Silicon Cluster Formation Studied by REAPDOR NMR

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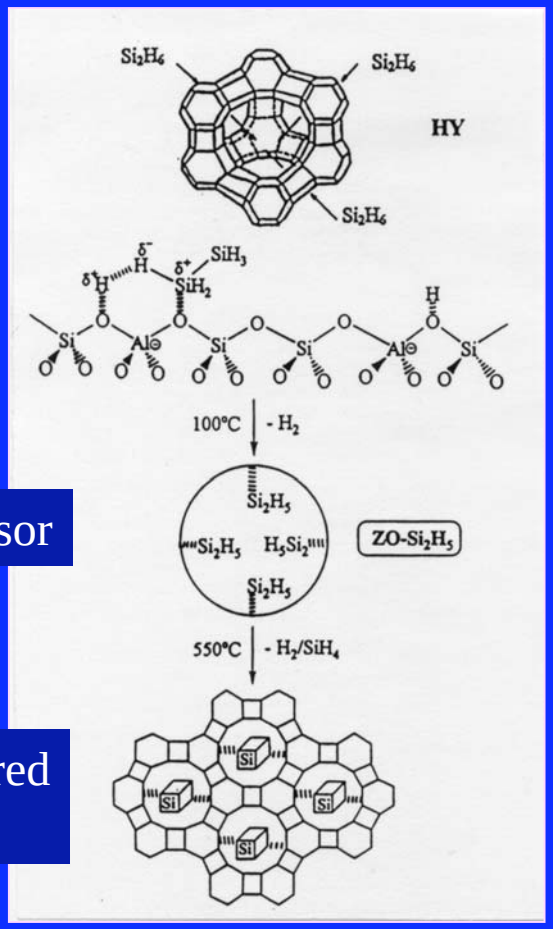
Ba, Yong; He, Jiliang; Ratcliffe, Christopher I.; Ripmeester, John A., Structure and Mechanism of Silicon Cluster Formation in Y Zeolite from 1H-Enhanced 29Si-27Al REAPDOR NMR Spectroscopy, (Communication) J. Am. Chem. Soc., 121, 36, 8387-8, (1999).

Ba, Yong; Ratcliffe, Christopher I.; Ripmeester, John A., Double Resonance NMR Echo Spectroscopy (Invited research News Paper), Advanced Materials, 12, 8, 603-606, (2000).

Encapsulation of silicon nanoclusters

- Uniform arrays of silicon clusters with mono-dispersion of cluster diameters
- Cages of zeolites
  - nano-reactors



Precursor

Nano-clustered material

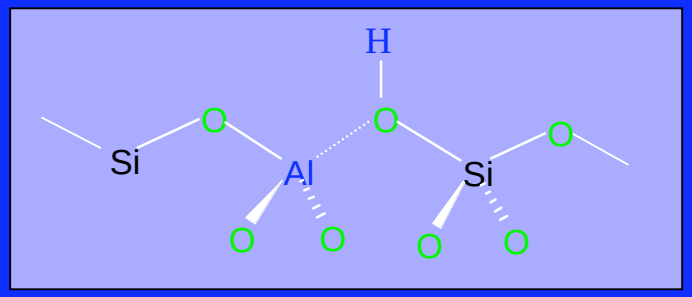
G. A. Ozin, O. Dag, A. Kuperman, P. M. Macdonald, *Stud. Surf. Sci. Catal.* **84** (1994) 1107.
J. He, Y. Ba, C. I.Ratcliffe, J. A. Ripmeester, D. D. Klug, J. S. Tse, K. F. Preston, *J. Am. Chem. Soc.* **120** (1998) 10697.

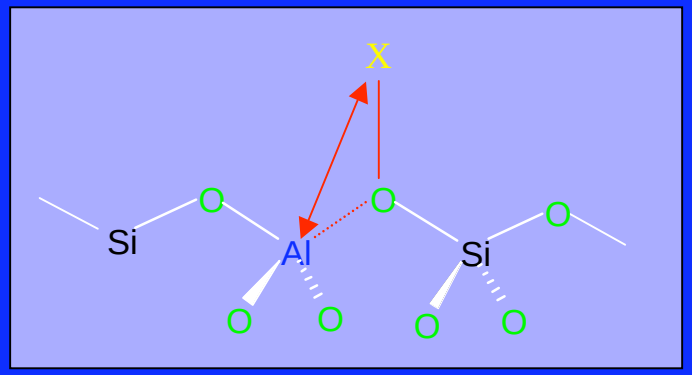
Characterization of silicon nanoclusters

- Structure and formation mechanism of the silicon nanoclusters?
- X-ray powder diffraction
  - Only the framework structure
  - But no silicon nanoclusters
- NMR
  - ^{29}Si CP MAS
  - ^{29}Si-^{27}Al REAPDOR

Why ^{27}Al REAPDOR?

