Direct Observation of a New Type Imperfection in Mordenite: Overgrowth of the Different Structure on MOR {110}

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A new type imperfection in mordenite, overgrowth of the different structure on MOR {110}, was observed by transmission electron microscopy(TEM). The overgrowth structure is a very small amount and/or minute, and would be a new zeolite structure produced *locally*.

Zeolites contain various types of imperfections such as dislocations, twins and intergrowths, which can affect catalytic and adsorptive properties depending on the structure and the amount.[1,2] As for mordenite, c-axis fault was confirmed by electron[3] and X-ray diffractions.[4] In this report, we will show the TEM observation of a new type imperfection in mordenite, overgrowth of the different structure on MOR {110}, and discuss the overgrowth structure (MOR means the structure type code of mordenite, space group Cmcm).

Commercial mordenite (SiO_2/Al_2O_3=200,TOSOH Corporation) was dispersed in acetone without crushing and then collected on a microgrid. High resolution observation was carried out at 200 kV using a JEM-2000FX electron microscope with a spherical aberration C_S=2.3 mm. Electron micrographs were recorded at approximate Scherzer focus condition. An X-ray powder diffraction pattern was also obtained to estimate the amount of the overgrowth structure. The pattern was examined in a MAC SCIENCE MXP3 diffractometer with Cu K α radiation

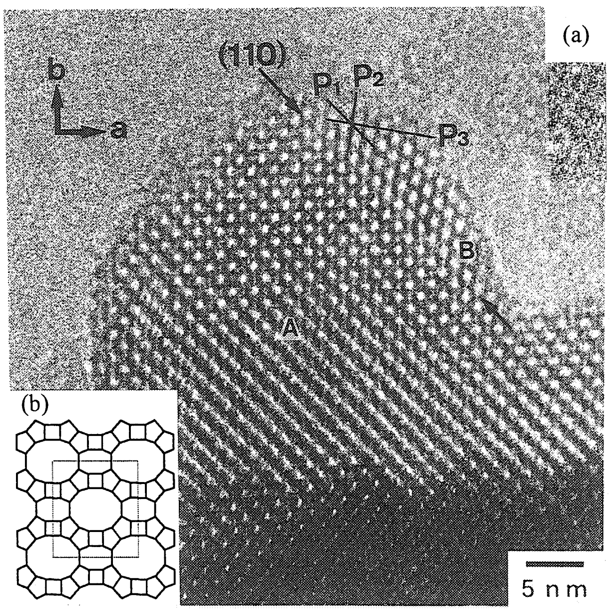

Figure1. The high resolution TEM image of the overgrowth structure on MOR {110} taken with [001] incidence for MOR(a), and the structure model of MOR(b).

Table1. The interplanar spacings of the overgrowth structure

	The interplanar spacings/ Å			
	crystalNo.1	No.2	No.3	No.4
P_1	12.8	12.9	12.3	12.6
P_2	10.5	11.1	11.0	10.4
P_3	7.80	7.85	7.85	7.66

Table2. The interplanar angles of the overgrowth structure

	The interplanar angles/			
	crystalNo.1	No.2	No.3	No.4
P_1^P_2	52	58	54	55
P_2^P_3	92	87	87	91
P_3^P_1	36	35	39	34

at a step of 0.02° in 2 Θ and refined the crystal structure by Rietveld analysis using the program RIETAN.[5,6] The interplanar spacings and angles of the overgrowth structure were measured from images, after a correction of magnification by comparing the lattice parameter, which was determined by the X-ray analysis, with the lattice spacings observed in the image.

Figure 1(a) shows a high resolution TEM image taken with [001] incidence for MOR. The crystal consists of two regions, A and B. They differ from each other in the arrangement of white dots. Region A is MOR. White dots in the region correspond to main channels of MOR with 12 membered rings, and black parts correspond to 8, 5 and 4 membered rings (see Figure 1(b)). The overgrowth structure, observed in region B, growths on the (110) of MOR. The (110) fault plane is situated on the black parts, not the white dots. It indicates that some structural changes occurred in 8, 5 and 4 membered rings of MOR, and then the overgrowth structure grew on them. Additionally, it appears that the overgrowth structure is tilted slightly from the incident, because the white dots in region B, which may correspond to 12 membered rings, are elliptical. In other parts, white spots were observed in nearly circle.

