JOURNAL OF CATALYSIS **178,** 94–100 (1998)
ARTICLE NO. CA982130

# Structure Analysis of the Mesopore in Dealuminated Zeolite Y by High Resolution TEM Observation with Slow Scan CCD Camera

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Received October 23, 1997; revised March 31, 1998; accepted April 28, 1998

**The microstructures of a dealuminated zeolite Y were observed with a transmission electron microscope (TEM) under a very low electron dose condition using a high sensitivity SSC camera for the purpose of elucidating the formation mechanism of the mesopores. Mesopores were distributed three-dimensionally. They were closely related with the preexisting (111) twinning planes. The possibility of controlling the distribution of mesopores by controlling the distribution of twins during synthesis is also mentioned.** © 1998 Academic Press

## 1. INTRODUCTION

Zeolite Y has been used extensively as a catalyst for refining oil and as a material for absorbing emitted gases. In order to extend the applications of zeolite Y, it is necessary to improve its heat resistance. Control of the Si/Al ratio of zeolite Y with a dealumination treatment has been attempted to meet this demand. However, during the dealumination treatment pores with a diameter of approximately 20 nm have been formed in the zeolite grains simultaneously. Such pores are called mesopores. Several studies on the mesopores formed in the zeolite grains have been reported (1, 2), but the formation mechanism has not been clarified yet.

One of the most effective methods of analyzing mesopore microstructure should be TEM observation, especially high resolution electron microscopy (HREM). However, since zeolite is very sensitive to electron beam irradiation, HREM observation under usual conditions is quite difficult. In the present study a TEM equipped with a high sensitivity SSC camera was used to observe microstructure of zeolite Y (3–5).

## 2. EXPERIMENT

HSZ-320NAA and HSZ-360HUA (made by TOSOH corporation) were used as the zeolite Y samples in this study. HSZ-360HUA, which is a dealuminated zeolite Y, was prepared from HSZ-320NAA using an ion exchange with $NH_4^+$ ions and a steam treatment at high temperature (2).

A scanning electron microscopy (SEM) image of the sample of HSZ-360HUA is shown in Fig. 1. This micrograph was taken with a JSM-6000F (JEOL) SEM. As seen from Fig. 1 HSZ-360HUA is built up of 0.2 $\mu$m to 0.3 $\mu$m-sized regular-octahedron grains formed by {111} planes. These particles were dispersed on a copper mesh (#1000) without any mechanical treatments such as crushing. So prepared samples were dehydrated for 2 h at 350°C in a vacuum of $1 \times 10^{-3}$ Torr (1 Torr = 133.3 N/m$^2$). This treatment was carried out to suppress the electron beam radiation damage during the subsequent observation in a TEM. The dehydrated sample was mounted on a specimen holder, and inserted in a TEM with no atmospheric contact.

TEM observations at low magnification were carried out at an accelerating voltage of 400 kV in a JEM4000FX (JEOL) electron microscope, HREM observations were conducted at an accelerating voltage of 200 kV in an EM-002B (TOPCON) electron microscope equipped with SSC camera (model 679 GATAN). The electron beam density used in the present HREM observation was 0.2 A/cm$^2$ at a magnification of 390,000. This electron density was approximately 1/50 of that used for an HREM observation under usual conditions with ordinary photographic films. HREM observations of the dehydrated zeolite Y by using such a low dose condition could be carried out for several minutes without producing any radiation damage. These HREM images were recorded at 1024 × 1024 pixels and exposure time was 2 seconds. Some of the TEM images were treated by FFT method to get clearer information on geometric relation in the microstructure of the zeolite.