- Brønsted-acid sites
  - Chemically active sites for molecular adsorption and reaction
  - Associated with aluminum atoms
- ^{27}Al good for double resonance
  - 100% natural abundance
  - $\gamma = 6.9706*10^{-7}$ rad $T^{-1}s^{-1}$
- Correlation of adsorbed molecules to Al sites provides structural information
- ^{27}Al spin-5/2 quadrupolar nucleus
  - ^{27}Al REAPDOR



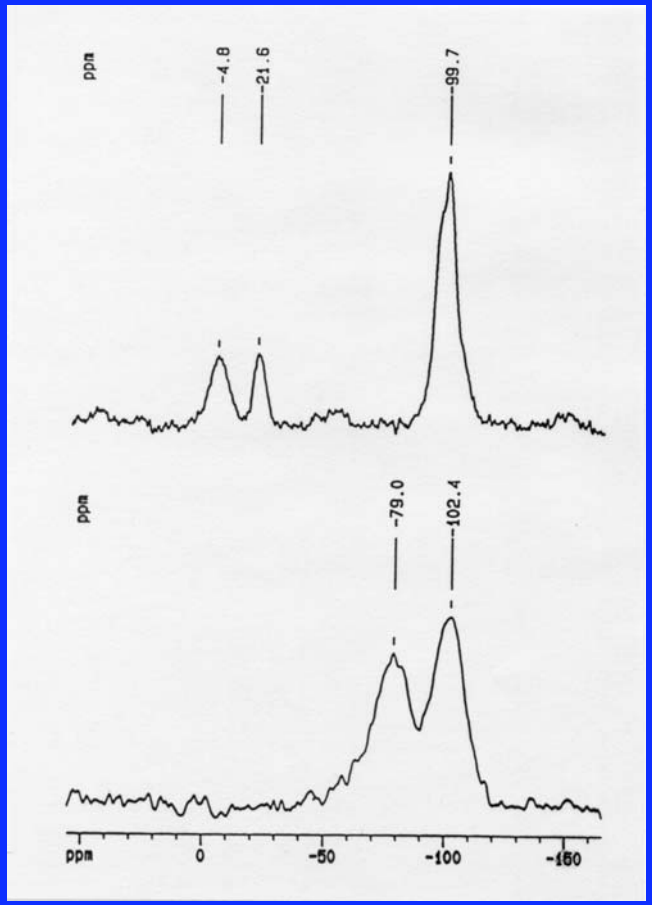


Y. Ba, J. He, C. I.Ratcliffe, J. A. Ripmeester, *J. Am. Chem. Soc.* **121** (1999) 8387.
Y. Ba, J. He, C. I.Ratcliffe, J. A. Ripmeester, *Advanced Materials*, (xxxxxx).

^{29}Si CP MAS Spectra

Precursor: disilanes anchored in the α-cages of the HY zeolite

The HY zeolitic-inclusive silicon nano-clustered material

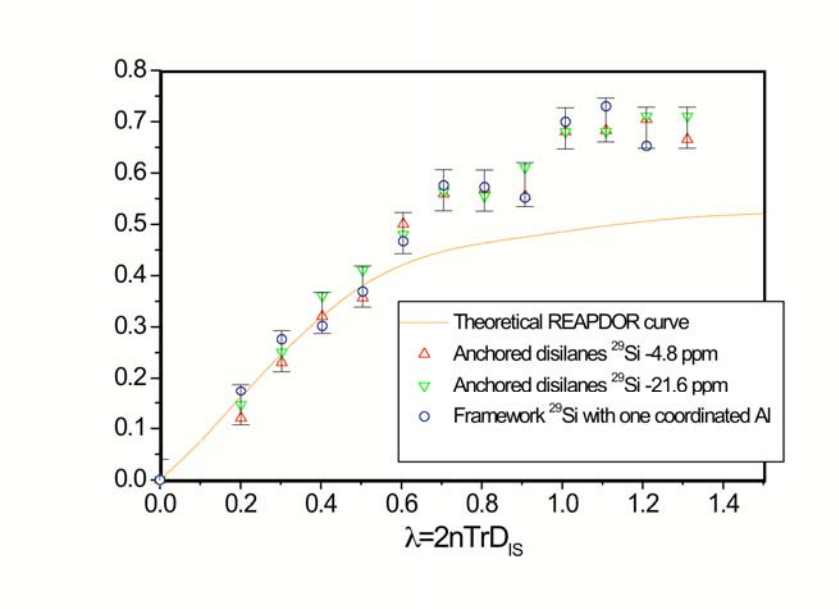


Problems and Solutions

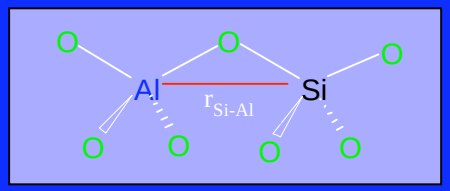
- Assignment of the ^{29}Si spectra
- Disilane anchoring site and mode
- Structure of the silicon nano-clusters
- Formation mechanism of the silicon nano-clusters

