Development and Application of 3-Dimensional Transmission Electron Microscopy (3D-TEM) for the Characterization of Metal-Zeolite Catalyst Systems

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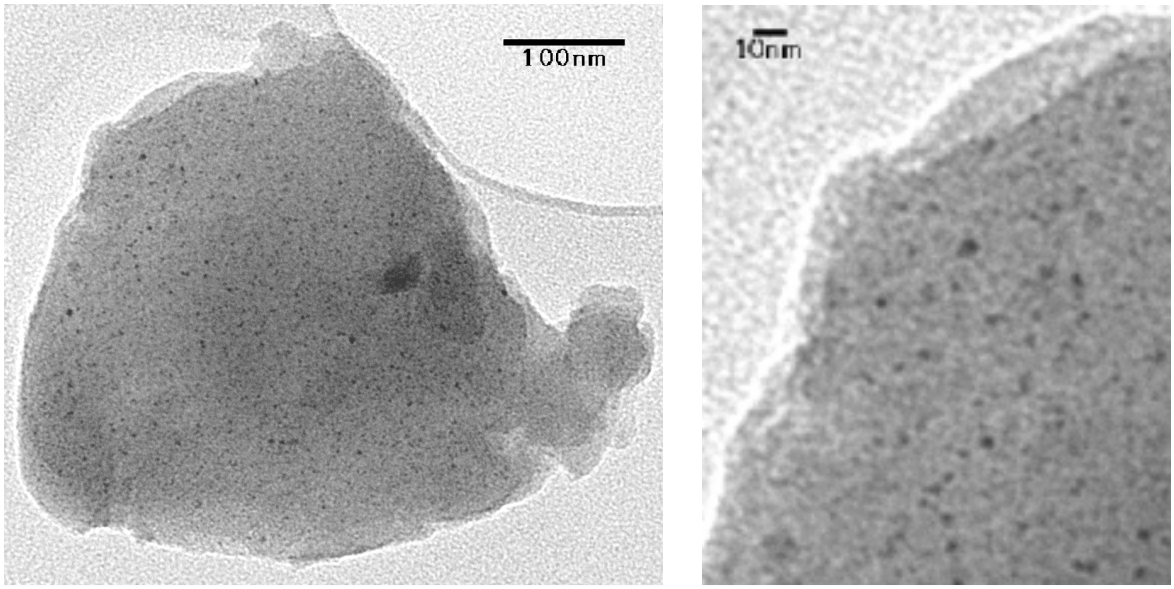
With electron tomography (3D-TEM) a 3D-reconstruction is calculated from a series of TEM images taken at a tilt angle range (tilting range) of +70° to –70°. The reconstruction can be visualized with contour surfaces that give information about the surface of the sample as well as with slices through the reconstruction that give detailed information on the interior of the sample. Electron tomography gives much more information than Scanning Electron Microscopy (SEM), since SEM gives only information about the surface of a sample. As a case study, the imaging of silver clusters on zeolite NaY is given. The reconstruction shows silver particles at the external surface as well as a silver particle in a mesopore of the zeolite crystallite. It is concluded that 3D-TEM comprises a breakthrough in the characterization of nano-structured solid catalysts.

1. INTRODUCTION

Solid catalysts are of tremendous importance for economy and environment. The drive towards clean and efficient technology calls for precise design and characterization of catalysts. Today, many solid catalysts can be considered as sophisticated, three-dimensional nano-structured materials [1,2]. Especially zeolites and mesoporous materials are well known for their three-dimensional structures. To date, however, no method has been reported that is able to provide structural information in three dimensions with 1-30 nm resolution. In two dimensions, Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) can provide a surface image of a material at atomic resolution. Scanning Electron Microscopy (SEM) can provide a high-resolution image of a surface in three dimensions (topography), but the material below the surface is not imaged. Transmission Electron Microscopy (TEM) does give high-resolution information of a sample, but the three-dimensional information is projected into a 2D image. The information in the third dimension is lost. Figure 1 shows a TEM image of a Pt/NaY catalyst, which illustrates the absence of three-dimensional information. From Figure 1 it cannot be determined where the Pt-particles are located: inside the zeolite crystal or at the external surface. However, with the development of electron tomography (3D-TEM) it has become possible to get a 3D image of both the surface and the interior of a sample.