## 3. RESULTS AND DISCUSSION

### 3.1. *Configurations of a Mesopore*

A TEM image of a dealuminated zeolite Y (HSZ-360HUA) particle is shown in Fig. 2a. White vein-like

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0021-9517/98 $25.00

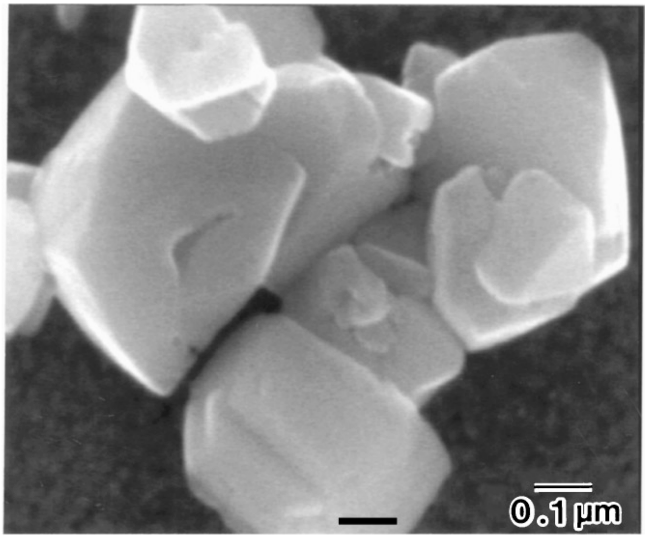

**FIG. 1.** SEM image for the sample of HSZ-360HUA. The grain size of the fine powders is around 0.2–0.3 $\mu$m, and the form of the particles is approximately octahedron formed by (111) plane.

contrasts are observed in the particle. The particle was observed while the sample was being tilted by 10° steps to 50°. A series of the TEM images is shown in Figs. 2b–2f.

When the sample was tilted, the white contrasts (such as $A_1$ and $A_2$) changed their shapes. The particular white contrasts denoted by $A_1$ and $A_2$ which were initially perpendicular to the rotation axis shortened their lengths in a ratio of sin$\theta$ ($\theta$: the rotation angle), and eventually they appeared as two round pores (denoted by $A_1'$, $A_2'$) after being tilted by 50° (Fig. 2f). From these observations, we conclude that those white contrasts are mesopores.

Figure 3 is enlarged a part of Fig. 2f. Lattice images of zeolite Y are shown in Fig. 3. Measurement of the lattice fringe spacing reveals that these lattice images correspond to the (111) plane in zeolite Y crystal. Therefore, it can be concluded that the mesopores are formed on the (111) plane. The distribution of mesopores in zeolite Y particles is summarized schematically in Fig. 4.

From images of mesopores, the diameter of mesopores is estimated to be approximately 15–20 nm. In this case, the influence of diffraction contrast due to the disorder of crystal structure around the pore surface should be taken into account. The diameter of the mesopores did not depend on the size of the zeolite particles that contained them. On the other hand, the length of the mesopore changes from one mesopore to another. From these results, it is concluded that the diameter of the mesopores is almost a constant (15–20 nm), and irrespective of the length of the mesopores. This value is in good agreement with the average value of the diameter of the mesopores measured by the $N_2$ adsorption method (6). Thus, it is predicted that 15–20 nm

