

# CHEMICAL REACTION OF SILICON CLUSTER IONS WITH ETHYLENE BY USING FT-ICR MASS SPECTROMETER

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Mass-selected silicon cluster ions were levitated in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer and monitored during chemisorption reaction with ethylene ( $C_2H_4$ ). Through measurements of "time-dependency" of this reaction process, drastic change of the reactivity depending on the number of absorbed ethylene was observed, in addition to the strong dependency to silicon cluster size.

Silicon cluster is the one of the most important subject of the cluster science, because bulk silicon is the most important semiconducting material in the electronics industry. Among many experimental and theoretical studies on silicon clusters, measurement of reactivity to gases is one of the most useful experimental techniques. Jarrold et al.<sup>1</sup> investigated the reaction kinetics for the addition of the first ethylene molecules with use of injected ion drift tube techniques. Maruyama et al.<sup>2</sup> reported that "laser-annealing" is possible by the excimer laser excitation of the silicon clusters levitated in the magnetic field of a FT-ICR spectrometer. In this study, we have implemented a FT-ICR spectrometer directly connected to a laser-vaporization supersonic-expansion cluster beam source and mass-selected silicon cluster ions were levitated in a FT-ICR spectrometer and monitored during chemisorption reaction with ethylene.

Fig. 1 shows a example of FT-ICR mass spectra of the reaction process for  $Si_{15}^+$ . The top panel Fig.1(a) shows the FT-ICR mass spectrum of silicon cluster cations in the 11-23 atom size range as injected from a laser vaporization supersonic cluster beam source. In order to observe the chemisorption reaction product on a clean baseline, all clusters except for  $Si_{15}^+$  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 5 seconds before and after SWIFT. Fig. 1(b) shows the mass spectrum measured after this mass selection. Fig.1(c) shows the results of exposure of  $Si_{15}^+$  to ethylene at  $1 \times 10^{-4}$  Torr for 0.5 seconds. Successive chemisorption of ethylene molecules are observed. It is interesting that  $Si_{15}E_1^+$  is observed as stronger signal than the parent  $Si_{15}^+$ . It means that silicon cluster becomes less reactive after an absorption of one ethylene molecule. Fig.1 (d) shows more drastic change of the reactivity depending on the number of ethylene molecules. It is obvious that  $Si_{15}E_1^+$  and  $Si_{15}E_4^+$  are considerably less reactive. It is also possible that there are several isomers of  $Si_{15}^+$  with different reactivity.

Similar studies for parent silicon clusters from 11 to 20, 25, 30 atoms shows a special stability of  $Si_xE_y^+$  when  $x + y = 19$ , such as  $Si_{15}E_4^+$ . Such information

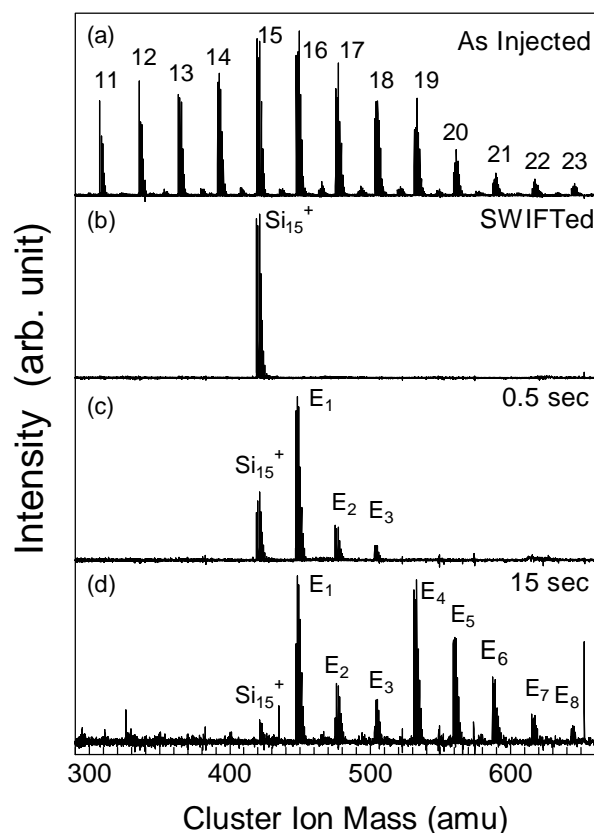


Fig.1 FT-ICR mass spectra of the reaction process, (a) silicon cluster cations as injected from a laser vaporization supersonic cluster beam source, (b) after selective SWIFT ejection, (c) after an exposure of  $Si_{15}^+$  to ethylene at  $1 \times 10^{-4}$  Torr for 0.5 seconds [the  $Si_{15}(C_2H_4)_n^+$  chemisorption products are marked as  $E_n$ ]. (d) after an exposure of  $Si_{15}^+$  to ethylene at  $1 \times 10^{-4}$  Torr for 20 seconds.

should be important to discuss the geometrical or electronical structure of silicon clusters.

## Reference

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2. S. Maruyama, L. R. Anderson and R. E. Smalley, J. Chem. Phys., **93**, 5349, (1990).