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From Average to Local Structure: A Rietveld and an Atomic Pair Distribution Function (PDF) Study of Selenium Clusters in Zeolite-NdY

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Synthesis of metal/semiconductor nanoparticles with narrow size distributions is a significant challenge in nanoscience. One promising approach to achieve such narrow distributions is to employ a crystalline host framework, such as a zeolite, to constrain the size and the shape of the nanoparticles.[1−3] Several examples of this method have been reported, and the advantages relative to other techniques used to fabricate semiconductor nanoclusters discussed.[4−6] In guest−host methods, short-range ordering of the guest molecules and distortions of the zeolite framework in the vicinity of these molecules, which can be observed in the form of diffuse X-ray scattering, makes the structural analysis nontrivial. Here, we describe the structure and short-range ordering of Se clusters in a zeolite Nd−Y and show how a detailed structure can be obtained by combining Rietveld and pair distribution function analysis.

The long-range ordering of a crystalline structure can be always accurately determined with a high degree of accuracy by analysis of the Bragg intensities and positions. But analyzing the short-range order is difficult due to the low absolute intensity of the diffuse scattering and the fact that it is widely distributed in the reciprocal space. The Rietveld method[7] extracts information only from the Bragg peaks leading to an *average* structure neglecting any local distortions except as reflected in Debye−Waller factors. The pair distribution function (PDF) technique,[8−11] originally developed to analyze liquids and glasses,[12−14] is a method for analyzing the short-range order using powder diffraction data. The PDF is obtained by Fourier transforming the properly corrected and normalized diffraction data into real space. Since the Fourier transform of the data includes both Bragg and diffuse scattering intensity, the PDF produces long-range and short-range order structural information simultaneously, albeit in a one-dimensional projection. A structural model can be refined by fitting the Fourier transformed data (PDF)[6−8] to determine the deviations of the local structure from the *average*. In r-series PDF modeling the *average* structural model is refined at different real space intervals against the experimental PDF to obtain details of crossover from local to average structure.[15]

Clusters of Se in NdY zeolite were synthesized using chemical vapor deposition.[1] X-ray diffraction measurements at 41 keV (λ = 0.298 Å) were performed using 1 mm sealed capillaries in transmission geometry at the beamline ID-31 of the European Synchrotron Radiation Facility (ESRF). Measurements were carried out up to a 2θ maximum of 110° to minimize termination ripples in the PDF. The PDF was then obtained using the corrected and normalized X-ray diffraction data in the program PDFGetX2.[16] GSAS/EXPGUI[7,18] and the PDFgui[6,19] were used for the Rietveld refinement and for r-series[2,6] PDF modeling, respectively.

At the first stage of the data analyses, a Rietveld refinement was used to obtain an *average* structural model for the dry NdY/Se system. The diffuse scattering (see Supporting Information (SI)) was subtracted together with the capillary background by fitting a shifted Chebyschev polynomial function. A structural model was obtained by fitting Bragg peaks with a pseudo-Voigt profile function. During the initial refinement, the Se site occupancies were constrained according to the reaction stoichiometry. During the last cycles of the refinement, all atomic coordinates, U_{iso}, cell parameter, zero shift, and the unconstrained occupancies of the Se sites were refined simultaneously to determine an *average* structure. The results of the Rietveld refinement are shown in Figure 1, and the details are given in the SI. A large isotropic thermal parameter (U_{iso}∼0.5 Å^2) for the Se atoms was required to model the static disorder. The specific static displacements of the Se atoms are determined in the PDF model below.

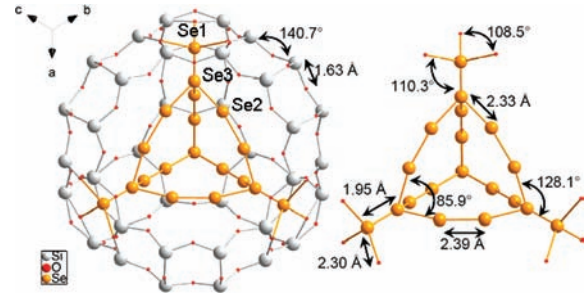

Figure 1. Resulting structural model of the Se cluster in the dry zeolite Nd−Y cage. The Se cluster is bonded to the framework through O atoms. Note that the local distortions of the framework are not visible in this model.

In the PDF analysis, the site occupancy was constrained so that only 1 out of 2−3 selected sites about the *average* can be filled at a given time. The statistical disorder of the Se sites due to the missing atoms in the cluster (when there is an unoccupied site in the cluster, neighboring atoms tend to relax and occupy sites displaced from the average) was included in this way. The *average* structure of zeolite Nd−Y from the Rietveld refinement was confirmed over a PDF length scale, 8−50 Å (Figure 2a).