During the last five years automated electron tomography has been developed in the field of biology [3,4], although the theory has been developed much earlier. Due to the automation of the data collection and the increased performance of personal computers, electron tomography can now be applied for practical assays with reasonable investments in time and hard- and software.

In this paper the first application of electron tomography in material science is presented. A concise introduction in the theoretical and practical aspects of 3D-TEM is described. As a case study, the 3D imaging of an Ag/NaY catalyst is given. This system is of fundamental interest to assess metal mobility under reducing and oxidizing environment in zeolites as is apparent from the work of Beyer et al. [5]. In this paper, however, we will restrict ourselves to the study of a freshly reduced Ag/NaY sample.



a **b**

Figure 1a and b: (2D)-TEM image of Pt/NaY. Figure 1a is taken at a magnification of 27.5k, Figure 1b is an enlargement of the left side of Figure 1a.

2. THEORY OF 3D-TEM

A TEM image is in good approximation a projection of the 3D structure of the sample. This causes that information about the 3D ordering of the structure is lost. This is shown in Figure 2, where the projections of several 3D structures are depicted. Although stereo images of a sample can contribute to the understanding of the 3D ordering of the sample, electron tomography is the only technique that is able to provide a 3D electron microscope image of a sample.

With electron tomography a 3D image is reconstructed from a series of (2D) TEM images, taken at different tilt angles. The resolution of a 3D reconstruction is approximately given by the relation: Resolution = π * thickness of the sample / number of images, assuming that a tilt series is taken over the full tilt range ($\pm$ 90°) with a constant tilt increment [3,4]. For example, when 150 images are taken of a 100 nm thick object, a resolution of 2 nm is obtained.

In practice, however, the tilting range is limited to about $\pm$75°, due to physical limitations of the sample holder. This causes that the resolution of the 3D reconstruction is direction

dependent and that structures are slightly elongated in the direction of the angular gap. Therefore, the tilting range should be chosen as large as possible. However, at high tilt angles the travelling path through a non-spherical sample may increase, thus causing loss of contrast due to multiple scattering of the electrons. For example, the path through a 200 nm thick sample will be 580 nm at 70° tilt.

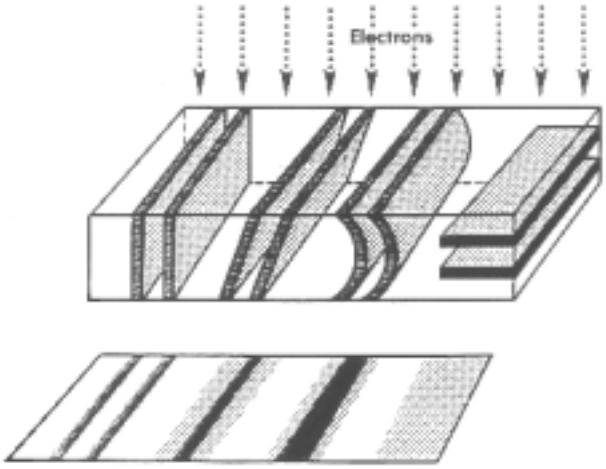


Figure 2: Loss of information when projecting 3D structures into 2D images.

Changing the specimen tilt angle causes a change of focus and shifting of the sample. These changes have to be corrected in order to obtain a pre-aligned data set. Correcting these changes manually is tedious, time-consuming and prune to error. Fortunately, with automated electron tomography [3], these corrections are carried out automatically. An essential aspect of this method is that the electron microscope images are collected digitally with a slow scan CCD camera. The digital images are used for the automatic compensation of image shift and focus change.

After the acquisition of a pre-aligned data set, the data series has to be aligned more accurately. This can be done with the help of fiducial markers. Gold beads sprinkled on the grid or metal particles in/on the sample can serve as markers. By least-squares fitting of the positions of these fiducial markers, the data series is aligned.