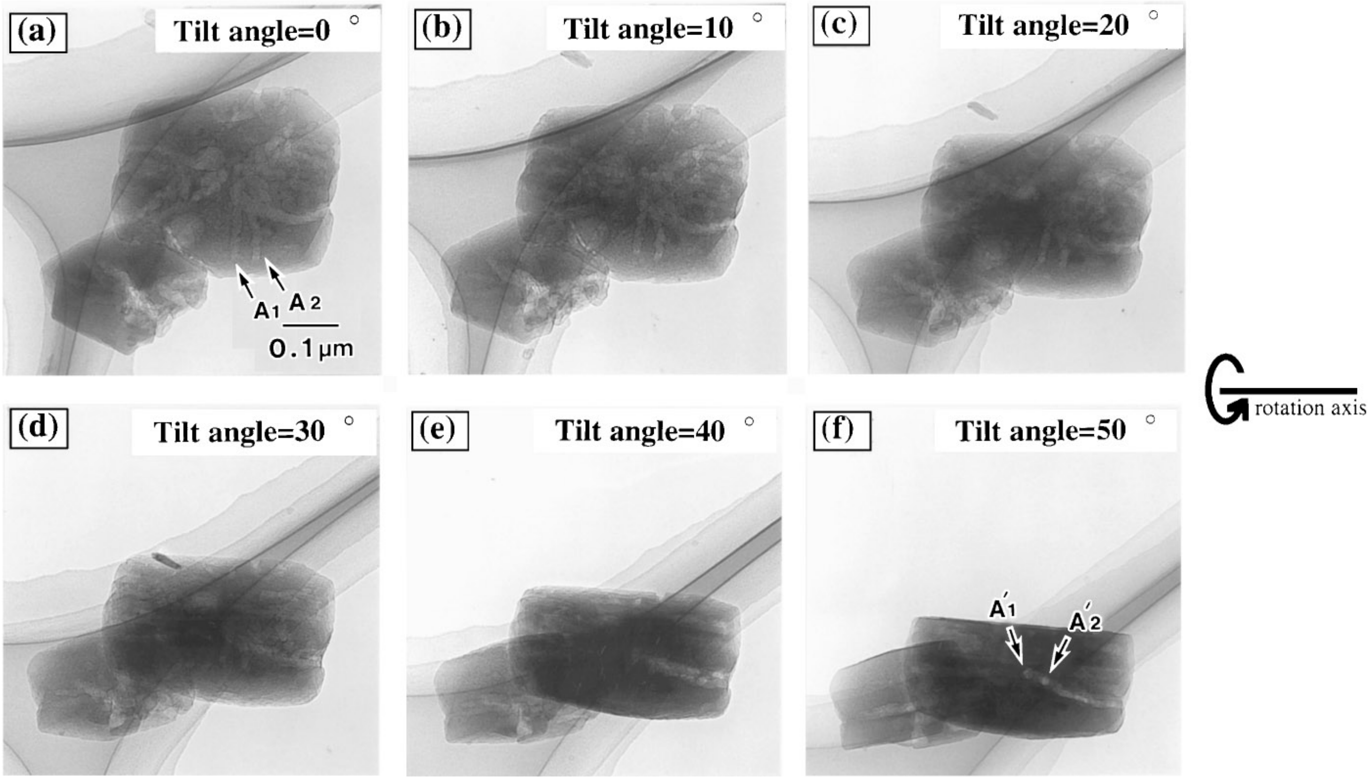

**FIG. 2.** A series of TEM images for the mesopore in zeolite Y (HSZ-360HUA). These images were observed while the sample was being tilted by 10° steps to 50°.

