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Stabilization of Quantum Size CdSe Clusters in Zeolite-Y
EXAFS and X-ray Diffraction Studies

by

+Karin Moller, +Thomas Bein, Mike Eddy, Galen Stucky, #Norman Herron
to be submitted to the Journal of the American Chemical Society

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Abstract:

Small (<15Å) CdSe clusters have been synthesized within the cage system of zeolite-Y. Cluster size and connectivity patterns are controlled by cadmium ion concentration, selenium source and residual water. Analysis of Cd-edge EXAFS and powder synchrotron X-ray diffraction data, in addition to model calculations reveal the presence of $\text{Cd}_4(\text{O,Se})_4$ cubes within the sodalite units of the zeolite structure.

Cadmium Selenide (CdSe)



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Abstract

Small ($<15\text{\AA}$) CdSe clusters have been synthesized within the cage system of zeolite-Y. Cluster size and connectivity patterns are controlled by cadmium ion concentration, selenium source and residual water. Analysis of Cd-edge EXAFS and powder synchrotron X-ray diffraction data, in addition to model calculations reveal the presence of $\text{Cd}_4(\text{O},\text{Se})_4$ cubes within the sodalite units of the zeolite structure.

Introduction

Semiconductor particles are known to change their electronic, optical and photochemical properties with particle size. Neither bulk nor molecular properties are encountered in the size regime from 10Å to 50Å. The large band gap and occurrence of isolated absorption peaks for semiconductor 'clusters' in this size range have been explained by considering quantum size effects and exciton formation¹.

The synthesis of well defined, homogeneous semiconductor clusters is necessary to understand the origin of these quantum size effects. Preparation has been achieved by wet colloidal methods², by growth in dielectric glassy matrices³ or in polymers⁴. Characterization of cluster size and structure are often difficult to accomplish, especially with cluster sizes smaller than 20Å. Particle sizes are usually not uniform and agglomeration of individual particles often occurs⁵. Thus, the effect of particle size on the optical properties is obscured. In recent papers we reported an alternative approach to stabilize well-defined semiconductor clusters. Selenium and cadmium sulphide moieties were encapsulated in a crystalline microporous host framework⁶. In this paper we present structural evidence for the stabilisation of closely related, CdSe, in zeolite-Y. Colloidal CdSe is of interest for photosensitized electron transfer reactions utilized for solar energy conversion and photocatalysis⁷.

The constraints provided by the rigid, crystalline aluminosilicate framework of a zeolite offers a considerable improvement in size definition over other preparative environments. Zeolites consist of corner-sharing AlO_4 and SiO_4 tetrahedra connected such that well defined cavities and channels are formed (figure 1). Metal cations can be introduced by ion exchange of the sodium ions present in the original material. The intrazeolite location of these cations is limited to sites close to the framework as shown in figure 1 for zeolite-Y. Sodalite subunits are connected via six-ring windows to form the large supercages of zeolite-Y. The sodalite unit contains four SI' and four SII' coordination sites with three framework oxygen serving as ligands. Very small charged species such as Na_4^{3+8} or Ag_3^{2+9} in addition to the neutral palladium(0) ensembles containing only four atoms¹⁰ have been observed in the cavity system of zeolite-Y.

In this paper we illustrate the complementarity of powder X-ray diffraction (XRD) and X-ray absorption (EXAFS). Both techniques have been applied to the elucidation of the structure of CdSe loaded zeolite-Y. Rietveld¹¹ refinement of powder diffraction data determines the statistical locations of the atoms, while EXAFS yields crucial information on bond formation by monitoring the local environment of the absorber atoms.

Experimental

The Cd zeolite-Y samples were prepared by a standard ion exchange procedure. The starting material was commercial LZY-52. 10g of LZY-52 was slurried into 1000cm³ distilled water. The pH was adjusted to 5 and an appropriate ?? amount of cadmium nitrate added. The slurry was stirred overnight at room temperature, filtered and finally washed. The sample was then dried at 673K in flowing oxygen, followed by evacuation as the sample

cooled to room temperature. Hydrogen selenide was then passed over the dried zeolites for one hour. A final evacuation was performed at 323K before storage under inert atmosphere.

Chemical analysis gave the following unit cell contents:

CdY: $\text{Cd}_{18.3}\text{Na}_{19.4}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$
CdSe2: $\text{Cd}_{5.9}\text{Se}_{4.8}\text{Na}_{44.2}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$
CdSe6: $\text{Cd}_{17.2}\text{Se}_{11.4}\text{Na}_{21.6}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$

Extended X-ray absorption fine structure (EXAFS) analysis was carried out on all three samples, powder X-ray diffraction (XRD) was performed only on sample CdSe6.

