JOURNAL OF SOLID STATE CHEMISTRY 84, 171–177 (1990)

LETTERS TO THE EDITOR

On Crystal Structure Imaging of Silicalite by HREM

V. ALFREDSSON, O. TERASAKI,* AND J.-O. BOVIN

National Center for HREM, Chemical Center, University of Lund, P.O.B. 124, S-221 00 Lund, Sweden

Communicated by A. Rabenau, October 6, 1989

High-resolution electron microscopy (HREM) images of silicalite (ZSM-5) along [010] were taken with a 400-kV EM with a resolution of 1.6 Å. The images contain a dark contrast in the centers of the main channels, where there are no atoms. This contrast is an artifact and is not appreciable in the HREM images which have been published so far. That this problem can be overcome by choosing the proper experimental conditions was confirmed by both computer-simulated and experimental HREM images. Computer image processing is also applicable to this kind of problem. © 1990 Academic Press, Inc.

Introduction

HREM is one of the best techniques for characterizing materials which are incorporated into the voids of zeolites (*1*). Chan *et al.* have recently simulated HREM images to investigate the visibility of a 13-atom Pt cluster in the channels of zeolite-Y (FAU) along [110] for a 200-kV EM and pointed out a new problem for which intuitive interpretation does not work; i.e., dark patches appear even in empty channels of the zeolite (*2*). Experimental conditions for HREM must therefore be carefully chosen to obtain an intuitively interpretable image. As far as we know there is no report on the solution of this and here we show by experiment and image simulations a way to overcome this problem for silicalite.

ZSM-5 crystallizes in the space group *Pnma* with the cell parameters a = 20.07, b = 19.92, and c = 13.42 Å (*3*). Along [010] there are straight channels with openings defined by 10-membered rings of a diameter of about 5.5 Å. This direction is suitable for HREM image recording. These main channels are surrounded by eight five-membered rings (5R) and two six-membered rings (6R). The axis passing through the centers of the main channel or through those of the 6R is a twofold rotational axis. This is the only visible difference along [010] between ZSM-5 and ZSM-11 which has a closely related structure. The latter has a mirror-plane in the yz-plane.

Experimental and Image Simulation

HREM images of silicalite were taken along [010] by use of a JEM-4000 EX (C_s = 1.0 mm, resolution = 1.6 Å) with objective apertures of two different sizes (1.0 and 0.3 $Å^{-1}$). The image simulations were carried

* Permanent address: Department of Physics, Tohoku University, Sendai 980, Japan.

0022-4596/90 $3.00
Copyright © 1990 by Academic Press, Inc.
All rights of reproduction in any form reserved.