After the alignment of the data series the 3D reconstruction has to be computed. The basics of the method were already proposed in 1917. It was stated that the projection of a 3D object is equal to a central section of the Fourier transform of that object. A data series thus provides many different central sections of the Fourier transform of the sample, thus filling the 3D Fourier space. By inverse Fourier transform of the obtained 3D Fourier space a 3D image of the original object is obtained. An algorithm that is often used for the computation of the 3D reconstruction is resolution-weighted back-projection [4].

Finally, the 3D image can be visualized in different ways. One way is to build a contour model in which the outer surface of the object is visible. Another possible way of visualization is cutting the 3D image in thin, nm-thick, slices. By looking at the individual slices one can exactly locate metal particles inside zeolite crystals in three dimensions with high resolution.

If the sample is dose-sensitive, methods are available to collect datasets under low-dose conditions and at cryo-temperatures.

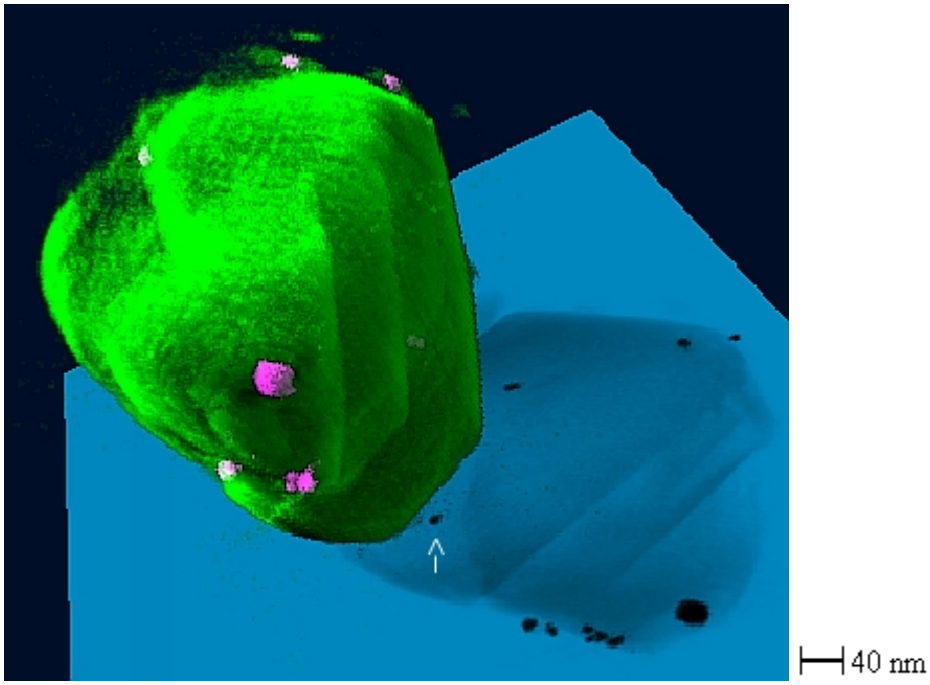


Figure 3: Contour surface of an Ag/NaY crystal. Silver particles are coloured pink, the zeolite is coloured green. On the blue surface a black shadow-projection of the zeolite with silver particles is shown. The white arrow indicates the shadow of a silver particle that is located inside the zeolite.