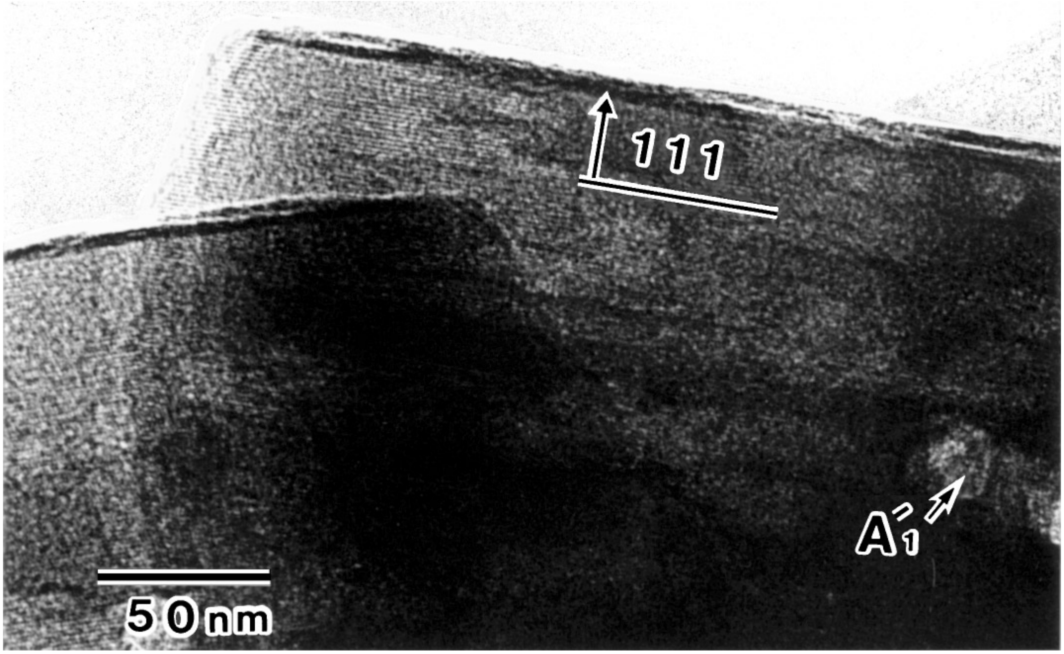

**FIG. 3.** TEM image that a part of Fig. 2f is magnified. Lattice images can be seen. The lattice fringe spacing correspond to the (111) plane in zeolite Y crystal.

is a unique size for the diameter of a mesopore in the dealuminated zeolite Y. It should depend only on the structure property of zeolite Y.

The microstructures of zeolite Y were observed at a higher magnification using an SSC camera. An HREM image of the zeolite Y particle (HSZ-360HUA) is shown in Fig. 5. The white contrast with columnar shape corresponds to the mesopore. Close observation of these micrographs shows that microtwins exist along the mesopores. The twin planes are indicated by arrows; the twins are very thin. From this result, it is concluded that formation of mesopores is closely related to existence of twin planes; the twin plane is selected as the creation site of the mesopore.

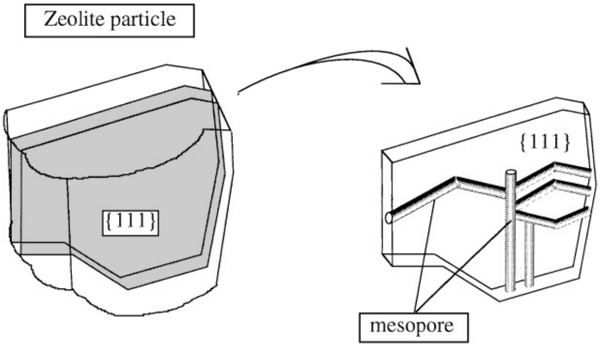

**FIG. 4.** Schematic drawing of the dealuminated zeolite Y. A distribution of the mesopores in the dealuminated zeolite Y is shown.

### 3.2. *HREM Observation of a Twin in the Zeolite Y*

An HREM image of a typical twin in HSZ-320NAA is shown in Fig. 6. This type of twin has been often found in zeolite Y and the density depends on the synthesis condition (7). An image simulation of the twin was calculated using the multi-slice method (8), based on the structure model shown in Fig. 7a, and the result is shown in Fig. 7b. We used the following parameters for this calculation; thickness 10 nm, defocus −35 nm, Cs 0.4 mm, Acc. voltage 200 kV. The observed image agrees with the calculated image very well. Therefore it can be concluded that the twin has a structure shown in Fig. 7a. In this model structure, the twin boundary consists of the oxygen atoms of the T−O−T (T elements are Si or Al) bond in a double six-membered ring. The density of T−O−T bonds is lowest at this twin plane among any planes parallel to the {111} plans. Furthermore, the ordering of the chemical bonds changes in the twin boundary and it is speculated that the T−O−T bond on a twin plane is more unstable than other T−O−T bonds. Zeolite is constituted by bonds between T elements through T−O−T bonds. Therefore, the mesopores should be formed by the dissociation of these bonds. Then, the dissociation of the bonding is most likely to be localized in the twin plane.

### 3.3. *Cross-Sectional Observation of the Mesopores in Zeolite Y*

An HREM image of a mesopore in HSZ-360HUA observed from the ⟨110⟩ zone axis is shown in Fig. 8. The growth