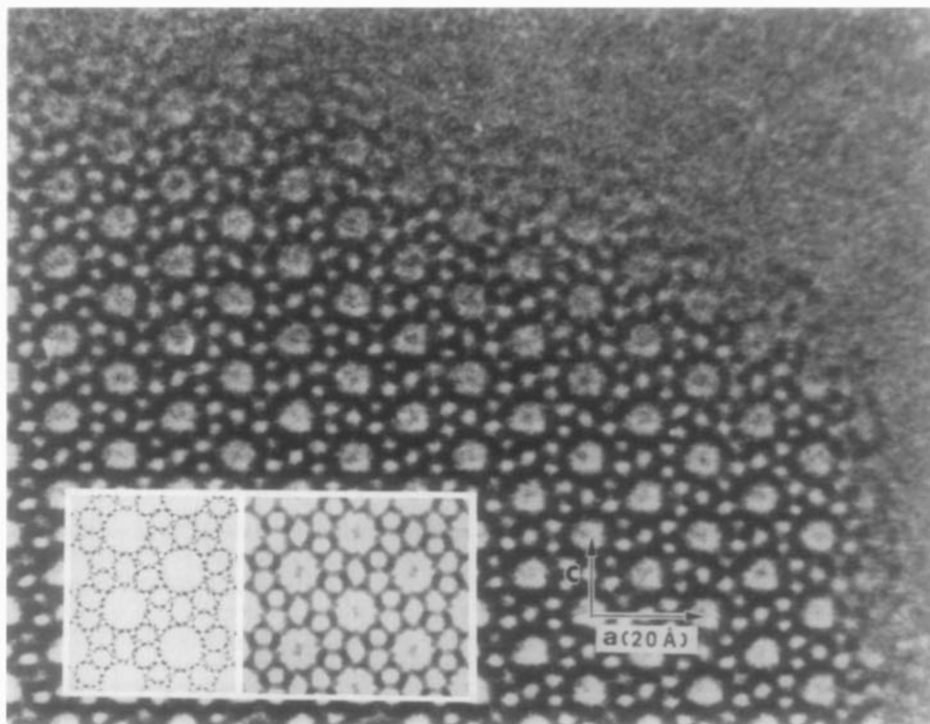

FIG. 1. High-resolution electron micrograph of silicalite recorded along [010] with a 400-kV microscope. Inserted are a simulated image at Scherzer focus and a drawing of the framework structure. An objective aperture of 1.0 $Å^{-1}$ was used.

out with a local version of the SHRLI programs (*4*).

Results and Discussion

An experimental image of silicalite of the [010] incidence is shown in Fig. 1. It was taken with an objective aperture of 1.0 $Å^{-1}$ and close to Scherzer focus. Inserted in the image are the corresponding simulated image and a drawing of the framework structure. In the micrograph the big channels as well as the smaller channels are clearly seen and the twofold axes are recognizable from the distribution of two different sizes of 5R. In the centers of the channels there are dark patches, although there are no atoms.

The contrast in an HREM image from a thin crystal is roughly proportional to the projected potential (or charge) density convoluted with the contrast transfer function (CTF) and with the objective aperture function. Thus, it has been simply believed that an HREM image will be closer to the projected potential density if the resolution of the electron microscope is improved, and therefore that the incorporated materials are imaged as dark contrast with well-resolved framework structures in the HREM images. The projected potential density is the Fourier sum of the crystal structure factors for the electrons and these have for the $\{h0l\}$ reflections the relations

$$F(h0l) = F(-h0-l) = F(h0-l) = F(-h0l) \quad \text{for } h+l=2n$$

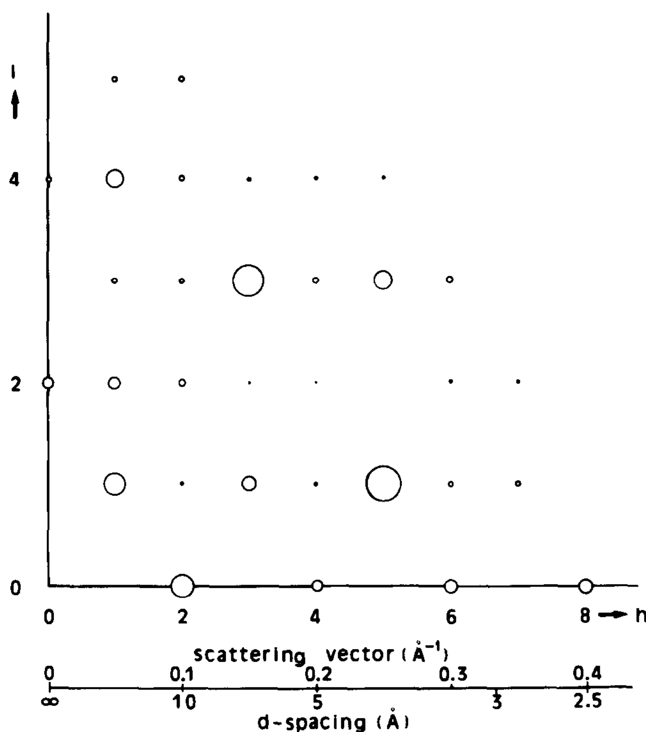

FIG. 2. Diagram showing sizes and locations of the different reflections important in creating the image. By using different objective aperture sizes one can choose which reflexions to include in the micrograph.

$$F(h0l) = F(-h0-l) = -F(-h0l) = -F(h0-l) \quad \text{for } h+l = 2n+1,$$

and their magnitudes are schematically shown in Fig. 2 for the reflections which have d-spacings larger than 2.5 Å. The reflections with $h + l = 2n + 1$, such as {102} and {104}, do not contribute primarily to the contrast at the center of the main channels but to give the correct symmetry of the image (5). The contrast at the center of the channels is built up by the reflections with $h + l = 2n$, mainly by {101}, {303}, {503}, {200}, and {501} reflections. It becomes clear from the consideration of their magnitudes and signs that the contribution from {101} is important for obtaining the correct contrast. The CTFs for two different conditions (−500 and −800 Å) are shown in Fig. 3. As can be seen from the figure, transmission for the {101} reflections at 500 Å underfocus, which is close to the condition for Fig. 1, is lower than that of the other reflections. This will make the dark contrast outweigh the bright one and there will thus be dark patches in the center of the main channels. To get rid of these patches the contribution from the {101} reflections must be enhanced. A way to accomplish this is to change the shape of the CTF by lowering the focus (see Fig. 3 at −800 Å). The reflections with small scattering vectors are given higher transmission but the reflections above zero cross give contradictory information to the image. A smaller objective aperture (r = 0.3 Å^{-1}) will remove this contribution. Although some resolution will be lost (see Fig. 2), the reflections needed to