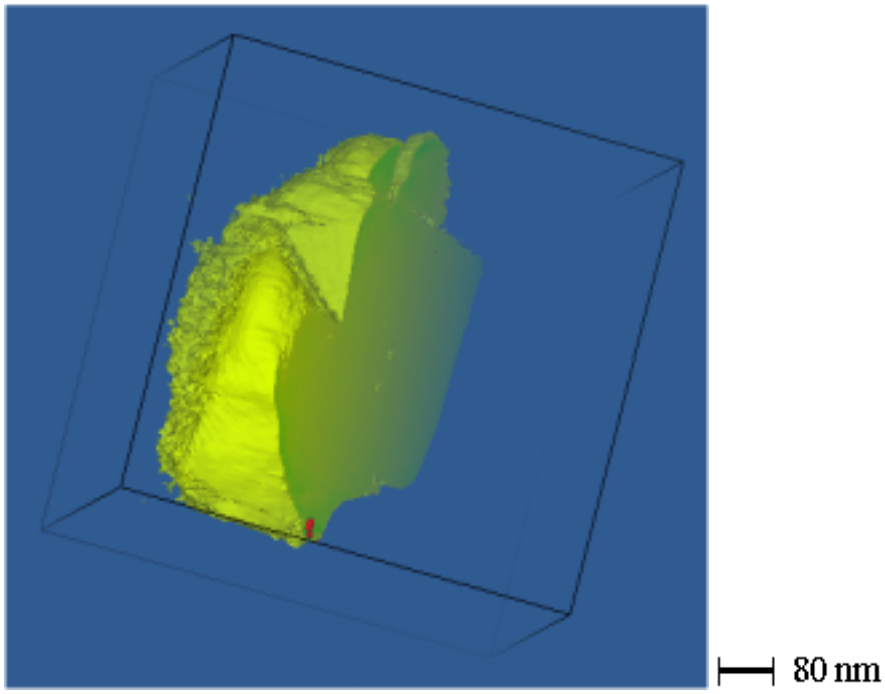


Figure 4: Intersection of Ag/NaY showing a silver particle (red) at or near the surface of the zeolite (yellow).

A drawback of 3D-TEM (just as is the case with 'normal' TEM) is that one investigates only a very small part of the sample. Therefore, additional (macroscopic) characterization techniques, such as XPS, are needed in addition to electron microscopy.

3. APPLICATION TO METAL/ZEOLITE SYSTEMS

Ag/NaY was made by suspending 500 mg NaY (LZY 54 from UOP, Si/Al ratio is 2.5) in 100 ml 4.0E-4 M $AgNO_3$. An exchange efficiency of 100% results in a 0.9 wt% Ag catalyst. The suspension was stirred overnight at room temperature. After centrifugation from the solution, the loaded zeolite was washed and centrifuged two times with de-mineralised water and dried at room temperature. The material was dried at 150°C in argon and subsequently reduced at 150°C in hydrogen.

A tilt series of Ag/NaY was taken at a magnification of 11.5k on a Philips CM 200 FEG microscope with a 1024 x 1024 CCD camera (pixelsize 1.12 nm). From a representative Ag/NaY crystal 143 images were taken from +70° to –72° with 1 degree intervals. For alignment purposes 7 dark features (silver particles) that could be followed throughout the whole tilt series were chosen as fiducial markers. The 3D reconstruction contains a volume of 1150x1150x1150 nm and has a resolution of 11 nm.

