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## The nature of encapsulated silicon nanoclusters in zeolite Y

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Luminescent silicon clusters have been synthesized by chemical vapor deposition of  $Si_2H_6$  into the supercages of H<sub>32</sub>Na<sub>24</sub>Y zeolite. The encapsulated Si clusters are air stable and exhibit a room-temperature photoluminescence in the green-yellow region. The electronic band gap of the cluster is determined to be about 2.4 eV from photoelectron and photoabsorption spectroscopies. A saturation loading of seven disilane molecules per supercage was determined *directly* from multiple quantum <sup>1</sup>H nuclear magnetic resonance spin counting of the precursor material. Intrazeolitic  $Si_n$ clusters are formed after heating with loss of SiH<sub>4</sub> and H<sub>2</sub>. The new quantitative spin counting result is consistent with an average value of 12±2 Si/cluster obtained from previous indirect measurements using x-ray photoelectron spectroscopy and Si K-edge x-ray absorption near-edge spectroscopy [J. He, D. D. Klug, J. S. Tse, C. I. Ratcliffe, and K. F. Preston, Appl. Phys. Lett. 71, 3194 (1997)]. This observation reveals a mechanism for the conversion of gaseous Si<sub>2</sub>H<sub>6</sub> into silicon nanoclusters. © 1999 American Institute of Physics. [S0003-6951(99)02506-1]

The encapsulation of semiconductor nanoclusters in the pores of zeolite molecular sieves has been actively explored as a means of producing tunable light-emitting materials.<sup>1–5</sup> The well-defined and well-organized cavities provided by a zeolite host serve as an ideal environment to control the encapsulated cluster's size and shape and to assemble the clusters in an ordered array. There is also the advantage of stabilizing the normally very unstable nanosized clusters through encapsulation and coordination to the host framework. While encapsulated II-IV semiconductor clusters in zeolites have been extensively studied,<sup>6-10</sup> relatively little work has been systematically carried out on III-V (Ref. 11) and IV (Refs. 12 and 13) clusters, particularly Si clusters, in such systems.

The synthesis of Si nanoclusters in dehydrated HY zeolite through the chemical vapor deposition of disilane (Si<sub>2</sub>H<sub>6</sub>) gas was reported recently.<sup>10</sup> This encapsulated Si cluster exhibits strong room-temperature photoluminescence and the optical absorption edge was found to shift to higher energy with respect to bulk silicon.<sup>15</sup> The exact nature of the electronic structure, the origin of the luminescence, the cluster formation mechanism and, perhaps more importantly, the size of the clusters remain uncertain. These key issues are investigated in the present work. For the framework structure, we chose to prepare the Si clusters in a partially exchanged acidic form of the Y zeolite (H<sub>32</sub>Na<sub>24</sub>Y-NaHY), because this starting material has a much better thermal stability than the HY zeolite used previously.

Silicon clusters were prepared by chemical vapor deposition (CVD) of disilane gas (98%, Matheson) within the pores of NaHY zeolite, to a saturation loading determined previously. The disilane gas was transferred into a closed vessel containing the dehydrated-deamminated zeolite powder and the mixture was then heated at 100 °C for 40 h. This treatment produced intrazeolitic Si cluster precursors. The loading of Si2H6 was roughly estimated according to the quantity of zeolite used and the amount of Si<sub>2</sub>H<sub>6</sub> reacted. After removal of the generated H<sub>2</sub> and unreacted Si<sub>2</sub>H<sub>6</sub> by pumping at 100 °C for 1 h, the precursor was further heated to 550 °C at 1 °C/min and held at this temperature for 2 h to eliminate more H<sub>2</sub> and some SiH<sub>4</sub>. The resulting solid is stable in air and is pale yellow in color. Analysis of all these zeolitic materials by x-ray diffraction (XRD) reveals that the crystallinity and integrity of the zeolite host is maintained with no sign of diffraction peaks characteristic of crystalline silicon (c-Si).

The encapsulation process of Si clusters within the pores of zeolite includes the anchoring of Si<sub>2</sub>H<sub>6</sub> followed by the clustering of the entrapped disilane precursor via the elimination of the H atoms as hydrogen. These chemical processes were monitored by in situ infrared (IR), thermogravimetric analysis-mass spectrometer (TGA-MS), and solidstate <sup>29</sup>Si magic angle spinning (MAS) NMR spectroscopy. The appearance of new vibrational bands characteristic of  $O-SiH_m-SiH_n$  stretching after the initial reaction of disilane with the zeolite indicate the anchoring of Si<sub>2</sub>H<sub>6</sub>. Upon pyrolysis, the clustering of the anchored disilane is indicated by the elimination of gaseous silane (SiH<sub>4</sub>) and hydrogen as monitored by mass spectrometry, and the gradual decrease of the Si-H stretching IR intensities. The formation of new Si–Si bonds is clearly shown from the observation of <sup>29</sup>Si NMR resonances at  $\sim -79$  ppm relative to tetramethylsilane (TMS), which are characteristic of Si nuclei directly bonded to 3-4 Si atoms. All the spectroscopic evidence unequivocally substantiates the formation of Si clusters inside the pores of the zeolite.

