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The structure of an iron oxide cluster incorporated into zeolite Y, determined by HRTEM and SAED

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Abstract. The atom positions of an iron cluster (Fe_6O_n) inside the framework of a zeolite (FAU, $Na_{48}(Fe_2O_3)_{38}Al_{48}Si_{144}O_{384}$) were determined through the use of electron crystallography methods for three-dimensional reconstruction of atomic positions within the cluster from high-resolution electron micrographs and selected-area electron diffraction. The iron-containing FAU structure was determined in the space group $Fd3m$ ($a = 24.7$ Å) by the use of 42 unique reflections. The Fe_6O_n molecule is situated in the sodalite cage with the iron atoms facing the square windows of the cage. The iron–iron distance is 3.6 Å and the distances between iron atoms and the nearest oxygen atoms in the sodalite cage are close to 2.2 Å. As a verification of the method, the same technique was used for the dermination of the structure of $Na_{48}Al_{48}Si_{144}O_{384}$ without iron, and the Si/Al atom positions of the zeolite framework were found to coincide with those determined from single crystal X-ray diffraction methods.

PACS. 61.14.-x Electron diffraction and scattering – 61.14.Rq Other electron diffraction and scattering techniques for structure analysis – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

1 Introduction

Zeolites are a group of framework aluminosilicates with well-defined channels and cavities that are of a suitable size for the incorporation of small molecules and clusters. Iron-containing zeolite crystals of the FAU type are of great interest, since they show interesting catalytic properties. When the NO_x gas content in the exhaust from cars is reduced, FAU containing iron can be used as a catalyst. Synthesis of carbon nanotubes through the use of an FAU catalyst containing iron or cobalt has also been reported [1].

The location of the incorporated clusters is important for the understanding of the properties of these materials. The most common technique for structure determination, X-ray diffraction, cannot always be employed because of the small crystal size of most zeolites. High-resolution transmission electron microscopy (HRTEM), combined with image processing and selected-area electron diffraction (SAED), is a more suitable method for small crystals. Recent developments in image recording, such as slow-scan CCD cameras and imaging plates, suitable for low-dose imaging and linear recording of images and, more importantly, diffraction patterns, have made it possible to use HRTEM techniques for beam-sensitive materials, such as zeolites. Ultramicrotomy of embedded crystalline samples can be used to provide large, evenly thin (less than 200 Å) areas suitable for this type of investigation. So far, most structure determinations by HRTEM have been derived from two-dimensional data recorded along a short unit cell axis [2]. The atom positions along the short axis have then been deduced from geometrical and chemical considerations. This method is not suited for many zeolites, which often have three long unit cell axes. Instead a full three-dimensional reconstruction [3], the combination of HRTEM data from several crystallographic directions is to be preferred.

This investigation uses HRTEM images and SAED amplitudes to determine the positions of small iron oxide clusters in the FAU zeolite, $Na_{48}(Fe_2O_3)_{38}Al_{48}Si_{144}O_{384}$ (in the following text called (Na,Fe)Y). The same compound without implanted iron oxide, $Na_{48}Al_{48}Si_{144}O_{384}$ (hereafter NaY), was subjected to identical procedures, and the structure was determined as a control experiment.

2 Experiment

The (Na, FeY) crystals were prepared according to a method published elsewhere [4]. The crystals contained 76 $FeO_{1.5}$/unit cell, according to energy-dispersive X-ray spectroscopy (EDX) analysis of several crystals. (Na,Fe)Y and NaY crystals were dried at 300 °C for 24 h and embedded in an epoxy resin (Spurr) [5]. Ultrathin sections, less than 200 Å, were prepared using an ultramicrotome (Leica Ultracut UCT) equipped with a diamond knife, and the sections were supported on lacy carbon film on copper grids.

The ultrathin sectioned samples were investigated in a JEM-4000EX, operating at 400 kV with a structural resolution of about 1.6 Å ($C_s = 1.0$ mm, $C_c = 2.7$ mm, with a spread of focus about 60 Å and semiconvergence angle 0.50 mrad). Structure images were recorded at very low electron doses (<50 electrons/Å^2 $\times$ second) at 250 000 times magnification (3.3 pixels/2 Å) with a slow-scan CCD camera (Gatan 694). Diffraction patterns from the same crystals as those used for the HRTEM images were recorded on the slow-scan CCD; the smallest condenser aperture and smallest spot size of the microscope were used.

3 Structure determination

NaY is cubic, and its space group is $Fd3m$ ($a = 24.7$ Å) if Si/Al ordering is disregarded. The iron-containing zeolite was assumed to have the same space group, which was consistent with the symmetry of the images and recorded diffraction patterns. For NaY crystals, two different directions, [110] and [111], were imaged, resulting in 57 reflections out of 101 unique ones extending to a resolution of 1.7 Å. For crystals of (Na,Fe)Y, only images in the [110] direction were recorded, giving 38 reflections out of 67 unique ones extending to a resolution of 2.0 Å, and giving a good coverage of the 3D reciprocal space because of the high symmetry of the space group. The lower resolution and fewer detected reflections in the latter case are mostly due to the more electron beam-sensitive nature of the (Na,Fe)Y, which gave a lower signal-to-noise ratio in the images, meaning that fewer of the weak reflections could be extracted from the slow-scan CCD recordings.

