X-Ray absorption and photoelectron spectroscopic observation of intrazeolitic silicon nanoclusters

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The Si-K near-edge absorption spectra and X-ray photoelectron spectra of silicon nanoclusters encapsulated in the pores of zeolite Y are measured; the intrazeolitic Si clusters display a blue shift of the K-edge (0.5 eV) relative to that of bulk Si and a strong room-temperature photoluminescence, which is consistent with the quantum confinement effect; the number of Si in the as-prepared sample is estimated to be 20 atoms per unit cell of zeolite Y from both XPS and Si K NEXAFS analysis.

The drive towards nanoscale technology has motivated intense research on Si clusters and nanocrystals.[1] These are new forms of Si that exhibit quantum confinement effects and novel optoelectronic properties, such as efficient room-temperature photoluminescence. Several chemical approaches have been used to prepare these nanostructured forms of Si, including solution-phase synthesis *via* the dehalogenation of halosilanes by alkali metals[2,3] or by the Zintl compound KSi,[4] ultrasonic fracture of electrochemically etched Si wafers (porous Si),[5] gas-phase depositions by either slow combustion[6] or microwave plasma[7] of silanes and molecular sieve encapsulation *via* chemical vapour deposition of gaseous silanes.[8] Except for the molecular sieve encapsulation, these methods produce Si clusters with broad size distribution ranging from several Ångstroms to hundreds of nanometres. With well defined and well ordered cavities and channels, molecular sieves provide a ready access for synthesizing single-sized clusters and assembling cluster arrays periodically.[9]

Recently, Ozin *et al.* reported the synthesis of intrazeolitic Si nanoclusters.[8a] Dehydrated zeolite HY was employed to anchor disilane. FTIR spectroscopy showed that the disilane selectively reacted with the hydroxy group of the Brønsted-acid sites within the supercages. Subsequent thermal treatment of the silane-containing zeolite precursor led, *via* H_2 elimination and Si clustering reactions to intrazeolitic Si nanoclusters. The overall process is believed to occur *via* eqn. (1), where Z represents the zeolite framework and Y is zeolite Y.

$$\text{Z–OH} + \text{Si}_2\text{H}_6 \xrightarrow[-\text{H}_2]{} \text{Z–OHSi}_2\text{H}_5 \xrightarrow[-\text{H}_2]{\text{heat}} (\text{Si}_n\text{H}_m)\text{Y} \qquad (1)$$

The dimensions of such nanoclusters are too small for standard microscopic (*e.g.* TEM) and diffraction (*e.g.* XRD) techniques to provide detailed structural information. Here, for the first time, we describe direct evidence for the formation of intrazeolitic Si clusters, their electronic properties and average cluster size from the study of Si-K near-edge absorption fine structure and core-level X-ray photoelectron spectroscopy.

The intrazeolitic silicon clusters used in this work were prepared by a procedure similar to that reported previously.[8a] Known quantities of disilane gas were transferred into a closed vessel containing zeolite HY through a vacuum line equipped with a pressure meter.† The mixture was then heated at 100 °C for 40 h. After removing the generated H_2 and unreacted disilane, the sample was heated to 550 °C at 1 °C min^{-1} and held at this temperature for 2 h under vacuum (10^{-3} Torr). The resulting solid is an air-stable pale yellow powder. X-Ray diffraction analysis showed that the long-range lattice of the zeolite framework was distorted but that the order of zeolite cavities remained intact.

Si K-edge absorption measurements were performed at the Syncrotron Radiation Center at University of Wisconsin at Madison, WI, using the CSRF beamline and a double-crystal monochromator with InSb(111) crystals.[10] All data were obtained with total electron yield detection and an effective sampling depth of *ca.* 700 Å.[11] Fig. 1 shows Si-K near-edge X-ray absorption fine structure (NEXAFS) data from both as-prepared intrazeolitic silicon clusters and zeolite HY. The edge at 1847 eV is due to the framework SiO_2 in zeolite. Two additional absorptions are found in the as-prepared intrazeolitic silicon clusters, *i.e.* at *ca.* 1839 and 1845 eV, respectively. The former is characteristic of a non-oxidized form of silicon and can be unambiguously attributed to the presence of silicon clusters. The intensity of this absorption is size-dependent and increases with the disilane loadings.[12] In their NEXAFS study of surface-oxidized silicon nanocrystals, Schuppler *et al.* assigned the absorption edges at ⩾1843 eV between the crystalline Si (c-Si) and SiO_2 thresholds to the interfacial SiO_x ($x < 2$) species.[13] Similarly, the absorption edge at 1845 eV can be attributed to ≡SiO and =SiO_2 species which connect silicon clusters to the framework. This assignment was further supported by the *in situ* FTIR study of the encapsulation process indirating that both $HSiO(Si)_2$ and $HSiO_2(Si)$ were found in the intrazeolitic Si clusters.[12] Soft X-ray photoemission spectroscopy of the as-prepared sample showed the presence of SiO_2 only and no detectable non-oxidized form of Si in the outer 25 Å of the zeolite particles. This provides confirmation that essentially all of the silicon clusters are within the zeolite pore structure.

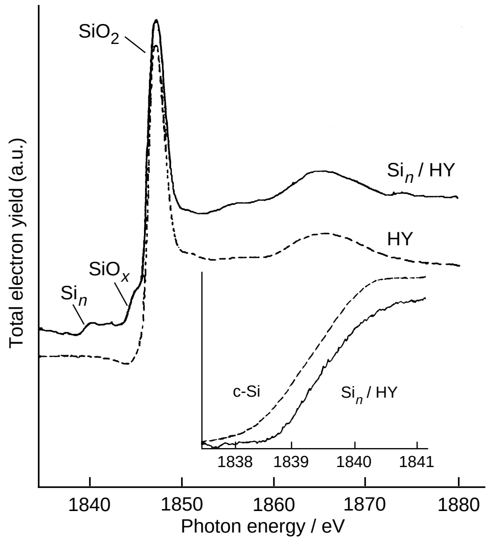

Fig. 1 Si K-edge NEXAFS data from intrazeolitic silicon clusters (Si_n/HY) and zeolite HY. Inset shows the comparison of the Si absorption edges between crystalline Si (c-Si) and silicon clusters.

