

## FT-ICR study of chemical reaction of silicon clusters

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It is crucial to understand the surface reaction of semiconductor materials such as silicon and germanium for the current nanotechnology. The semiconductor clusters can serve as the important model material of surface reaction. Furthermore, the structural and chemical information of semiconductor cluster is directly important for the generation and characterization of the quantum dot. Here, experimental measurements of chemical reaction of silicon clusters  $\text{Si}_n^+$  ( $10 \leq n \leq 20$ ) to ethylene was performed with the Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer.

Silicon clusters generated by the laser-vaporization supersonic-expansion cluster beam source were directly injected to the 6 Tesla superconducting magnet of FT-ICR mass spectrometer. Fig. 1(a) shows the FT-ICR mass spectrum of the injected and trapped clusters. Each thick peak corresponding to clusters  $\text{Si}_n^+$  were made of 6 to 8 lines of 1 amu apart. This isotope distribution pattern agreed well to the distribution calculated from the natural abundance of silicon isotopes. The small peaks between silicon cluster peaks were due to addition of a carbon or an oxygen atom to each cluster. In order to observe the chemisorption reaction product on a clean baseline, all clusters except for  $\text{Si}_{17}^+$  were excited away from the ICR cell by the selective RF excitation called "SWIFT" (Stored Waveform Inverse Fourier Transform) technique. It was especially crucial for reaction of ethylene that has the same mass of silicon atom. Clusters were well thermalized to the room temperature by exposures to argon at a pressure of at  $1 \times 10^{-5}$  Torr for 10 seconds after SWIFT. Fig. 1(b) shows the mass spectrum measured after this mass selection. Fig. 1(c) shows the results of exposure of  $\text{Si}_{17}^+$  to ethylene at  $1 \times 10^{-5}$  Torr for 0.2 seconds. Successive chemisorption of ethylene molecules were observed. Even though most of  $\text{Si}_{17}^+$  chemisorbed one or two ethylene already at 0.2 s, some  $\text{Si}_{17}^+$  still remained unreacted at 5 s. The existence of less reactive isomer was suggested.

For the chemisorption of first ethylene, kinetic reaction process was explored for  $\text{Si}_n^+$  ( $10 \leq n \leq 20$ ) by changing the reaction time. The pseudo-first-order kinetics of the reaction is expressed as

$$\ln(I/I_0) = -k[\text{C}_2\text{H}_4]t,$$

where  $I_0$  and  $I$  were initial and final abundance of  $\text{Si}_n^+$  in a reaction for time  $t$ , respectively. Except for  $\text{Si}_{14}^+$ , all clusters did not follow this pseudo-first-order kinetics. The over-all trend in dependence of the rate constant  $k$  on cluster size was in good agreement to Jarrold's ion drift tube experiments. The remarkable discrepancies of experimental results between ion drift tube experiments by Jarrold et al.<sup>(1)</sup> and FT-ICR experiments of Smalley's

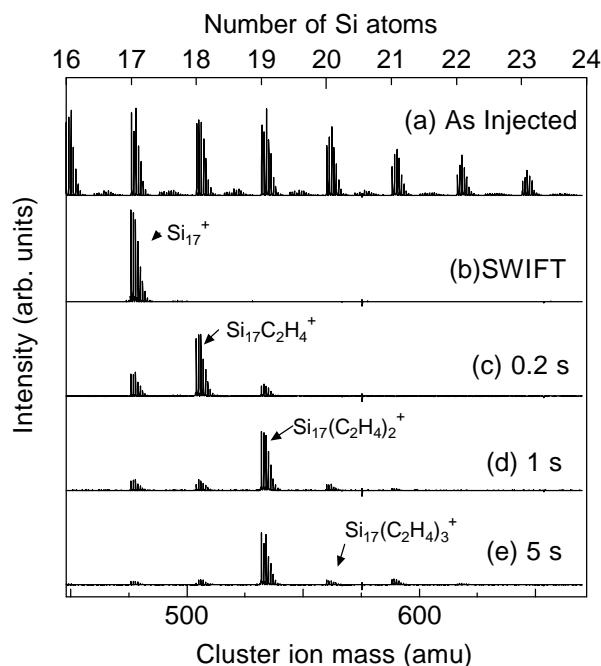


Fig. 1 FT-ICR spectra of reaction of  $\text{Si}_{17}^+$  with ethylene. (a) silicon clusters as injected from the cluster source, (b) after SWIFT ejection to keep only  $\text{Si}_{17}^+$ , (c) after an exposure of  $\text{Si}_{17}^+$  to ethylene at  $1 \times 10^{-5}$  Torr for 0.2 s, (d) 1 s, (e) 5 s.

group<sup>(2)</sup> was not realized in this size range. In general, present experimental results showed less abundance of less-reactive isomers compared to Jarrold's experiments. Furthermore,  $\text{Si}_n^+$  ( $n = 11, 18, 19$ ) did not show the first-order-kinetics in contrast to Jarrold's.

As shown in Fig. 1(d) and (e), the product distribution became almost the same after some time of reaction process. These final product distributions were summarized for all cluster size. It was directly demonstrated that the final distribution was not from the chemical equilibrium. The final product distribution was the result of the isomers of  $\text{Si}_n^+$  or isomerization due to the chemisorption of ethylene molecules. A remarkable special stability of  $\text{Si}_x(\text{C}_2\text{H}_4)_y^+$  when  $x + y = 19$  was observed in these final product distributions. The selectivity of reaction site was strongly suggested from the result.

## References

- (1) K. M. Creegan and M. F. Jarrold, *J. Am. Chem. Soc.*, 112, 3768, (1990).
- (2) S. Maruyama, L. R. Anderson and R. E. Smalley, *J. Chem. Phys.*, 93, 5349, (1990).