EXAFS

All EXAFS experiments were carried out on beamline X-11a at the National Synchrotron Light Source, Brookhaven National Laboratory. Data on the Cd K-edge (26711eV) were collected in transmission using a Si(400) crystal monochromator. The ionization chambers were filled with Ar(I0) and Kr(I).

The zeolite samples are moisture sensitive and consequently were sealed in a 1:1 dodecane/octadecane mixture under an inert atmosphere. Data collection was done at liquid nitrogen temperature, scanning up to 1500eV above the absorption edge. At least two scans (20 minutes each) were taken.

The sample thickness was calculated to give an absorption step μx between 0.7-1.0 and a total absorption less than 2.0. The data were analysed using the EXAFS programs developed at the University of Washington following published procedures¹². Background removal was accomplished using a cubic spline function. The resulting EXAFS modulations were weighted by k^3 (k , electron wavevector) and then Fourier transformed over the range $k=2-15\text{\AA}^{-1}$. The data for reference and unknown samples were treated identically throughout the work-up process to avoid artefacts. The inner potential, E_0 , was varied stepwise and was always in the range $-3 < E_0 < +3\text{eV}$.

CdS, CdSe (both amorphous) and PdO were used as reference materials. EXAFS reference parameters were extracted as follows: PdO was used a) as reference for the Cd-O coordination sphere (reference values $R=2.01\text{\AA}$, $N=23^{13}$) and b) as reference for the Cd-Cd contribution (reference values $R=3.01$, $N=4$). Phase and amplitude transferability can be assumed since Pd and Cd are close in the periodic table.

CdS provided reference data for the Si/Al contribution from the zeolite framework (reference values $R=2.52\text{\AA}$, $N=4^{14}$). The use of CdS as reference for Cd-Si/Al 2nd shell interaction is assumed to introduce only minor errors since Cd-O-Si are less than 150° and therefore do not contribute significantly to multiple scattering. A mean free path correction was applied when there was a large discrepancy ($>0.2\text{\AA}$) between the reference and actual bond distances. The CdSe gave reference data for the selenide scatterer ($R=2.62\text{\AA}$, $N=4^{15}$).

Geometric model calculations for cadmium arrangements in the zeolite framework have been carried out based upon crystallographic data for faujasite¹⁶ and bond distances from our EXAFS results.

Synchrotron Powder X-ray Diffraction

Synchrotron radiation has opened up exciting new possibilities in all aspects of powder diffraction. The high peak to background ratio and

excellent resolution enables a well resolved pattern to be collected in about 12 hours for most samples. The simple peak shape and high resolution allows deconvolution of the powder pattern for structure determinations¹, or application of the profile method devised by Rietveld². Consequently the past two years has seen a rapid increase in the number of problems being tackled by this technique³. This is particularly true in the zeolite field, where large single crystals are difficult to prepare, and a detailed knowledge of the framework structure is essential if improvement in the shape selectivity of a zeolite is desired. Thus several molecular sieves of commercial importance have recently been investigated by high resolution synchrotron powder x-ray diffraction⁴.

Powder Synchrotron X-Ray Diffraction

High resolution x-ray powder data were collected for CdSe in zeolite-Y (CdSe6) on the powder diffractometer at beam line X13A at the Brookhaven National Synchrotron Light Source. A perfect Ge(111) crystal scattering in the horizontal plane was used to monochromate the incident x-ray beam. The sample and LiF(400) analyzer crystal scatter vertically. For a full description of the diffractometer geometry at X13A see reference ⁵. The wavelength was determined to be 1.53668Å by calibration with a Si standard. The sample was packed into a flat aluminum holder, sealed with thin beryllium foil to exclude moisture and data collected by step-scanning from 5° to 73° in intervals of 0.01° for periods of 2 to 10 seconds. Larger counting times are required at higher scattering angles to counteract the fall-off in the form factor. The sample container was rocked 2° at each data point to reduce the effects of preferred orientation. To monitor the incident beam intensity an ion chamber filled with nitrogen was placed before the sample. The beam size was 2.5x1mm in the horizontal and vertical directions respectively and the intensity at the sample position was ca. 10¹⁰ photons/sec for a storage ring current of 100mA.