All the image processing (Fig. 1) was performed with the Semper software (Synoptics, Ltd). The images were in each case Fourier-transformed and corrected for the effect of the contrast transfer function (CTF) of the objective lens. Both the amplitudes and the phases of the diffraction peaks are affected by the CTF. In areas where the CTF is positive, atoms are imaged as white, and in areas where the CTF is negative, atoms are imaged as black. Amplitudes are dampened by multiplication with the value of the CTF. Only the position of the zeros in the CTF, and not its actual shape, influenced the final result in this case, since the image amplitudes were replaced with measured electron diffraction amplitudes in the reconstruction, and thus only the phases of the reflections were deduced from the images. Nevertheless, both the amplitudes and phases were corrected using a Wiener filter [6] so that it could be verified that all images gave comparable results after focus correction. The image defocus was estimated from the Fourier transform of the amorphous material present on the surface of the zeolite crystals. Amplitudes and phases of diffraction peaks with a signal-to-noise ratio better than 3 were extracted from the focus-corrected Fourier transform. The unit cell origin was shifted to the correct phase origin of the projection, the symmetry of the projection was imposed on the amplitudes and phases, and the amplitudes and phases (0 or π) were extracted.

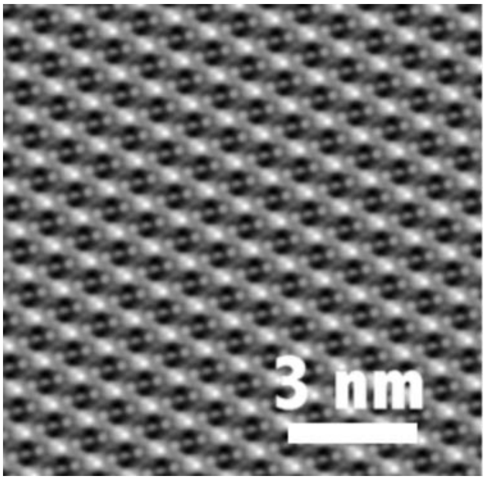

Fig. 1. Symmetrized and averaged HRTEM image of an NaY crystal along [110], recorded close to Scherzer defocus with a slow-scan CCD camera.

Diffraction amplitudes were then measured from the SAED patterns. The background was subtracted from the recorded patterns, the integrated intensities in the whole diffraction spots were measured, the amplitudes (square root of intensity) calculated, and the correct space group symmetry imposed. The amplitudes from different SAED patterns were scaled to each other with the use of common reflections, and an average was calculated. The extracted diffraction amplitudes were combined with image phases (a reflection list is available on request via e-mail: Jan-Olov.Bovin@oorg2.lth.se).

Image simulations performed for NaY and (Na,Fe)Y show that multiple diffraction in these zeolites starts to alter the relative amplitudes of the reflections at thicknesses above 200–300 Å for 400 kV accelerating voltage. Based the settings of the ultramicrotome and comparisons of recorded images with simulations, the section thickness was estimated to be around 150 Å for the samples used in the structure determination. Images of several crystals (8 different crystals for NaY and 5 for (Na,Fe)Y) from different sections, recorded at different defoci, showed the same measured phases (0 or π, since the structure is centrosymmetric) after focus correction. The only exceptions were four weak reflections for NaY, and two for (Na,Fe)Y. This consistency is important, since a phase reversal for a single strong reflection can change the appearance of the calculated crystal structure completely. The maximum difference in diffraction intensities between crystals in differ-

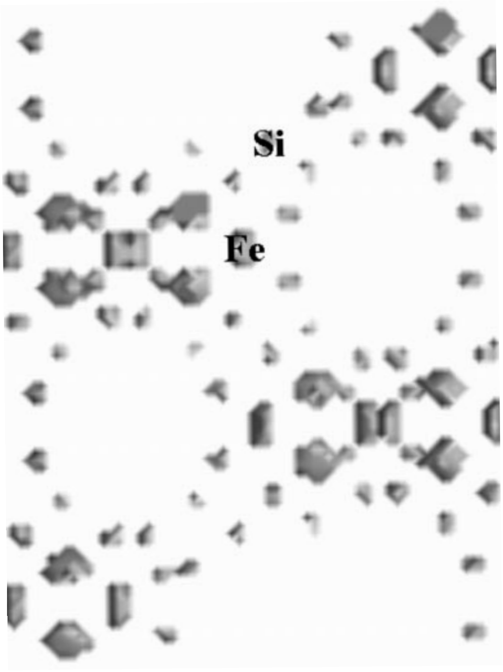

Fig. 2. Three-dimensional reconstruction, that is the inverse Fourier transform of one unit cell of (Na,Fe)Y, projected along [110]. Si denotes one silicon atom position of the super cage, and the location of one iron atom (Fe) in the Fe_6O_n cluster is marked.

ent ultramicrotomy sections was 26% after scaling, further supporting the assumption that all crystals used in the calculations were of similar thickness. The known structure of the zeolite framework for NaY also provides a way for one to determine how reliable the structure determination is, by comparing the silicon positions from the inverse Fourier transform with those from the X-ray determination.