A detail of the Si K-edge absorption for as-prepared intrazeolitic silicon clusters and c-Si is presented in the inset of Fig. 1. From this it can be seen that the absoption edge for the silicon clusters is *ca*. 0.5 eV higher than that of c-Si. A blue shift in the absorption edge is indicative of a quantum confinement effect where the bottom of the LUMO orbitals (or conduction band) is raised relative to the 1s core level. A similar observation has been reported in the Si K-edge absorption studies of porous-Si (p-Si) samples, whose absorption edge is *ca*. 0.4–0.5 eV higher than that of c-Si.[14]

X-Ray photoelectron spectroscopy (XPS) was used to determine the chemical composition. Fig. 2 shows the XPS spectra from both intrazeolitic silicon clusters and zeolite HY samples. In addition to the peak at the Si 2p binding energy of 102.9 eV, corresponding to SiO_2, a weak peak centred at 99.2 eV appears in the intrazeolitic silicon clusters. This peak is characteristic of the Si 2p binding energy for unoxidized Si, reflecting the presence of silicon clusters. The SiO species, indentified by the NEXAFS above, is not observed because its concentration is so low that its peak is overlapped by that of SiO_2 in the XPS spectrum. Within the XPS detectable range (the outer 50 Å of the zeolite particles), the contents of SiO_2 (framework of zeolite) and Si (silicon clusters) were determined to be 93.19 and 6.81 atom%, respectively. This comparison enables an approximate estimate of the minimum occupancy of Si (as silicon clusters) in the zeolite pores, *i.e. ca.* 20 Si atoms per unit cell.‡ This number is similar to that obtained from the edge jump of the X-ray absorption spectrum.‡

The as-prepared intrazeolitic silicon clusters exhibit a strong room-temperature photoluminescence. Remarkably, its broad spectrum with a peak energy of 2.28 eV (with 488 nm excitation) closely resembles that of the organosilicon cluster, *syn*-tricyclooctasilane (2.25 eV).[15] This tentatively suggests that the structure of the intrazeolitic silicon clusters resembles that of *syn*-tricyclooctasilane. Further investigation into the cluster size and shape is in progress.

In summary, we have demonstrated that Si K-edge absorption spectroscopy is a useful tool for the direct observation of the encapsulation of silicon clusters in zeolite Y and for the study of their electronic properties. XPS provides a means of estimating the content of Si in each unit cell of zeolite.

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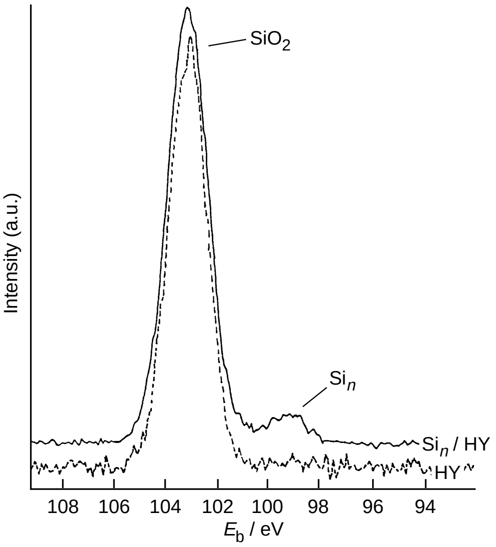

Fig. 2 XPS data from intrazeolitic silicon clusters and zeolite HY

Footnotes

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† Zeolite HY was prepared from commercial zeolite Y (LZ-Y52, $SiO_2/Al_2O_3 = 4.74$) by (*i*) fully exchanging the Na content with NH_4 cations to generate NH_4Y, (*ii*) slowly heating the NH_4Y to 460 °C at 1 °C min^{-1} increments, (*iii*) maintaining this temperature for 10 h, and then (*iv*) gradually cooling to room temperature; all steps at a pressure $< 10^{-3}$ Torr except (*i*). The HY zeolite contains eight supercages per unit cell. The disilane loadings were calculated according to $4Si_2H_6$ per supercage.

‡ XPS spectra were recorded on the XPS Kratos Axis Instrument, using monochromated Al-Kα radiation. The effective sampling depth is 50 Å. The unit-cell formula for a dehydrated zeolite HY can be expressed as $H_{56}(AlO_2)_{56}(SiO_2)_{136}$. Because the photoemission experiment shows that the non-oxidized form of Si is undetectable in the outer 25 Å of the zeolite, the actual Si content in the body of zeolite should be at least twice as much as that measured by XPS, when compared with the measured SiO_2 content in the same sampling depth (50 Å). Therefore, the number of Si atoms per unit cell can be calculated as follows: $2 \times 6.81 \times (135/93.19) \approx 20$.

In Si K-edge absorption spectra, the relative concentrations of Si and SiO_2 in the intrazeolitic Si clusters are also directly proportional to their individual edge jumps.[16] Since each unit cell of zeolite contains 136 units of SiO_2, the number of Si can thus be estimated to be 13 atoms per unit cell from its edge jump relative to that of SiO_2. By adding the contribution of SiO_x species to Si clusters, the Si atoms per unit cell would be *ca*. 20, in agreement with the estimation by XPS data.

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