The interplanar spacings and angles of the overgrowth structure were measured from the images in order to analyze the structure. The planes were termed P_1, P_2 and P_3 for convenience as indicated by black lines in Figure 1(a). Observations from four

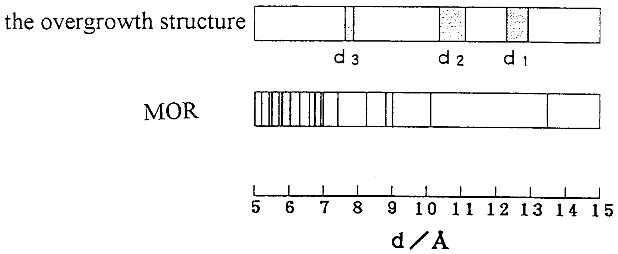

Figure2. The interplanar spacings of the overgrowth structure and MOR. The spacings of the overgrowth structure are plotted as a band from the minimum to the maximum.

different overgrowth structures including one of Figure 1(a) are shown in Table 1 and 2. It is conjectured that four structures are the same overgrowth structures, because the interplanar spacings and angles are in agreement each other . The small differences would be caused by two reasons; the errors due to the differences of the tilted angles from the incidence as mentioned above, and the elasticity of the framework structure.

Figure 2 schematically shows the interplanar spacings of the overgrowth structure and MOR. For the overgrowth structure, the spacings are plotted as a band from the minimum to the maximum shown in Table 1. The spacings are different from each other, and so it is clear that the overgrowth structure is not MOR. And therefore, the possibility of other zeolite structures were examined. The interplanar spacings and angles of seventy five silicate zeolite structures mentioned in ZEOLITE ATLAS[7] were calculated. But taking the size of channels into account, none of them corresponds to the overgrowth structure.

The observed and calculated X-ray powder diffraction patterns are shown in Figure 3(a)(b) respectively, and the difference in Figure 3(c). Assuming that the sample consists of MOR, the Rietveld analysis gave a fit of Rwp=0.109. The difference dose not indicate the presence of any other structures, therefore the amount of the overgrowth structure is under the detection limit by X-ray powder diffraction, that is to say, it is a very small amount and/or minute. In fact, the frequency which we could observe the overgrowth structure by TEM was one per several tens of mordenite crystals. And the domain size was also small.

As described above, the overgrowth structure is not a known zeolite type, and a very small amount and/or minute. It is possible that the overgrowth structure is just a quite distorted MOR. Some studies have been carried out about distorted zeolite structures by TEM. G.W.Qiao et al. observed A-type zeolite which has about one third of misfit along the [010] direction.[8] This distortion is in two-dimension. O.Terasaki reported that Y-type zeolite has twins which dose not penetrate a whole crystal.[9] Dozens of lattices where the twin fades out are distorted, and the degrees of distortion are different. The overgrowth structure differs from reported ones in the dimension. It spreads regularly in three-dimension. For that reason, the overgrowth structure would be a new zeolite produced *locally*. But the amount of the overgrowth structure is quite small, and so the clarification of the structure has not performed. Further investigations are needed.

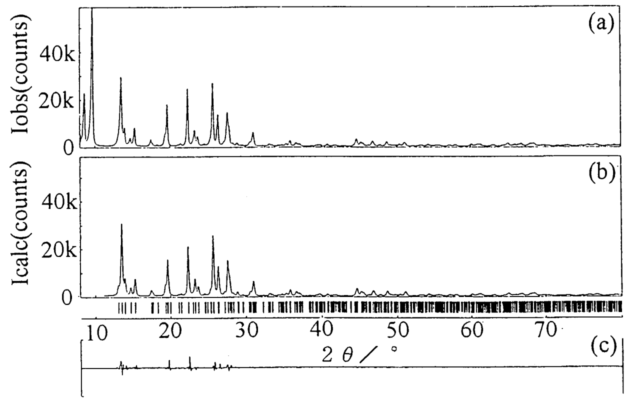

Figure3. The observed X-ray powder diffraction pattern(a), the calculated pattern(b) and the difference(c).

References and Notes

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