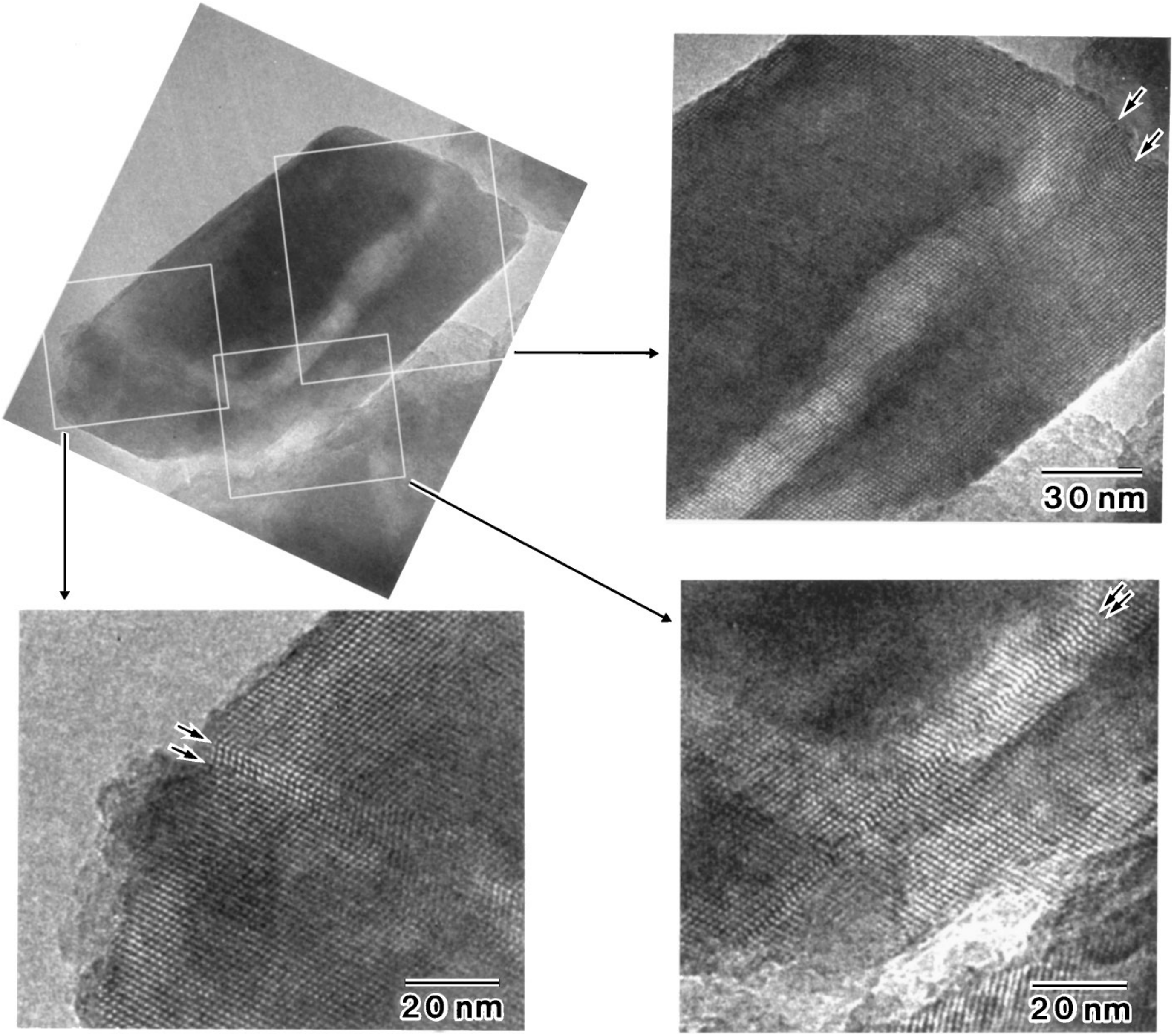

**FIG. 5.** HERM image for the dealuminated zeolite Y (HSZ-360HUA) observed along the [110] zoon axis. The white contrast with columnar shape shows the mesopore.