Prior to the measurement of the photoluminescence (PL) of intrazeolitic  $Si_n$  clusters, the luminescent behavior of the pristine NaHY host was evaluated. Only a weak emission that may be associated with the hydroxyl groups in the zeolite host was observed around 500 nm at room temperature. Figure 1 shows the room-temperature PL spectrum of intrazeolitic Si<sub>n</sub> clusters prepared from a saturation loading of disilane. The emission is found to peak at 560 nm-in the green-yellow region of the visible spectrum. Samples prepared with smaller disilane loadings, and hence, smaller Si clusters, also display strong room-temperature photoluminescence in the same region. The PL intensity increases with the

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FIG. 1. Room-temperature photoluminescence spectrum for the Si clusters/NaHY sample (with 488 nm  $Ar^+$  laser excitation).

amount of Si but the peak energy does not appear to shift appreciably. This observation indicates that discrete Si clusters are formed only inside the cages, and that they become more homogeneously dispersed in the zeolite host with increase of Si loading.

For the intrazeolitic semiconductor nanocluster systems, where the atomic compositions of the constituent semiconductor cluster are different from those of zeolite (Al, Si, and O), chemical (or elemental) analysis is generally applied to quantify the size of the cluster per unit cell of zeolite. Furthermore, in the case of II-VI nanoclusters,<sup>6,10,11</sup> it is also possible to measure the coordination shell of the cluster by using extended x-ray ray absorption fine structures (EXAFS) or anomalous x-ray scattering (AXS).<sup>25</sup> This, in combination with chemical analysis, can be employed to study the size and shape of the cluster. However, neither chemical analysis nor EXAFS is applicable to the intrazeolitic Si cluster system, owing to the overlap of the Si peak from both cluster and zeolite host. Furthermore, AXS is impracticable for Si due to the comparatively low-energy K-shell absorption edge. The two-dimensional (2D) multiple quantum <sup>1</sup>H NMR spin-counting technique is employed here to determine the number of entrapped disilane precursors in the supercage of zeolite.

In multiple-quantum (MQ) <sup>1</sup>H NMR, individual spins (protons) become correlated with each other through their dipolar couplings as a function of time.<sup>14</sup> Such MQ coherences are generated by applying an appropriate radiofrequency pulse sequence to the sample for a time  $\tau$ , thus inducing a Hamiltonian to force the spins to act collectively. For a finite coupled proton system (e.g., in the form of a cluster), the growth of coherences levels off at a value corresponding to the number of protons in the cluster. A plot of the number of correlated spins as a function of time for the sample of disilane entrapped in NaHY is shown in Fig. 2. The correlated spin numbers were obtained by fitting the experimental intensities of the MQ coherences to a Gaussian distribution model. As expected, the correlated spin number increases with MQ excitation time and finally levels off at  $N(\tau) \approx 38 \pm 1$  after 1500 µs. The error associated with the



FIG. 2. Number of correlated protons vs MQ excitation time for the entrapped  $Si_2H_6$  precursor in NaHY.

Gaussian fit is estimated to be less than 0.8 proton. Since the NaHY host can only provide four acidic sites for anchoring  $Z(eolite)O-Si_2H_5$ , i.e., 20 H/supercage, the remaining 18 protons come from three chemisorbed Si<sub>2</sub>H<sub>6</sub>···NaHY. Within the error limit, 4 ZO-Si<sub>2</sub>H<sub>5</sub> and three chemisorbed Si<sub>2</sub>H<sub>6</sub> giving a total of 38 H is a realistic possibility. This structural model accounts for a total of seven disilane molecules entrapped in each supercage, and implies that the maximum number of Si available to form a cluster is 14 Si/supercage. The MQ NMR spin counting technique was also used to determine that a maximum of five protons remain in the final Si clusters after thermal treatment at 550 °C. Taking into consideration the elimination of H<sub>2</sub> and some  $SiH_4$  during the pyrolysis step, the average cluster size of the disilane precursor is quite consistent with the estimated average size of  $12\pm 2$  atoms in the final cluster estimated reported earlier.<sup>15</sup> The mechanism of the anchored disilanes can be envisioned as follows:

chemisorbed

 $\begin{array}{c} \downarrow \\ \text{ZO}-(Si_2H_5)_4(Si_2H_6)_3 \rightarrow \text{ZO}-(Si_{12}H_5)+12.5 \text{ H}_2\uparrow+2SiH_4\uparrow. \\ \uparrow \\ \text{anchored} \\ \text{intrazeolitic cluster} \end{array}$ 