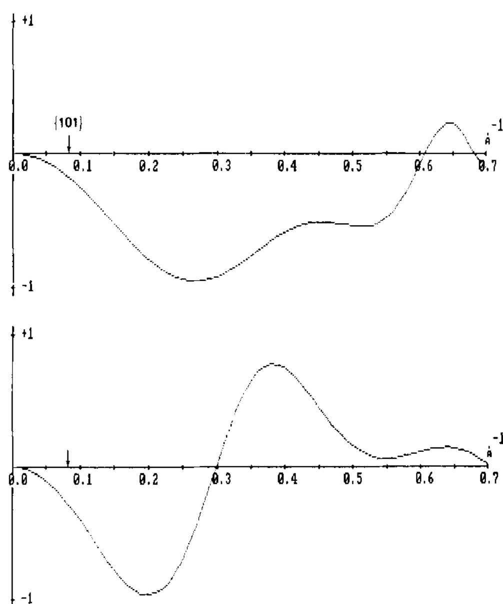

FIG. 3. Contrast transfer functions of the microscope used (C_s = 1.0 mm, C_c = 1.7 mm, α = 0.0003 rad) at different focuses; top at −500 Å, below at −800 Å. The position of the {010} reflection is marked.

create the essential part of the image, that is the contrast of the channels and the true symmetry of the framework structure, are within the area of the small objective aperture. This simple consideration was confirmed by fully dynamical image simulations. The computer-simulated images in Fig. 4 were calculated for an objective aperture of 1.0 Å^{-1}, crystal thickness 40 Å, and focus values ranging from 0 to −1100 Å with intervals of 100 Å. The dark patches as well as the fine details of the framework structure in the observed image (Fig. 1) are well reproduced in the simulated images close to Scherzer focus. In Fig. 5 the same changes of focus as those in Fig. 4 have been made but with an objective aperture of 0.3 Å^{-1}. At an underfocus of 800 Å, the dark patches have disappeared and the twofold rotational axes are also clearly seen. These will be the conditions to use if the difference between an empty silicalite and a silicalite in which atoms have been implanted is to be discerned. The range of focus values where this could be accomplished is rather broad, from about −700 to −900 Å. An experimental micrograph taken under these new conditions is shown in Fig. 6. The channels do not contain any patches and the twofold axes are also clearly seen.

These dark patches observed in the HREM image are due to a type of termination effect for small scattering vectors through CTF. This is ironically enhanced by improving the EM resolution. We have noted, by using microscopes with different accelerating voltages (1000, 400, and 200 kV), that the stability of the zeolite is better in higher voltage microscopes. Image processing, by means of the Wiener filter method, applied to this type of problem improves the correctness of the experimental image (see Fig. 7). Higher resolution is of course desirable to give as much detail as possible in the image. A detailed discussion of the image processing will be published later.

Conclusion

The artifact problem in EM work with silicalite can be overcome either by working under the experimental conditions here described or by image processing. It will thus probably be possible to distinguish in a focal series of HREM images between an

FIG. 4. Computer-simulated images with an objective aperture of 1.0 Å^{-1}. Simulations are made from focuses of 0 to −1100 Å with intervals of 100 Å.

FIG. 5. Computer-simulated images with an objective aperture of 0.3 Å^{-1}. The same focus steps as those in Fig. 4.