- Probing Si-Al internuclear displacement

^{29}Si-^{27}Al REAPDOR Result

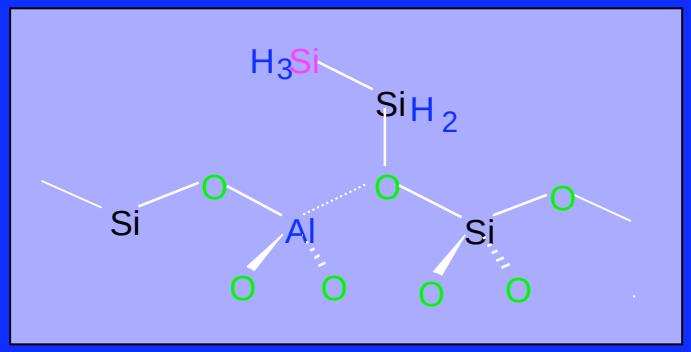


$r_{Si\text{-}Al}$=3.13 Å & D = 201.63 Hz



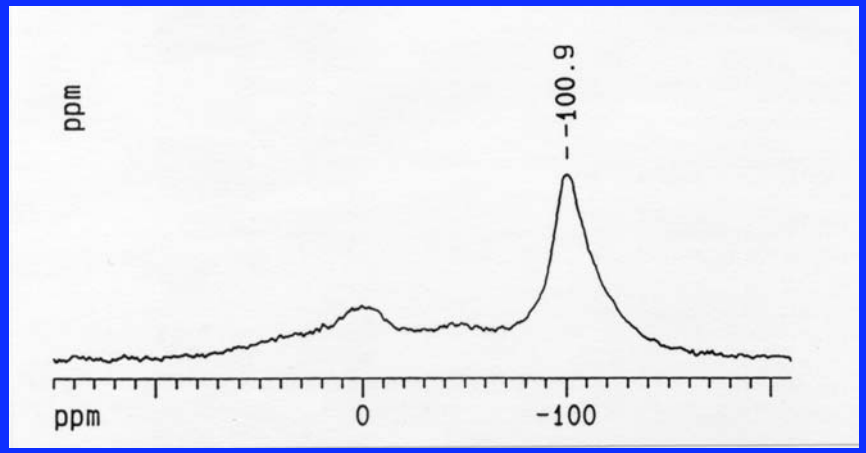
Implication

- Si's with CS at -4.8 ppm and -21.6 ppm have the same distance to Brønsted-acid-site Al's
- The distance is the same as that of neighboring Si to Al in the framework of NaHY zeolite



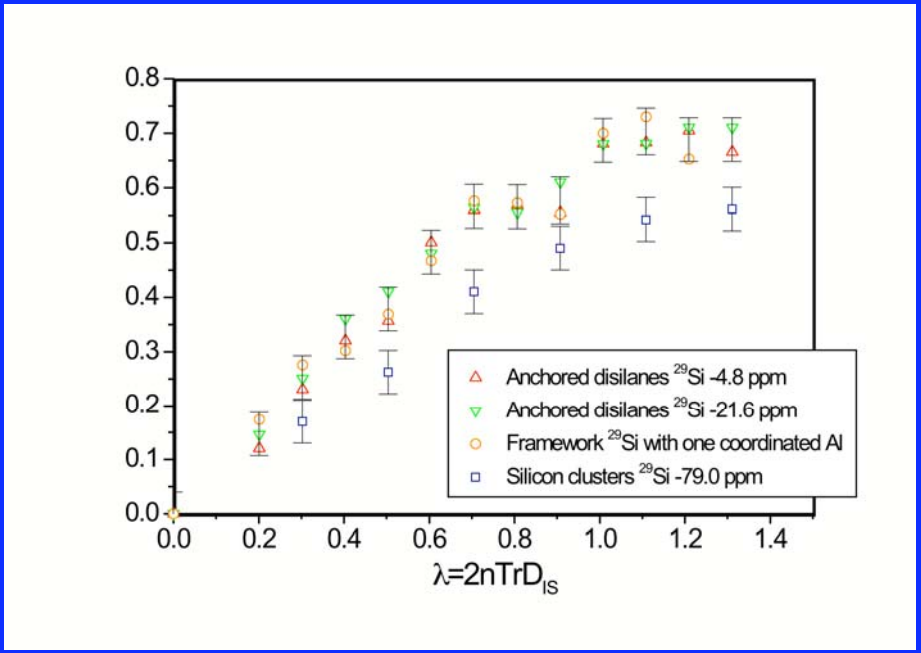
- Disilanes anchored in two structurally different modes
- The ^{29}Si CS of -SiH_3 should overlap in the CS region of the framework silicons

