

Stabilization of selenium in zeolites: an anomalous X-ray scattering study

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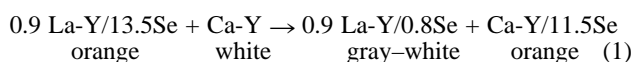
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The host–guest interactions in selenium/zeolite encapsulates are investigated with anomalous X-ray scattering (AXS) to rationalize the effects of the cation on the selenium incorporation.

The intriguing prospects of quantum confinement have stimulated many strategies to synthesize and investigate the properties of mesoscopic particles.¹ The encapsulation of semiconductor clusters within open-framework structures with large surface area like zeolites is particularly advantageous² since the zeolite itself can play the role of a solid support for these clusters, which is a prerequisite for prospective technical applications. Large arrays of quantum dots and wires with a narrow size distribution can be generated this way owing to the regular distribution of the cavities within the zeolite. The sorption of Se into molecular sieves is a typical example. Until now, studies of these systems^{3–7} have focused mostly on the structure and electronic properties of the encapsulated Se. However, little is known about the host–guest interactions in these selenium/zeolite encapsulates and the question of the driving force for the easy sorption of elemental Se into the zeolite cages has not been addressed. We note that the synthesis and characteristics of these Se/zeolite composites are distinct from those of ultramarine pigments,⁸ which are aluminosilicates with chalcogen radical anions trapped inside sodalite cages.

The sorption of elemental Se into zeolites is comparable to vaporization: the intermolecular bonds of the bulk material must be overcome to produce separate Se chains and rings inside the zeolite. The counter-cations, which counterbalance the negatively charged aluminosilica framework, are the anticipated binding sites and play a crucial role on the structure of the encapsulate as shown in our recent studies.^{9–12} In particular, the Raman spectra of Se in a number of cation-exchanged Y zeolites show the formation of Se₈ rings and predominant Se chains^{11,12} with the fraction of rings increasing along the series La-Y, Nd-Y, Ca-Y and Sr-Y. In the present work, we demonstrate that the counter-cations do not only act as structure directing agents but also contribute significantly to the stabilization of Se inside the zeolites.

A competition experiment was carried out in which La³⁺-ion exchanged zeolite La-Y (Na₃La₂₁Al₅₆Si₁₃₆O₃₈₄) was loaded with 13.5 Se atoms per supercage (La-Y/13.5Se = Se₁₀₈Na₃La₂₁Al₅₆Si₁₃₆O₃₈₄), close to the maximum uptake.¹⁰ A detailed description of the synthesis can be found elsewhere.^{10,11} This composite was then sealed in an evacuated quartz tube together with Ca²⁺-ion exchanged zeolite Ca-Y (Na₁₃Ca₂₁Al₅₆Si₁₃₆O₃₈₄), the two materials being separated by a frit. Upon heating to 350 °C, Se diffuses through the frit and is redistributed between the two zeolites. After a reaction time of 11 days, as indicated by color changes, Se was almost completely transferred to the Ca²⁺-ion exchanged zeolite Y according to the net reaction:



(La-Y/0.8Se = Se₆Na₃La₂₁Al₅₆Si₁₃₆O₃₈₄, Ca-Y/11.5Se = Se₉₂Na₁₃Ca₂₁Al₅₆Si₁₃₆O₃₈₄). The Na, Al, Si, Ca, and La content

were analyzed by atomic absorption spectroscopy (AAS). The Se uptake was determined from the weight balance (>99%). The only difference between the two forms of zeolite is the number and location of the metal ions.^{10,11} Rare-earth cations form oxygen bridged clusters inside the smaller sodalite cages (6.5 Å diameter), whose windows (1.4 Å wide) are too narrow to admit molecular Se structures. In contrast, alkaline-earth cations are found also in the large supercages (13 Å diameter, 7.5 Å windows) in close proximity to the Se encapsulates.^{10,11}