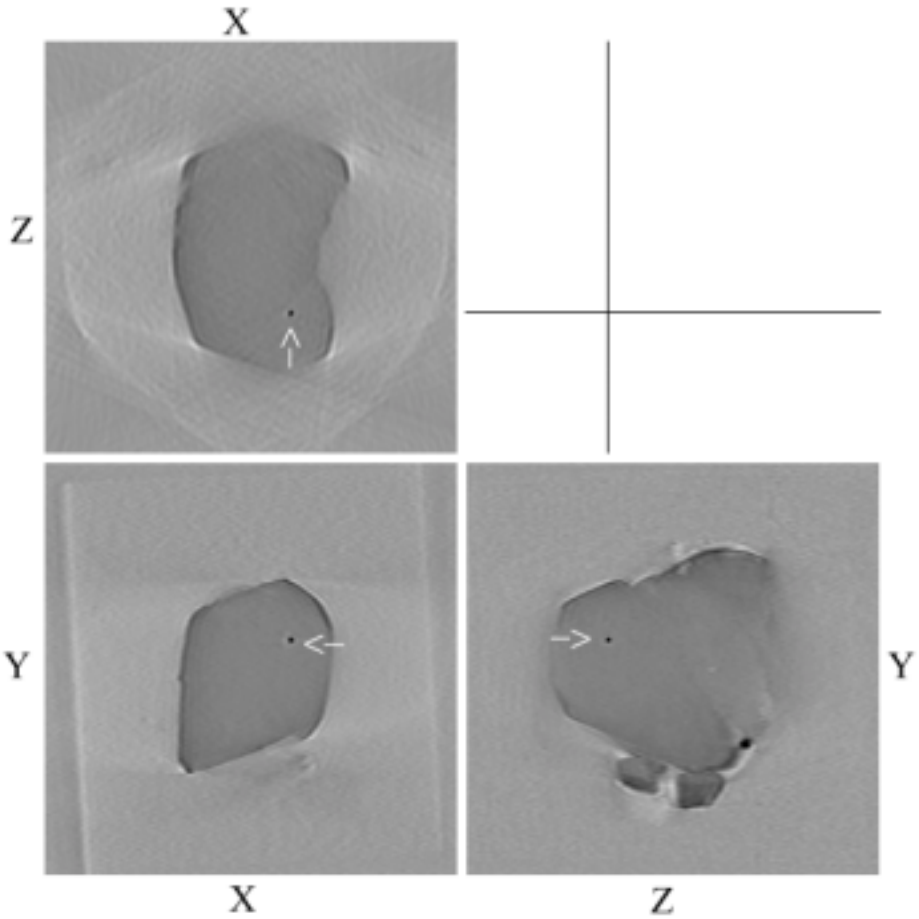


Figure 5: Slice through the reconstruction of Ag/NaY showing a silver particle (arrow) inside the zeolite.

In Figure 3 a contour model of the Ag/NaY sample is given. The colours of this model were obtained by selecting several bands of grey-values (e.g. the grey-values corresponding to the silver particles and the grey-values corresponding to the zeolite crystal) and assigning different colours to the different bands. The silver particles (shown in pink) are located at or near the external surface of the zeolite. The right-hand side of the image shows a shadow projection of the crystallite (black). In this shadow projection the shadow of a silver particle that is located inside the zeolite is also visible (white arrow).

In Figure 4 an intersection of the same crystallite is shown. The placement of a silver particle (red) at or near the surface of the crystallite is clearly visible.

The precise placement of the silver particles is best observed when the reconstruction is presented as a stack of thin slices. In Figure 5 one of these slices (X-Y) is given, showing a silver particle inside the zeolite. The orthogonal slices (X-Z and Y-Z) further support this conclusion.

4. CONCLUSIONS AND OUTLOOK

To date, no techniques were available that could characterize an individual solid catalyst structure in three dimensions at high resolution. With electron tomography (3D-TEM), however, it is possible to obtain a 3D high-resolution image of a sample. From a series of 2D-TEM images at different tilt angles a 3D reconstruction is calculated. The reconstruction can be visualized with contour surfaces and with slices through the reconstruction to investigate if particles are located inside or outside the porous material.

Future work will involve the further development of 3D-TEM by combination with element analysis (EDAX). The Ag/NaY material will be studied more extensively to assess metal mobility under oxidizing and reducing atmosphere. Other systems currently under study are metal-loaded carbon nanotubes and mesoporous materials.

ACKNOWLEDGEMENTS

This work has been carried out under the auspices of NIOK, the Netherlands Institute for Catalysis Research, Report No. UU-99-3-02. The authors would like to thank the Netherlands Organization for Scientific Research (NWO) for financial support, grant 98037. The research of one of us (AJK) has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences

REFERENCES

[1] K.P. de Jong, CATTECH **2** (1998) 87-94.
[2] K.P. de Jong, Current Opinion in Solid State & Materials Science **4** (1999) 55-62.
[3] A.J. Koster, R. Grimm, D. Typke, R. Hegerl, A. Stoschek, J. Walz, W. Baumeister, J. Struct. Biol. **120** (1997) 276-308
[4] J. Frank, Electron tomography, 1992, Plenum Press, New York
[5] H. Beyer, P.A. Jacobs and J.B. Uytterhoeven, J. Chem. Soc., Faraday Trans. I **72** (1976) 674.