direction of the mesopore is parallel to the observation direction. This mesopore is formed on one of the two (111) twin planes (indicated by arrows). The cross section of the mesopore is hexagonal and four of the six faces are parallel to the {111} planes and the other two faces are parallel to the {100} planes. Lattice images are observed inside the pore because this pore does not penetrate from the surface to the bottom of the particle. The $\beta$-sodarite cage, which is a unit structure of zeolite Y, is connected with the double six-membered rings, and ⟨111⟩ is the bonding direction of the T−O−T bond in the double six-membered ring. The lattice plane which is parallel to (111) plane can be formed with oxygen atoms of the T−O−T bonds in the double six-membered rings. The TEM image in Fig. 8 suggests that the mesopores are formed by the dissociation of the T−O−T bonds in the double six-membered ring. We can also find the planes constructed with oxygen atoms of the T−O−T bond parallel to the (100) plane in Fig. 7a. Two faces of the mesopore, which are parallel to the {100}, will be formed by dissociation of these T−O−T bonds. Furthermore, the (111) lattice image around the mesopore is disordered. This result suggests the presence of defects in the T−O−T bonds.

Figure 9 shows an early state in the growth of a mesopore in HSZ-360HUA. This mesopore assumes a wedge-shape

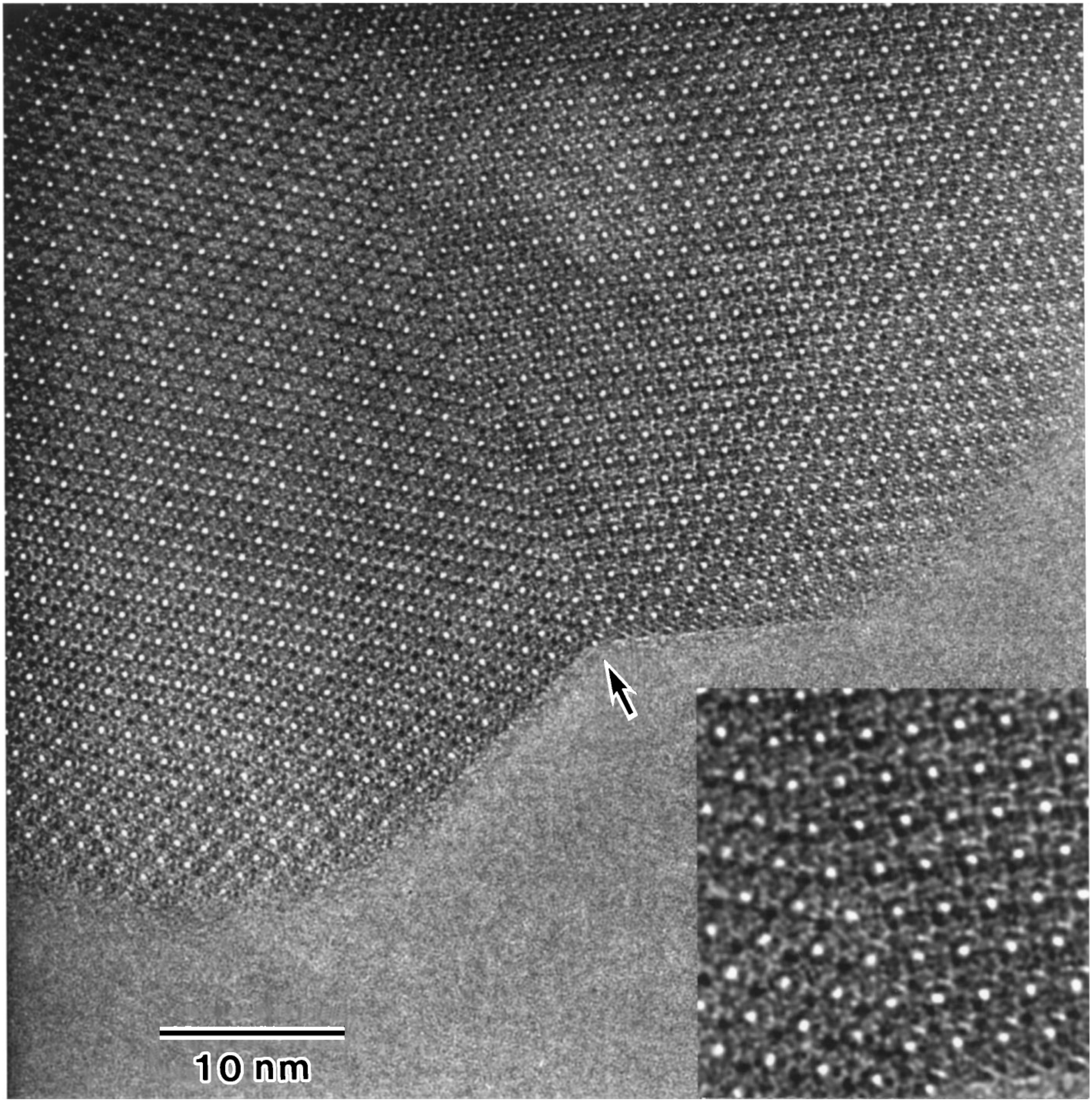

**FIG. 6.** HERM image of typical twin found in the zeolite Y (HSZ-320NAA) observed along the [110] zoon axis.

and the mesopore shape has not been completed. This defect which intersects the (111) twin plane at an angle of approximately 54.7° is formed along the (111) plane. The length of this wedge-shaped defect is approximately 15 nm and is similar to the diameter of the mesopores estimated from the TEM images. This result shows that the diameter of a mesopore is determined in an early stage of its growth.

## 4. CONCLUSION

The origin of the mesopores formed by the dealumination of the zeolite Y was studied. It was shown that a mesopore is formed along ⟨110⟩ directions in the preexisting (111) twin planes. The faces of a mesopore are hexagonal, consisting of the {111} and {100} planes. It is suggested that

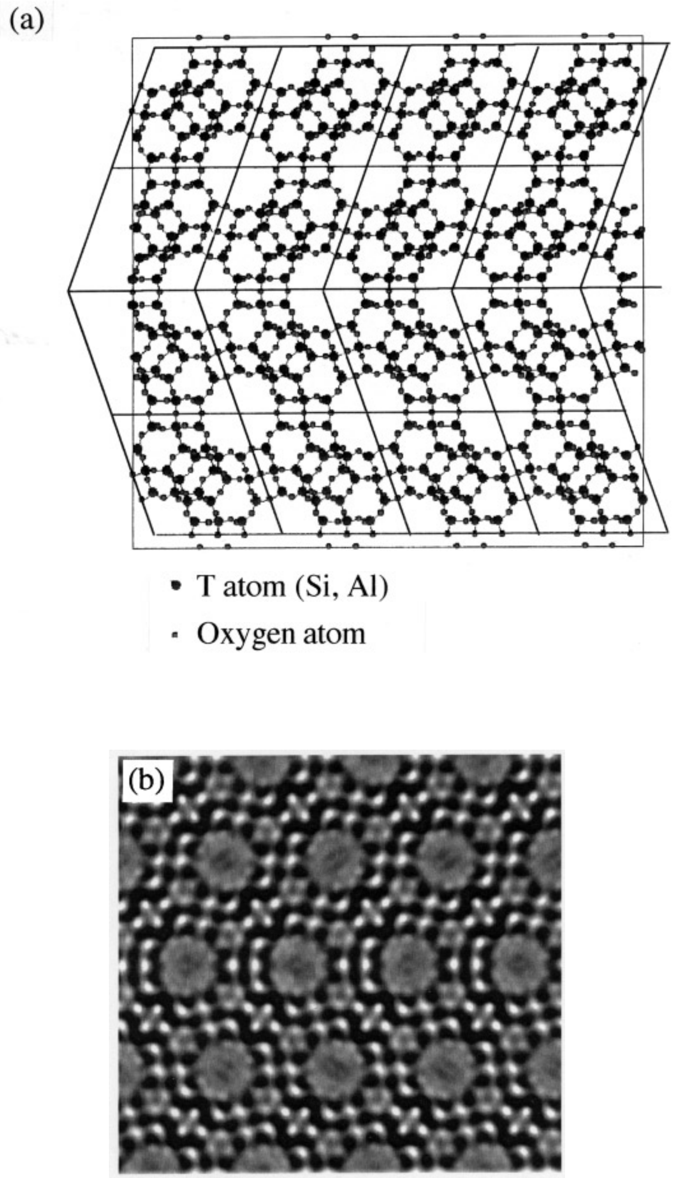

**FIG. 7.** (a) Structure model of a twin in the zeolite Y viewed along [110]. (b) HREM simulation image of the twin calculated at the following condition by multi-slice method. Thickness: 10 nm, Defocus: −35 nm, Cs: 0.4 mm, Acc. voltage: 200 kV.