The structural refinement was carried out using standard profile refinement techniques. The initial normalisation of the data was performed using programs available at Brookhaven and for structural refinement a modification of the original Rietveld program was employed. This program

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- ¹ (a) J.P.Attfield, A.W.Sleight, A.K.Cheetham, *Nature*, **322**, 620, (1986).
(b) M.S.Lehmann, A.N.Christensen, H.Fjellvag, R.Feidenhans'l, M.Nielsen, *J.Appl.Cryst.*, ****, (1987).
 - ² H.M.Rietveld, *J.Appl.Cryst.*, **2**, 65, (1969).
 - ³ D.E.Cox, *M.R.S. Bulletin*, **12**, ***, (1987).
 - ⁴ (a) B.Toby, M.M.Eddy, G.T.Kokotailo, C.A.Fyfe, D.E.Cox, submitted to *Zeolites*.
(b) N.Herron, Y.Wang, M.M.Eddy, G.D.Stucky, D.E.Cox, submitted to *J.Amer.Chem.Soc.*
(c) A.K.Cheetham, *Nature*, ****, (1987).
 - ⁵ D.E.Cox, J.B.Hastings, L.P.Cardoso, L.W.Finger, *Materials Science Forum*, **9**, 1, (1986).

incorporates the Voigt peak shape description that is essential for analysis of powder patterns collected using the two crystal configuration used at X13A⁶. The extra-framework material was revealed by standard Fourier methods.

Results

EXAFS analysis

The experimentally determined EXAFS modulations contain information about the local environment of the intrazeolite Cd(II) ions. By absorption of X-rays exceeding the binding energy of a core electron, photoelectrons are ejected from the absorber atom. These photoelectrons are backscattered from neighbouring atoms, thereby producing an interference wavepattern of the absorption coefficient. It follows that each spectrum is a superposition of contributions from different coordination shells around the Cd absorber. To abstract information about the atoms of interest, subtraction of the background and normalisation has to be performed. A Fourier transformation from energy into radial coordinate space (R-space) allows for a separation of different shells. Figures 2 and 3 show the EXAFS modulations of the original data after background removal and normalisation, and also the data of reference and unknown samples after Fourier transformation.

A comparison between the cadmium exchanged zeolite and those exposed to hydrogen selenide gas (figure 3) shows that major changes occur for the CdSe6 sample. Thus we will begin by examining this sample.

The Fourier transformation (figure 3b) shows three overlapping contributions. Normal Fourier filtering and curve fitting technique are difficult in this case, since the resulting chi function will always be composed of more than one neighbouring shell. On the other hand, a three shell fit over the entire data range would involve at least 6 variables to account for the bond distance (R), number of neighbours (N) and deviations from the Debye Waller factors (SS^2) in each shell. Assuming also that there is a distribution of cation positions in the zeolite structure illustrates the high demand on the fitting procedure. We have therefore used a file technique which has been employed very successfully by Koningsberger et al¹⁷ on similar complicated systems.

As discussed in detail in a recent publication⁶, the first and second peaks in Cd-zeolite-Y result from oxygen and Si/Al scattering from the framework with a concomitant Cd-Cd contribution convoluted into the second peak. CdSe6 is distinguished by an additional peak at 2.3Å in R-space, caused by the selenide in the system. Subtracting this from the system would isolate the the surrounding shells and thereby offer the possibility of carrying out single shell fits. To calculate a Cd-Se scatterer pair, the unknown parameters for the selenium neighbours were estimated by comparing the CdSe reference with CdSe6 and by inspection of the unknown sample after subtraction of the calculated Se data. The difference file is shown in figure 4a. The separation into two shells is now visible, but a remnant remains at 2.2Å.

Assuming only minor overlap of this residue with the first major peak a backtransformation was applied to this difference file, using a very narrow window of 1.5-2.1Å. The smooth shape of the resulting chi function seems to

⁶ D.E.Cox, B.H.Toby, M.M.Eddy, to be published in Aust.J.Phys.

justify this assumption (figure 5a). Still, a fit was only possible with two different oxygen distances (the final results are listed in table 1). Using these values a broader window of 1.3-2.4Å was then fitted with an additional CdSe shell. As can be clearly seen in figure 5b, this chi function now has a different envelope, due to the small amount of additional scatterer. In a third step, a backtransformation on the second major shell in the difference file was applied between 2.4-3.3Å. A fit was performed with CdS as reference for the presumed Cd-Si/Al neighbours (figure 5c). Finally, all results were included for a fit of the whole data between 1.3-3.3Å. Considering the complexity of the sample, a reasonable fit was obtained as illustrated in figure 5d. The results are listed in table 1. The FT on the calculated file shows good agreement with the original sample (figure 7a).