Since the structure of the incorporated Se is disordered with respect to the zeolite framework, crystallography does not yield information about the Se–cation interactions. Instead, we employed anomalous X-ray scattering (AXS) that has been successfully used for the study of bulk disordered materials.¹³ This method exploits the strong energy variation of the complex atomic scattering factor $f(Q, E) = f_0(Q) + f'(E) + if''(E)$ in the vicinity of an X-ray absorption edge. A differential structure factor $S_z(Q)$ associated with a particular element z can be obtained from the difference of two diffraction measurements performed with incident energies some ten and some hundred eV below the absorption edge.¹⁴ The scattering factors of the other elements in the sample do not change significantly over such an energy range. The differential pair distribution function $T_z(r)$, which is obtained from $S_z(Q)$ via Fourier transformation, gives information about the average spatial environment about the z atoms.¹⁴

In the present study we determined $S_{\text{Se}}(Q)$ for two zeolites with Se loading similar to those of eqn. (1): La-Y/11.7Se and Ca-Y/12.8Se. (The samples used for the competition experiment were too small for the X-ray measurements. Since we are presenting a difference of two measurements, the result should not be sensitive to the actual Se loadings as long as they are reasonably high and of similar magnitude in the two samples). The diffraction patterns were measured at energies 20 eV and 300 eV below the K absorption edge of Se (12658 eV). Although the Se concentration is <15 atom% in each compound, the quality of the $S_{\text{Se}}(Q)$ data (Fig. 1) is reasonably good. The two corresponding $T_{\text{Se}}(r)$ look similar (Fig. 2). The oscillations below 2 Å are due to truncation effects caused by the limited range of Q in the $S_{\text{Se}}(Q)$ data. The first real peak is centered at 2.34 ± 0.02 Å in both distribution functions: this distance is well within the range of intramolecular bond lengths observed for bulk Se forms: 2.33 Å (trigonal Se),¹⁵ 2.37 Å (monoclinic Se)¹⁶ and 2.35 Å (amorphous Se).¹⁷ The number of next-nearest neighbors was determined from the area in the radial distribution function $T_{\text{Se}}(r)$ corresponding to these peaks. The extracted coordination number $\text{CN}(1) = 2.2 \pm 0.3$ is consistent with the existence of either infinite chains or rings [both with $\text{CN}(1) = 2.0$] inside the zeolite pores, corroborating the conclusion of our earlier Raman spectroscopic studies.^{11,12} The second peak is located between 3.0 and 4.3 Å in both $T_{\text{Se}}(r)$ functions. At least two different types of interaction contribute to it,¹⁸ second-neighbor Se–Se interactions at a distance of 3.7 Å and Se–O (framework) interactions at a distance of 4 Å. From the first and second nearest Se–Se distances R_1 and R_2 , a bond angle of $\phi = 104 \pm 2^\circ$ can be deduced [$R_2 = R_1 \sin(\phi/2)$] which again is in the range of values found in bulk Se forms.¹⁸ In the region above 4.5 Å, the assignment of further interactions is impossible, but significant differences between the two sets of

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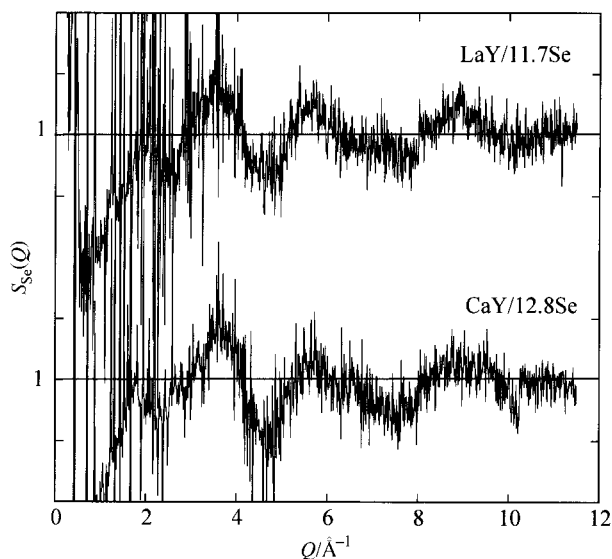


Fig. 1 Differential structure factors $S_{\text{Se}}(Q)$ of Ca-Y and La-Y loaded with 12.8 and 11.7 Se atoms per supercage, respectively, obtained from X-ray diffraction experiments at energies 20 and 300 eV below the K absorption edge of Se (12658 eV).

