5A-zeolite. The inset is the corresponding optical transform.

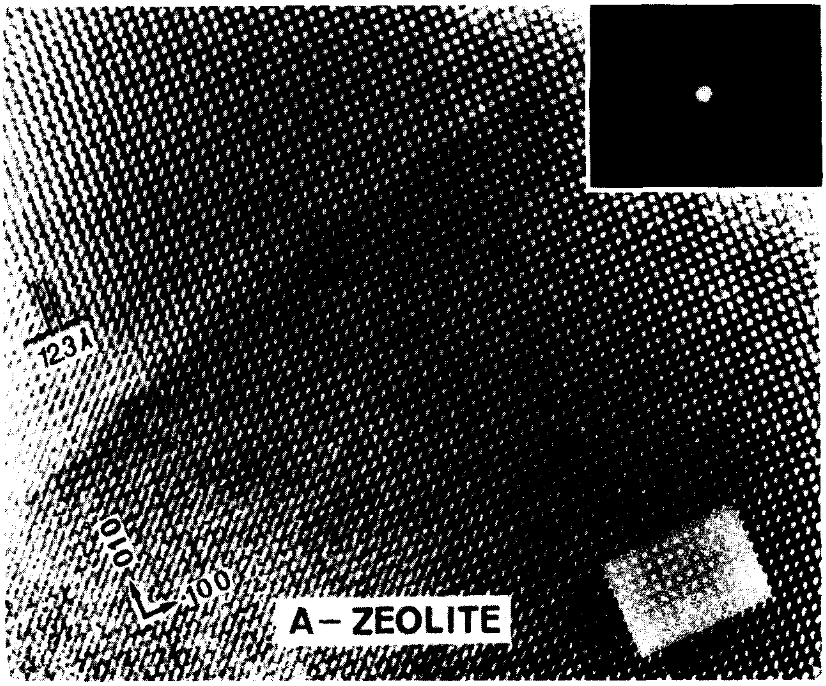

FIG. 6. HREM images of the same region as Fig. 5. It was taken 2 min after Fig. 5. The inset is the corresponding optical transform.

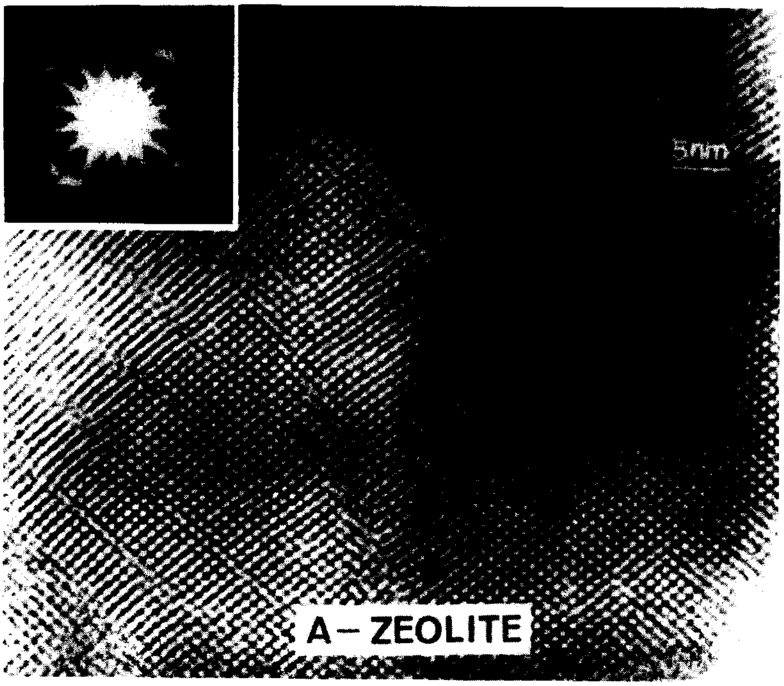

FIG. 7. The HREM image of another region in 5A-zeolite. The inset is the corresponding optical transform. The diffraction spots are diffuse.