CdSe₂, which contains only 6Cd²⁺/u.c. but a high Cd/Se ratio exhibits quite a different spectra to CdSe₆ (see FT in figure 3d). The intensity of the second major peak at 3Å is much larger than that seen for CdSe₆. A small contribution at about 2.3Å can be attributed to selenium as concluded from the analysis of the former sample. It is decreased in intensity, but much broader indicating a higher degree of disorder. The oxygen part of the first shell is similar to CdSe₆. A similar approach to that described above was carried out for this sample. After subtracting a Cd-Se calculated contribution (preliminary values $R=2.62\text{\AA}$, $N=0.8$, $SS^2=0.0023$), the FT of the difference profile (figure 4b) is similar to that of Cd-Y (figure 3f).

A fit of the first shell of this data set (1.5-2.1Å) again results in two different bond distances for oxygen (figure 6a). The second shell, when fitted only considering the Cd-Si/Al contributions results in a high number of neighbours (12.5 uncorrected) which is chemically unreasonable. Consequently there must be an additional contribution to this peak. A fit with an additional reference for the Cd-Cd interaction is shown in figure 6c. This brings the number of Si/Al atoms in the second shell down to 6.3 (uncorrected), a value expected for a cation in the SI' position. This also results in 2.6 Cd neighbours contributing to this peak. A fit over the data from 1.3-3.3Å is shown in figure 6d. The final values are listed in table 1.

Powder Synchrotron X-ray Diffraction

The observed, calculated and difference profiles for CdSe₆ are illustrated in figure 7. The refined atomic and profile parameters are given in table 2 with selected bond lengths and angles in table 3. An excellent refinement was obtained which is reflected in the small value of χ^2 .

The refined structure shows a zeolite framework which is essentially unchanged from the parent sodium zeolite-Y. The average T-O bond length (1.64Å) is in excellent agreement with that expected for a zeolite of this Si/Al ratio (2.61). Space group Fd3m (origin at center) was used throughout the refinement which assumes a random distribution of silicon and aluminum in the tetrahedral position and a suitable scattering length was calculated based on the Si/Al ratio. This proved adequate for refinement purposes. The powder peak shape could be accurately described by the convolution of Gaussian and Lorentz functions - the Voigt function. No asymmetry could be detected in the low angle reflections.

While the overall framework is as expected there are small variations in the individual T-O bond lengths. These are rationalised in terms of the approach of the cations to the framework oxygen. The sodium cations are located at SII, trigonally coordinated to three framework oxygen atoms. This location has been found to be the most energetically favorable for sodium¹⁸.

The Cd^{2+} is located primarily at SI'. This site, within the sodalite unit, is preferred by multivalent cations because some of the high charge density can be compensated by hydroxyl anions at SII' also in the sodalite unit. The cadmium at SI' has an octahedral coordination resulting from trigonal coordination to framework oxygens of the six-ring (which is part of the double six-ring interconnects of the zeolite-Y structure), $\text{Cd-O}(3)=2.41\text{\AA}$, and the three SII' atoms, $\text{Cd-O}(5)=2.42\text{\AA}$. The ratio $\text{Cd}(1)/\text{O}(5)$ of 1/3 indicates that the cube arrangement found in the CdS samples examined previously do not exist in this case. Remaining electron density, detected in difference Fourier syntheses, was found in the twelve-ring window $\text{Cd}(2)$. This site, SIII, is bound to two framework oxygen atoms at 2.70 $\text{\AA}$ and 2.74 $\text{\AA}$ and two non-framework atoms, which are presumed to be selenium. The many disordered sites present in this region make unequivocal assignment of the scattering density difficult. The total cadmium content based on the occupancy of these two positions is 16.6, in good agreement with that found from chemical analysis (17.2).

Discussion

The EXAFS and X-ray synchrotron powder diffraction results indicate that for sample CdSe2 there exists distorted $\text{Cd}_4(\text{O},\text{Se})_4$ cubes located within the sodalite units of the zeolite framework. This cube is disrupted in sample CdSe6.

From the combined presence of oxygen in the first shell and Si/Al neighbours in the second shell for both samples, Cd^{2+} ions must be located in extra-framework cation positions. This was confirmed by results of the Rietveld analysis, which shows the primary cation location as the SI' site. The Cd-framework oxygen bond distance of 2.39 $\text{\AA}$ from EXAFS is in excellent agreement with that found from XRD (2.42 $\text{\AA}$). In agreement with the X-ray diffraction data the occupancy of the double six-ring position can also be excluded.

The results of X-ray diffraction on these high symmetry systems gives only an average structure which is populated by partially occupied, disordered sites. The evidence for cluster formation is given by EXAFS, which can clearly show the presence of Cd-Cd interactions. This is evident in the CdSe2 sample, where a significant fraction of the second shell is due to Cd-Cd scattering at $R=3.36\text{\AA}$. The 2.9 neighbouring cadmium atoms strongly supports the simultaneous presence of four Cd atoms in one sodalite unit. In contrast, a similar metal-metal interaction could not be found in the CdSe6 sample.

