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ELECTRON MICROSCOPIC STUDY OF DEFECTS AND METAL PARTICLES IN ZEOLITES

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ABSTRACT

Zeolite-Y and ZSM-5 were studied with high resolution transmission electron microscopy. In Zeolite-Y only a (111) twin defect is frequently present. In ZSM-5 intergrowth of crystals of a completely different orientation often occurs. Artifacts due to intergrowth of two lattices and misorientations are shown. The presence of metal particles in ZSM-5 can be observed best by destruction of the zeolite lattice by the electron beam. No indication for a sintering of the metal particles due to the destruction of the zeolite lattice was observed.

INTRODUCTION

High resolution transmission electron microscopy (HRTEM) is a very powerful tool in the characterisation of catalytic materials [1,2]. In the investigation of zeolites by HRTEM the major problem is the high sensitivity of zeolites for the electron beam. Unless special precautions are taken it is not possible to select, orientate and take photographs of most zeolites. A number of preparations are reported which stabilize the zeolites [3]: dealumination, ion exchange to the H-form, ion exchange by \(\text{UO}_2^+\) ions. Until now, only a few papers have been published on HRTEM on metal particles in zeolites, mainly in Y-zeolite. A review is given in [4]. We are interested in defects in the structure, the frequency of their occurrence and their influence on the distribution of metal particles in the zeolite. Furthermore we are interested in the size, position and orientation of metal particles in the zeolite matrix. In this paper defects occurring in zeolite-Y and ZSM-5 are shown. Examples are given of artifacts which can easily lead to wrong conclusions and the depiction of small metal particles in ZSM-5 is discussed.
FIGURE 1 A [110] micrograph (a) of zeolite Y showing two (111) twin planes. The combination of the images of the twin and the matrix give a tripling of the period in the [111] direction (indicated by 0). b shows the image obtained by a (111) twin plane. The bar represents 10 nm.

EXPERIMENTAL

Several ion exchange experiments were carried out on a number of zeolite-Y samples to investigate which modification was most stable in the electron beam. Ion exchanges were carried out on Na-Y with NH₄Cl, LiCl, MgCl₂, PbCl₂ and LaCl₃. After calcination at 400°C the Li-form was found to be 2 to 10 times more stable than the other forms. Similar experiments on ZSM-5 using NH₄Cl, LiCl and CsCl showed no significant differences. Pt was introduced to NH₄-ZSM-5 (Si/Al ratio 70) by ion exchange with an aqueous solution of [Pt(NH₃)₄](OH)₂. The samples were oxidized in a He₂/O₂ flow by slowly increasing the temperature to 320°C. For the HRTEM study a suspension in methanol of the dry zeolite sample was brought on a carbon coated Formvar holy film on a copper grid. Only when no metal particles had to be detected the grid containing the zeolite particles was sometimes carbon coated again to reduce movement of the crystals due to the electron beam.

HRTEM was carried out with JEOL 200 CX microscope with top entry and double tilt of 10°.

RESULTS

One kind of defect only occurs very often in the zeolite-Y samples investigated: a (111) twin defect. Depending on the orientation of the (111) twin plane different images are obtained on photographs taken of zeolite-Y in the [110] orientation (Figure 1).

In ZSM-5 often intergrowth of completely differently oriented ZSM-5 is often observed (Figure 2).

Artifacts can occur relatively easily because the sensitivity to the electron beam of the zeolite crystals does not permit a thorough investigation of one given crystal. In Figure 3 two micrographs are shown of the same zeolite-Y crystal. The left micrograph is in a [110] orientation whereas the right one is tilted over 10°. It is evident that tilting the crystal out of the correct orientation leads to diffuse bands which may easily be interpreted as defects in the structure. With materials which are stable in the electron beam the orientation of the crystal photographed can be checked. This is often impossible for zeolite crystals.

Another artifact can be seen in Figure 1a. In the section indicated by 0, a tripling of the period in the [111] direction is seen. This is in fact a combination of the images obtained from the matrix and the twin.
FIGURE 2 Two micrographs of ZSM-5 partly in a [010] orientation and a complete differently oriented intergrowth. From the diffraction pattern it was found that the spacing of the intergrowth in a is from $d_{101}$ and that the orientation is about 10° out of [010]. The projection of [001] is given by the dashed line. The orientation of the intergrowth in b is not known. The spacing corresponds with $d_{101}$ and $d_{011}$. The combination of the both images leads to a Moiree pattern in b.
FIGURE 3 Micrographs of the same crystal of zeolite-Y in a [110] orientation and an orientation tilted 10° from [110]. Due to the misorientation diffuse bands occur. The distance between the diffuse bands depends on the angle of misorientation and the thickness of the crystal. The bar is 10 nm.

Detection of small Pt particles in ZSM-5 is hampered by the dominant image of the zeolite lattice. After destruction of the zeolite lattice, using the electron beam, the Pt particles can be seen much better. We did not observe changes in the metal particle size during destruction of the matrix. Figure 4 shows micrographs of the same area of ZSM-5 containing Pt particles. When the zeolite lattice is destroyed metal particles as small as 0.9 nm can be detected.

Knowing the positions of the metal particles from the image with the destructed zeolite lattice many of the particles can be seen in the micrograph with the undestroyed zeolite lattice. Since TEM images are a projection of both the zeolite lattice and the metal particles on a plane perpendicular to the electron beam, it is impossible to verify from one photograph whether the metal particles are in the zeolite crystalites or at the surface. This could be done taking stereo photographs.
However, for our experiments, it can still be concluded that the small metal particles observed are in the zeolite pore system because of two reasons. First, on none of the photographs small metal particles were seen on the edge of the crystals. When metal particles were seen on the edge they were very often larger than 4 nm. This is illustrated in Figure 5, where a micrograph is shown of Pt ion-exchanged ZSM-5, which has not been oxidized properly. This causes a migration of most of the platinum to the surface forming cubic crystals. Lattice fringes in such crystals and their morphology suggest these crystals to be PtO₂. Second, at the edge the thickness of the zeolite crystal is 5 - 30 nm. Since no metal particles are observed on the edge and a large number of particles is observed in an area of 5 - 30 nm width all over the crystal the particles cannot lie on the surface.

The positions of several metal particles in ZSM-5 are shown in Figure 6. Image simulations, using the Real Space method (5) suggest the white dots to be the intersections of two channels, running along the a and b axes respectively, and the thickness of the crystal to be smaller than 10 nm. Two metal particles, each probably occupying one intersection, can be seen at 1 and 2. Metal particles occupying two neighboring intersections can be seen at 3 and 4. The intensity of the much darker image of the particle at 4 may be caused by the orientation of the...
metal particle but can also be due to the occupation of four intersections, depicted as two intersections because of the projection. A micrograph taken after tilting the crystal over $5^\circ$ shows similar particles, with a slightly different distance between the particles.

\textbf{FIGURE 6} $[100]$ micrograph of Pt containing ZSM-5 showing the location of the metal particles in the zeolite matrix. The bar is 10 nm.

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\textbf{REFERENCES}