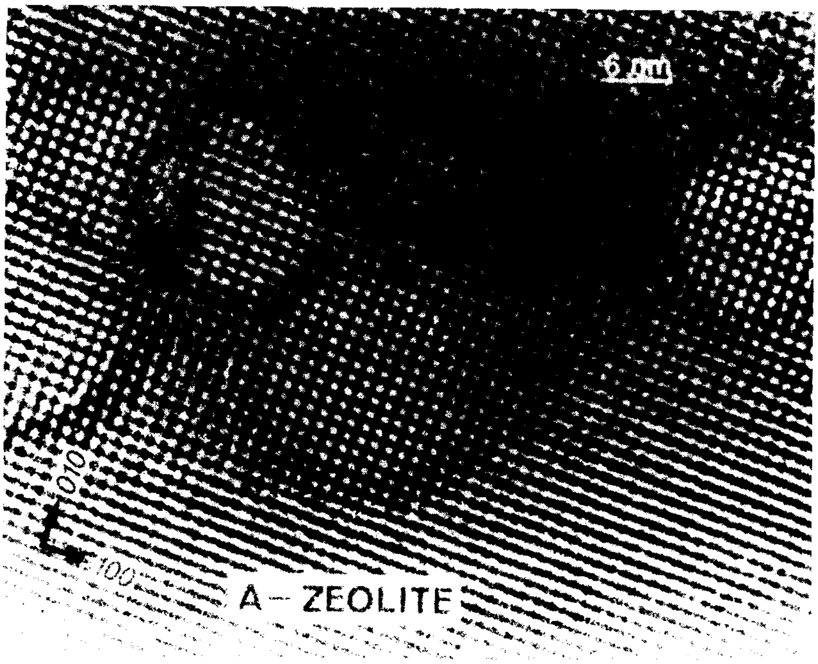

FIG. 8. The "coin structure" (domains) in 5A-zeolite.

taken by HREM as a square net of points with spacing ~12.3 Å. It is interesting to point out that a metastable structure which looks like a long-periodic one was observed in 5A-zeolite (chemical formula: $Na_2O \cdot CaO \cdot Al_2O_3 \cdot 2SiO_2$) as shown in Fig. 5. It can be seen that the atom row arrangement along the [100] direction repeats every five rows as indicated by the arrows, but there is about one third of misfit along the [010] direction. The optical transform result (lower right inset) indicated that the structure is not the common long-periodic one. The diffraction pattern can be considered as consisting of two sets of diffraction spots; one square set corresponding to the undistorted regions and the parallelogram set (vertex angle ~82°) corresponding to the distorted regions (distortion angle ~8°). These local distorted regions can also be observed in other patterns (Fig. 7). The distorted regions differ in their spacing and distortion angle and the corresponding optical diffraction spots became more diffuse (upper left inset of Fig. 7). It is also interesting to point out that the structure is not stable: it is a kind of elastic distortion. After about 2 min of electron beam illumination (excitation) the structure became a perfect cubic structure, as seen in Fig. 6 (the same region as Fig. 5, the inset is the corresponding optical transform). In addition, a kind of domain structure ("coin structure") with diameters of 10–20 nm was also often found in the 5A-zeolite (see Fig. 8). It can be seen that in small round domains the structure is rather perfect and has a little misfit with the matrix. However, the phenomena described above were not observed in 4A-zeolite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$).

Studies of the relations between catalytic activities and the structure imperfections have not been concluded as yet, but the observed structure imperfections may be one of the reasons which make the zeolites unstable in their catalytic activities as measured in experiments.

CONCLUSIONS

The channels and cages in zeolites can be resolved clearly by HREM. Both coherent and incoherent twinning boundaries have been observed in Y-zeolites. There is a tendency to form more incoherent twinning boundaries when Na is substituted by other cations, and the incoherent twinning boundary can be seen as a series of dislocations. Moreover, if the exchanged cations are in excess, they may form separate clusters as seen in Pd-Y zeolite with excess Pd. A metastable structure with elastic distortion was found in 5A-zeolite. Small domains of 10–20 nm diameter with perfect structure and some misfit to matrix were also observed in 5A-zeolite.

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