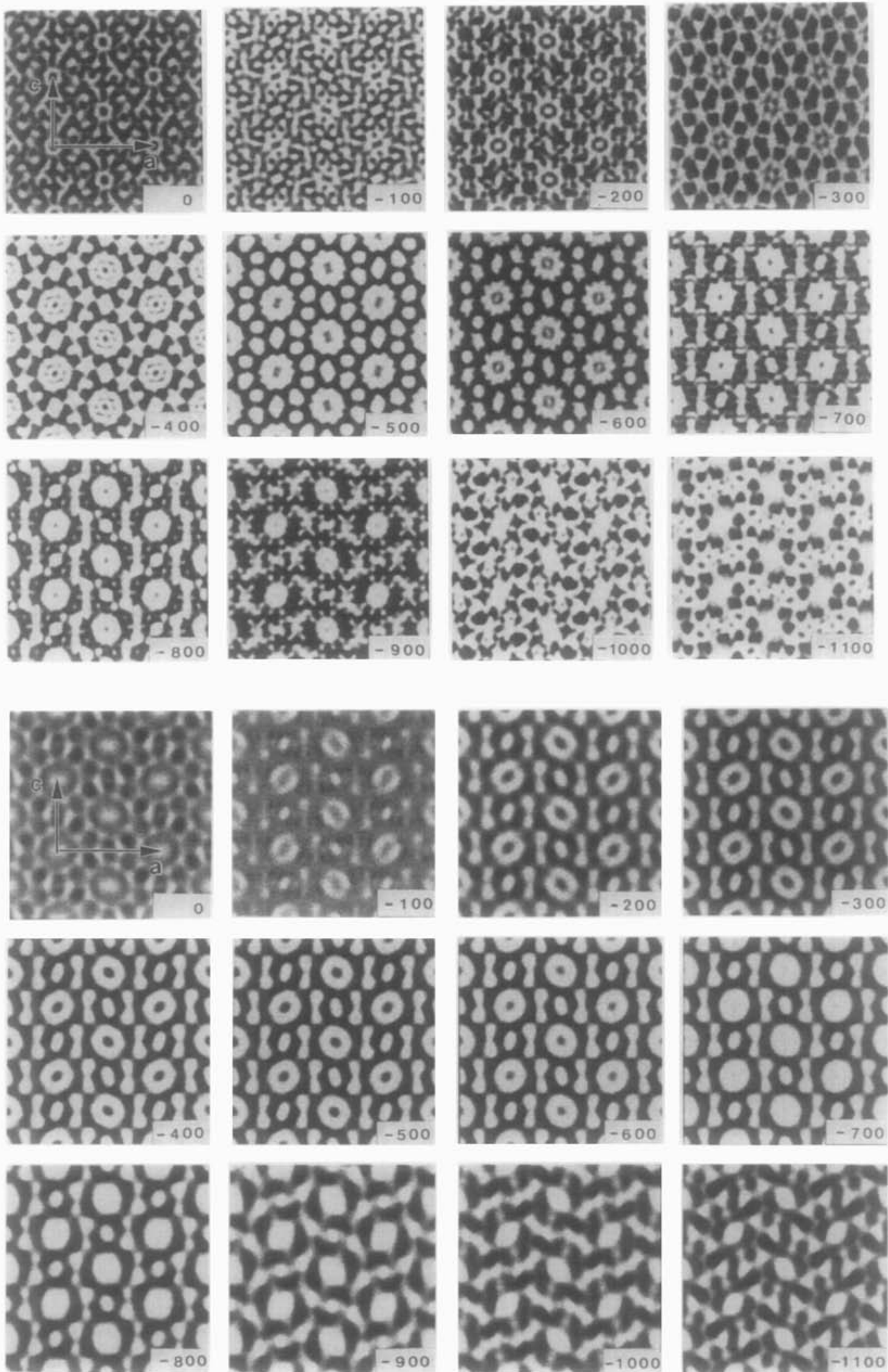

FIGURE 5.