Extra-framework oxygen atoms, presumably from water remaining despite the dehydration procedures, were found by both methods. The 2-3 oxygen atoms generate the cube arrangement within the sodalite cage. CdSe6 has less extra-framework oxygen present and may be the explanation for the disruption of the cubes.

The presence of selenium is clearly evident from the EXAFS data. The bond distance of 2.61 $\text{\AA}$, found for both samples is in excellent agreement with CdSe (2.62 $\text{\AA}$). From our previous arguments it follows that selenium is incorporated into the cube in CdSe2, replacing one oxygen atom. This stoichiometry would result in average coordination number of $\text{N:Cd-O}(\text{cube})=2.25$ and $\text{N:Cd-Se}=0.75$ as found in the fit. Such a formation is depicted in figure 8.

A similar cluster formation must be excluded in sample CdSe6 and it is at this point that some ambiguity over the location of the selenium exists. The analysis of the EXAFS data represents a simplification of the true atom

distribution within zeolite-Y. This arises from the limited data and hence variable parameters possible. Only one cation site, SI', is considered in the EXAFS analysis, and this is not the only cation location as shown by the X-ray diffraction results. There also exists a site within the 12-ring, designated SIII, and it is this location which appears to be coordinated to selenium.

As described in a recent publication on analogous materials similar results have been found for the location of small semiconductor particles of CdS within the zeolite-Y framework. Evidence from EXAFS and XRD analysis led to the conclusion that $\text{Cd}_4(\text{O},\text{S})_4$ cubes were formed within the sodalite cages. Cube or disrupted cube configurations have been proposed in related zeolite systems. Calligaris et al¹⁹ investigated the structure of cadmium exchanged zeolite-X and found Cd^{2+} at SI' and oxygen at SII'. The cadmium bond distances, to framework (2.40Å) and non-framework oxygen (2.36Å) are in good agreement with our results.

In conclusion, both EXAFS and XRD data show that the adsorption of hydrogen selenide in Cd^{2+} exchanged zeolite-Y does not displace cadmium from its position within the sodalite unit. Furthermore the formation of bulk CdSe can be ruled out. It is shown that selenium is located close to cadmium, however the total removal of all water molecules is difficult, and thus the amount of residual water present in the samples may vary.

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**Table 1 Refined Atomic and Structural Parameters
for CdSe6**
space group $Fd\bar{3}m$ (International Tables I No.227)
origin at center

T(1)	-0.0532(1)	0.1250(1)	0.0365(1)	1.01(4)	192
O(1)	0.0	-0.1047(2)	0.1047(2)	2.3(2)	96
O(2)	-0.0067(3)	-0.0067(3)	0.1423(4)	2.5(2)	96
O(3)	0.0730(2)	0.0730(2)	-0.0284(4)	1.7(2)	96
O(4)	0.0742(2)	0.0742(2)	0.3213(3)	0.8(2)	96
Na(1)	0.2391(4)	0.2391(4)	0.2391(4)	oi	15.8(4)
Cd(1)	0.0693(1)	0.0693(1)	0.0693(1)	oui	11.4(1)
Cd(2)	0.424(1)	0.212(1)	0.183(1)	ef	5.2(2)
O(5)	0.1646(4)	0.1646(4)	0.1646(4)	dfd	28.9(6)
Se(1)	0.132(2)	0.465(2)	0.098(2)	dfcf	3.8(2)
Se(2)	0.093(2)	0.018(2)	0.478(2)	fds	5.0(3)
a=b=c Å	24.6366(7)				
zeropt	1.76(5)				
U	406(31)				
V	-64(25)				
W	52(5)				
X	0				
Y	4.5(1)				
R _n	10.2%				
R _{pr}	21.0%				
R _{wpr}	21.6%				
R _e	18.2%				
x ²					

cdSe6

Framework

T(1) -O(1)	1.63(1)
-O(2)	1.64(1)
-O(3)	1.68(1)
-O(4)	1.62(1)
mean	1.643
expected	1.639

Extra-framework

Na(1) -3xO(2)	2.42(1)
cd(1) -3xO(3)	2.41(1)
-3xO(5)	2.42(1)
cd(2) -O(1)	2.74(2)
-O(4)	2.70(2)
-Se(1)	2.40(8)
	2.64(8)
	3.06
	3.25
-Se(2)	2.25(7)
	2.17
	2.82
Se(1) - Se(2)	2.81
	2.88
Se(2) - Se(2)	2.61
	2.61