The three-dimensional crystal potential (structure) was calculated by an inverse Fourier transform. The positions of the atoms, both iron and silicon (aluminium and silicon are disordered and cannot be distinguished), were directly determined from the positions of the highest intensities in the three-dimensional images for NaY and (Na,Fe)Y (Fig. 2). The rugged form of the dots, representing the atom positions, depends on the resolution of the calculations. The larger dot, the heavier the element..

4 Results and discussion

In the inverse Fourier determination of the NaY structure, the silicon (aluminium) atoms are placed at the 192(i) position ($x = 0.310, y = 0.125, z = 0.036$), which is a deviation of only 0.16 Å from the ($x = 0.3034, y = 0.1254, z = 0.0363$) position in the X-ray structure determination [7]. The two shortest Si−Si distances are 2.9 and 3.1 Å, which can be compared with the value 3.1 Å in the X-ray determination and the 3.1 Å distance between corresponding atoms in the mineral quartz. The Si−Si distance of 2.9 Å is unusually short and indicates the larger uncertainty in the position determination than in the X-ray case. The resolution of the images is not high enough to give clear oxygen position, even if there is some electron density at the expected positions.

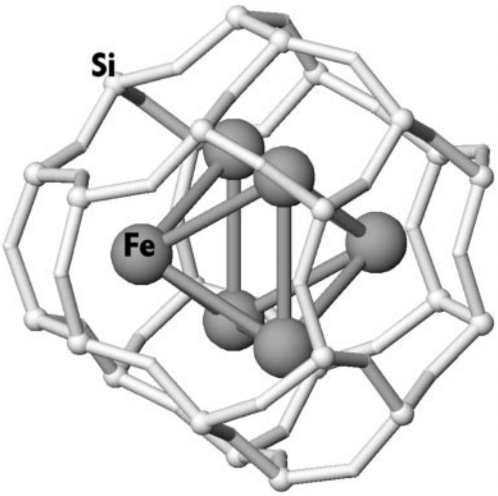

Fig. 3. The location of the Fe_6O_n clusters inside a sodalite cage. Perspective view close to [111].

For the (Na,Fe)Y structure, the silicon(aluminium) atoms are located at the same position, 192(i), with ($x = 0.318,\ y = 0.130,\ z = 0.033$), a deviation of 0.39 Å from the X-ray structure of NaY. The two shortest Si−Si distances here are 2.4 and 3.0 Å, again indicating the larger uncertainty in the determination of the silicon position as compared with the X-ray investigation. The iron atoms are located in the position 48(f) at ($x = 0.125, y = 0.125, z = 0.021$), thus forming an octahedron in the sodalite cage (Fig. 3). The iron–iron distances within the octahedron are close to 3.6 Å (the standard deviation can be estimated to 0.15), in reasonable agreement with the value 2.8–3.3 Å obtained by EXAFS before phase shift [4], but considerably longer than the 2.7–3.1 Å present in bulk iron oxides. The oxygen positions within the cluster cannot be determined from the inverse Fourier transform. If the framework oxygens are assumed to be in the same position as for NaY, the closest iron–framework-oxygen distance is 2.2 Å. The ionic radius of 8-coordinated Fe^{3+} in a perovskite-type structure has been calculated to 0.90 Å [8, 9], which gives an Fe−O distance of 2.3 Å, in good agreement with the 2.2 Å obtained above. It should be noted that only 63% (assuming full occupancy at the 48(f) site) of the implanted iron has been located in this investigation. The remaining iron atoms might be distributed at several other sites in the unit cell with low occupation, thus not giving enough electron density to be seen in the electron density maps.

5 Conclusions

The iron oxide cluster is hexanuclear, with the irons in an octahedron located inside the sodalite cage. The position of the framework silicon atoms is consistent with the known X-ray structure of NaY, thus supporting the results for the unknown location of the Fe_6O_n clusters. The distances within the cluster are in reasonable agreement with published EXAFS measurements.

Ultrathin sectioning of zeolite crystals gives large areas of even thickness, which is important for both the recording of HRTEM images and the electron diffraction of beam-sensitive materials, for which a large number of unit cells from areas of comparable thickness are required to give a high signal-to-noise ratio. The ultrathin sections can be made sufficiently thin so that severe multiple scattering may be avoided and electron crystallography of materials with low to medium atomic weight may be enabled.

A combination of HRTEM and SAED is clearly a possible method for structure determination of small crystals of inorganic materials. The accuracy is normally not as good as in X-ray refinement, and care must be taken when the results are evaluated, especially with regard to bond lengths and angles. However, the accuracy is good enough to show the location of implanted materials and the general shape of the framework. This work shows that it is possible to obtain reasonably accurate atomic positions from electron microscopy investigations, even for the very electron beam- sensitive zeolites.

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