X-ray absorption and photoemission spectroscopies can be used to measure the energies of the conduction- (CB) and valence- (VB) band edges of the Si cluster. From the energy shifts of the band edges relative to the values of c-Si, one should be able to characterize the band gap of the cluster. It was shown earlier that the onset of the K- and L-edge absorption edge for the Si cluster is blueshifted about 0.4 eV relative to that of c-Si.<sup>15</sup> Similar observations were also reported on other nanostructured Si systems, e.g., por-Si (Ref. 16) and layered polysilane.<sup>17</sup> Figure 3 shows the valenceband spectra for empty and Si cluster enclathrated NaHY zeolites. The two spectra are normalized by matching the maximum of the predominantly framework Si-O ionization at 14 eV. The difference of these two spectra yields a reasonable valence-band spectrum of the  $Si_n$  clusters. In order to compare the valence-band edge of the clusters to that of c-Si, we calibrated the respective spectra against their Si 2pcore level using a procedure described earlier.<sup>18</sup> The corrected valence band spectrum for the  $Si_n$  cluster is compared with that of c-Si, in Fig. 3. The energy of the valence- and L-band edge is determined as the intercept of the extrapo-



FIG. 3. Valence-band spectra for (a) pure NaHY and Si clusters/NaHY, and (b) *c*-Si and Si-clusters (obtained from the difference of the Si clusters/NaHY and NaHY). The valence-band photoemission spectra were measured using 150 eV synchrotron radiation with a Grasshopper Monochromator installed at the Canadian Synchrotron Radiation Facility, Synchrotron Radiation Center, University of Wisconsin, Madison.

lated linear part of the band edge just above the threshold with the base line.<sup>18,19</sup> The valence-band edge of the  $Si_n$ clusters shifts by 0.9 eV to higher binding energy when compared with c-Si. This observation suggests that the VB in Si<sub>n</sub> clusters is 0.9 eV lower than the valence-band maximum in c-Si. It is noteworthy that the shift of the VB energy level relative to c-Si is significantly larger than that of the CB energy level. This trend is consistent with recent experimental studies on porous Si (Ref. 18) and the calculations on hydrogenated Si clusters.<sup>20</sup> Taking the sum of the VB and CB band edge shifts of 1.3 (=0.9+0.4) eV and the indirect band gap of c-Si (1.1 eV), the band gap of the Si clusters is estimated to be 2.4 eV. This result is consistent with the PL peak energy (2.2 eV, see below) and the optical gap (2.22 eV) on similar Si<sub>n</sub> clusters in dehydrated HY zeolite.<sup>13(a)</sup> This value is much smaller than the 3-4 eV band gap for "free" Si clusters of similar size deduced from theoretical calculations.<sup>21,22</sup> Experimental studies have also strongly suggested that the relationship between the band gap and size of the cluster is not simple in small clusters.<sup>22</sup>

The maximum of the luminescence peak of the intrazeolite Si<sub>n</sub> cluster is found to be about 560 nm (2.2 eV). This value is very close to the estimated band gap. The consistency between the luminescence peak and the band gap suggests that the luminescence arises predominantly from the radiative electron-hole recombination between VB and CB levels, and no midgap surface states or defects are involved in the process. Incidentally, the position of the PL peak is very close to the luminescence at 2.25 eV observed in the syn-tricyclooctasilane molecule.<sup>23</sup> It is plausible that the intrazeolitic Si clusters may be a derivative of syntricyclooctasilane and have a similar basic ladder-like structure.<sup>24</sup> Molecular modeling calculations show that this In conclusion, a topotactic synthetic pathway has been used to assemble periodic three-dimensional arrays of  $Si_n$ clusters through the chemical vapor deposition of  $Si_2H_6$ within the supercages of NaHY zeolite. 2D multiple quantum <sup>1</sup>H NMR spin counting indicates that there are four anchored ZO- $Si_2H_6$  and three chemisorbed  $Si_2H_6$  units making a total of 14 Si in each supercage at saturation loading. Upon thermal treatment, a clustering reaction takes place. Taking into account the probable error in the measurement of the intensity in Si *K*-XANES, a cluster size of  $12\pm 2$  Si atoms is obtained. These  $Si_n$  clusters have a band gap of 2.4 eV and exhibit a room-temperature photoluminescence in the greenyellow region.

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