In general, weak correlations between two clusters in adjacent cages through the framework are possible. In this case, a remarkably

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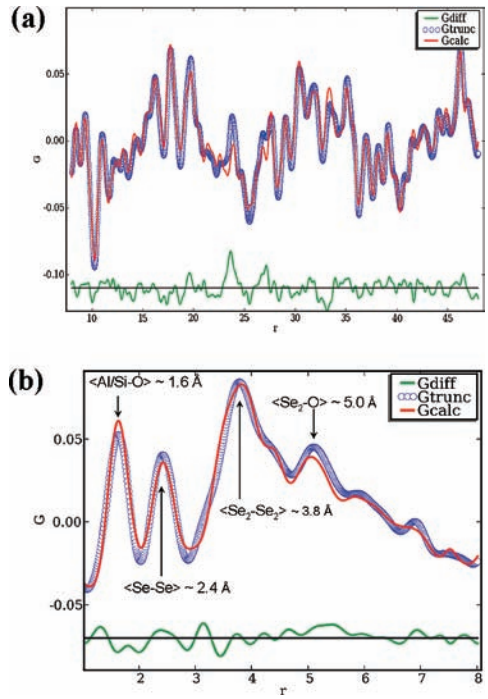

Figure 2. (a) An average structural model for the nondistorted zeolite framework was obtained at the PDF length scale, 8−50 Å. (b) Intracluster correlations and the distortions of the zeolite framework resulting in the pronounced diffuse scattering observed in our X-ray diffraction patterns were modeled at the PDF length scale 1.5−8 Å.

good fit could be obtained on the PDF length scale 8−50 Å with no indications of cluster−cluster correlations using only the calculated framework model.

The short-range order in the vicinity of the cluster was modeled on a PDF length scale of 1−8 Å (Figure 2b). A differential PDF was also obtained by subtracting the calculated framework PDF (using the PDF range 8−50 Å) from the total PDF. Both differential and the total PDFs were fit with structural models to obtain the proposed structure for the cluster.

To account for the correlations *between* the Se-clusters and the framework, however, it was essential to fit the *total* PDF with a structural model for the whole system on a length scale of 1−8 Å. The local framework distortions and the statistical disorder of the atoms so determined are shown in Figure 3. Since every pore is not filled (32% of the pores are filled according to composition), the framework distortions are averaged out with the unfilled pores.

In conclusion, we have prepared Se particles in the ∼13 Å diameter α-cages of zeolite NdY *via* a chemical vapor deposition technique and determined their structure. Rietveld refinement of the X-ray data with the diffuse scattering subtracted gives an average structure comprised of an undistorted framework containing clusters of 20 Se atoms. A considerable statistical disorder at the guest atom sites was evidenced by an unusually high Se thermal parameter (U_{iso} ∼0.5 Å^2). The Se clusters are weakly bonded to the framework oxygen atoms resulting in a short terminal Se−Se bond (Figures 1 and 3). The intracluster correlations and the cluster−framework correlations which give rise to diffuse scattering were modeled using an r-series PDF. Deviations of Si−O bond lengths and Si−O−Si angles from the average due to the effect of the Se clusters were observed in the PDF model (Figure 3).

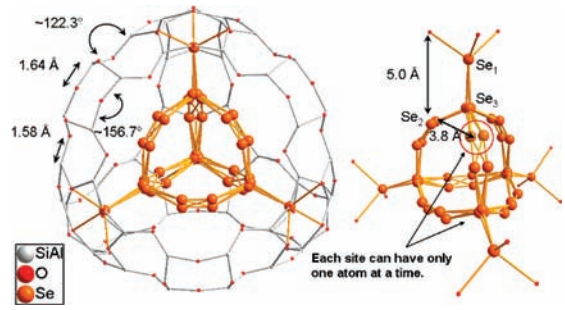

Figure 3. PDF model for the cluster. The diffuse scattering is mainly caused by static disorder among possible Se atoms sites in the cluster.

Statistical disorder due to occupational disorder has been introduced by assuming 2−3 sites about the average Se sites and constraining the occupancy so that only one of these 2−3 sites can be occupied at a given time. The average Se isotropic thermal parameter is only 0.02 Å^2 when the disorder is accounted for by including the diffuse scattering. Both PDF and Rietveld techniques are needed to determine the structure of such systems.

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Supporting Information Available: Sample preparation and details of the Rietveld and PDF refinements. This material is available free of charge via the Internet at http://pubs.acs.org.

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