these faces were formed by the dissociation of the plane constituted with oxygen atoms of T−O−T bonds. The diameter of a mesopore is approximately 15–20 nm, irrespective of the length. The size is likely to be determined at an early stage before the mesopore is completely formed. Thus, it is suggested that the density of a mesopore can be controlled by adjusting the density of the twins by adjusting the synthesis condition. Then, this technique may be applied effectively to improve the adsorption properties and catalysis properties of zeolite Y.

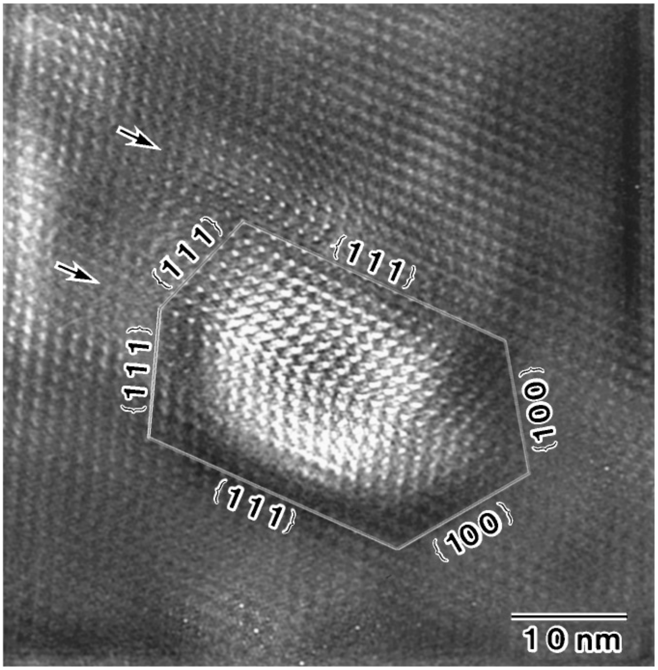

**FIG. 8.** HREM image for mesopore observed from $\langle 110 \rangle$ zone axis. The cross section of the mesopore is hexagonal and four of the six faces are parallel to the {111} planes and other two faces are parallel to the {100} planes.

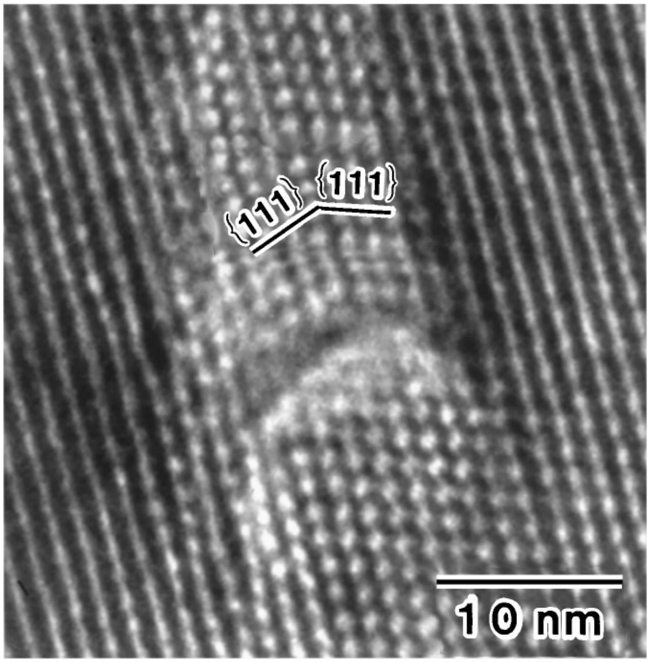

**FIG. 9.** TEM image shows early stage of the growth of a mesopore. A wedge-shaped defect is observed along the (111) plane on both sides of twin.

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