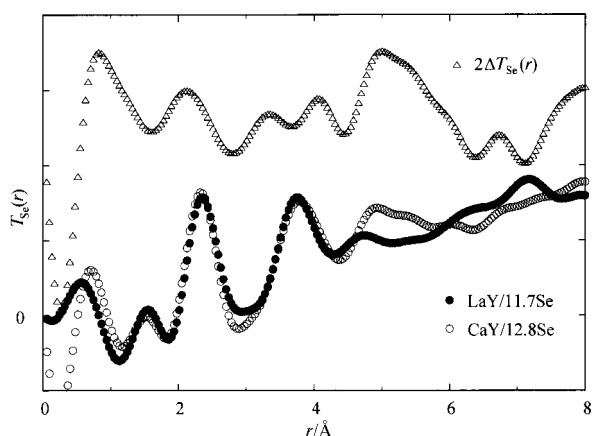


Fig. 2 Differential pair distribution functions $T_{\text{Se}}(r)$ of Ca-Y loaded with 12.8 Se atoms (open circles) and La-Y loaded with 11.7 Se atoms (filled circles) per supercage. The difference $\Delta T_{\text{Se}}(r)$ of the two $T_{\text{Se}}(r)$ functions is shown at the top: the peak around 5 Å is attributed to the Ca^{2+} -Se interaction, as discussed in the text.

$T_{\text{Se}}(r)$ functions in this region are noticeable and can be attributed to the Ca^{2+} -Se interaction, since, as discussed above, we believe that Se cation interactions exist in the Ca-Y zeolite and not in the La-Y zeolite. A corresponding peak emerges clearly around 5 Å in the difference $\Delta T_{\text{Se}}(r)$ of the two pair distribution functions (Fig. 2).

This long Ca^{2+} -Se distance is striking because it suggests a rather weak attraction. For comparison, the shortest possible Ca^{2+} -Se distance is given by the sum of the radii of Ca^{2+} (0.99 Å) and Se (1.17 Å). On the other hand, an interatomic distance of 2.965 Å is found in the ionic compound CaSe^{19} where strong binding forces exist between Ca^{2+} and Se^{2-} . The attraction between Ca^{2+} and a neutral Se chain would be expected to be much weaker inside the zeolite. Probably, the geometrical requirements of both the zeolite framework and the Se chain prevent a close approach. The bond distances and angles of the zeolite encapsulated Se chains do not vary considerably from those found in bulk forms¹⁸ and the dihedral angles are not expected to either. Thus, the short-range order appears to be rather robust and distortion of the Se chains towards the cations

becomes unfavorable. Also, the Ca^{2+} ions in the supercage bind strongly to the anionic framework oxygen. In fact, the favorite Ca^{2+} site in the faujasite supercage is only slightly (0.3 Å) out of the plane of the sodalite windows.²⁰ Thus, they are not easily accessible for a fairly rigid Se chain. Furthermore, the electronic repulsion between the Se and the anionic framework oxygen prevents a close approach of the Se chain to the framework counteracting the weak attractive forces between Se and Ca^{2+} . On these considerations, the observed Ca^{2+} -Se distance of 5 Å appears reasonable. However, these attractive forces acting over this long range are still capable of stabilizing the Se chain significantly in the Ca-Y as opposed to the La-Y zeolite, as shown by the competition experiment described above.

In this work, we have shown that cations play an important role in the stabilization of Se in the pores of zeolites. The nature of the binding interactions has been investigated with AXS, which has allowed us to highlight the environment of the encapsulated Se with an atomic concentration of < 15%: Se assumes a disordered arrangement within these porous materials. The attractive forces between the encapsulated Se and the zeolitic cations act over a surprisingly long distance of 5 Å.

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