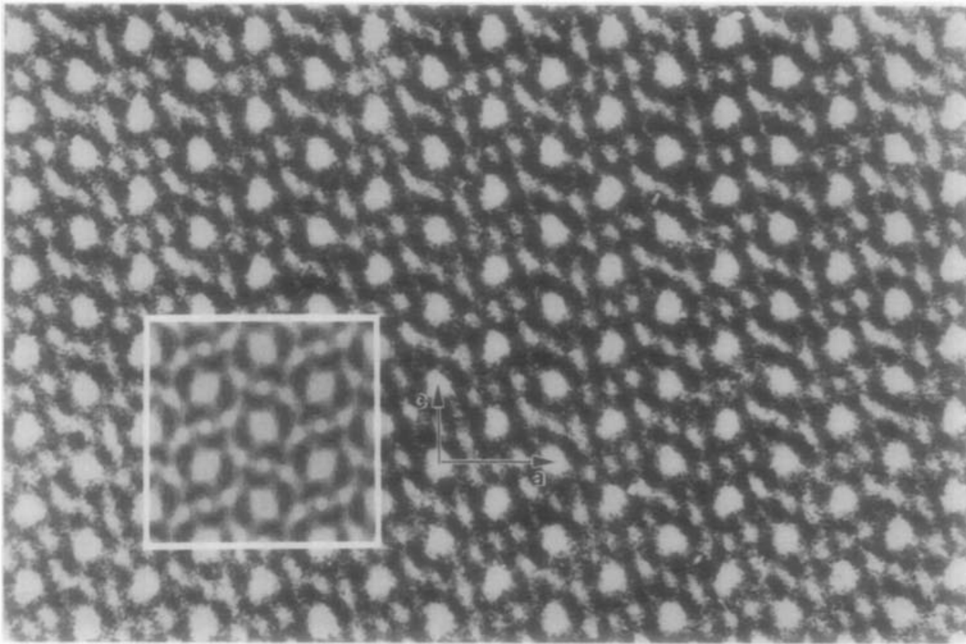

FIG. 6. High-resolution electron micrograph of silicalite recorded at 400 kV using an objective aperture of 0.3 Å^{-1}. The focus was about −800 Å. The inserted simulated image was computed for these conditions.

empty silicalite and a silicalite in which particles have been implanted.

It is also shown that it is necessary to carefully interpret HREM images of crystals with big unit cell constants, such as zeolites, and also of micrographs taken with electron microscopes of higher resolution.

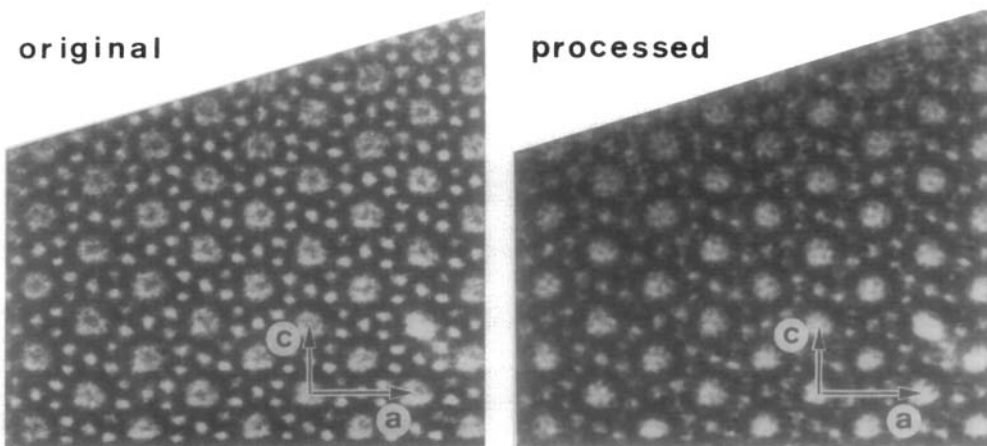

FIG. 7. Electron micrograph recorded under the same conditions as those in Fig. 1 (left). The same image after image processing with the Wiener filter method (right).

Acknowledgments

We thank the Swedish Natural Science Research Council (NFR) and the Board of Technical Development (STU) for financial support. O.T. thanks NFR for the support received as a visiting professor at Lund University and Professor S. Andersson for discussions. We also thank Dr. K. Tsuno at JEOL Akishima in Tokyo for help with the image processing.

References

1. O. Terasaki, K. Yamazaki, J. M. Thomas, T. Ohsuna, D. Watanabe, J. V. Sanders, and J. C. Barry, *Nature (London)* **330,** 58 (1987); *J. Solid State Chem.* **77,** 72 (1988).
2. I. Y. Chan, R. Csencsits, M. A. O'Keefe, and R. Gronsky, *J. Catal.* **103,** 466 (1987).
3. D. H. Olson, G. T. Kokotailo, S. L. Lawton, and W. M. Meier, *J. Phys. Chem.* **85,** 2238 (1981).
4. M. A. O'Keefe, P. R. Buseck, and S. Iijima, *Nature (London)* **274,** 322 (1978).
5. O. Terasaki, J. M. Thomas, G. R. Millward, and D. Watanabe, *Chem. Mater.* **1,** 158 (1989).