Direct Detection of the -SiH_3



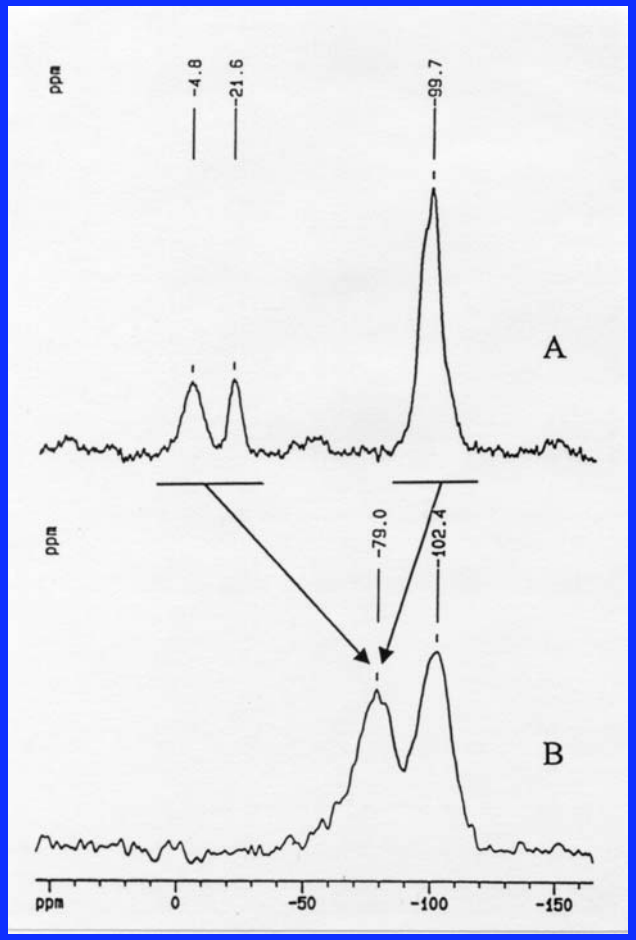
^{29}Si static CP spectrum from the precursor with short contact time (1 ms)

^{29}Si-^{27}Al REAPDOR Result



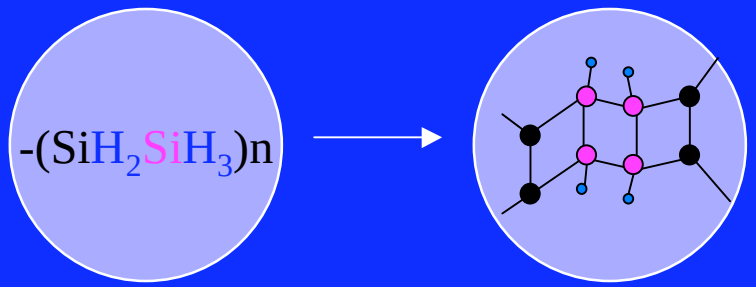
Implication

- The silicons with CS's at -4.8 ppm, -21.6 ppm and -100.9 ppm in the anchored disilanes formed the silicon clusters.



Implication

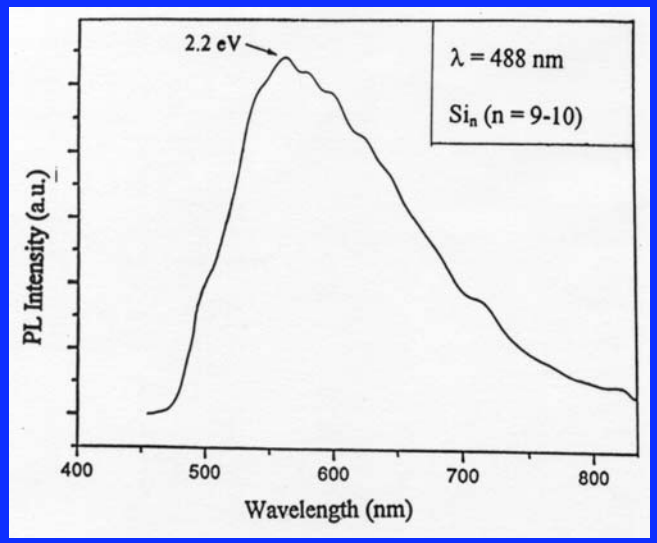
- The lower REAPDOR curve: -SiH_3 groups formed the cores of the silicon nano-clusters through forming Si-Si chemical bonds



- The nonzero REAPDOR curve: the silicon nano-clusters are indeed encapsulated in the α-cages of the HY zeolite

Photoluminescence Spectra

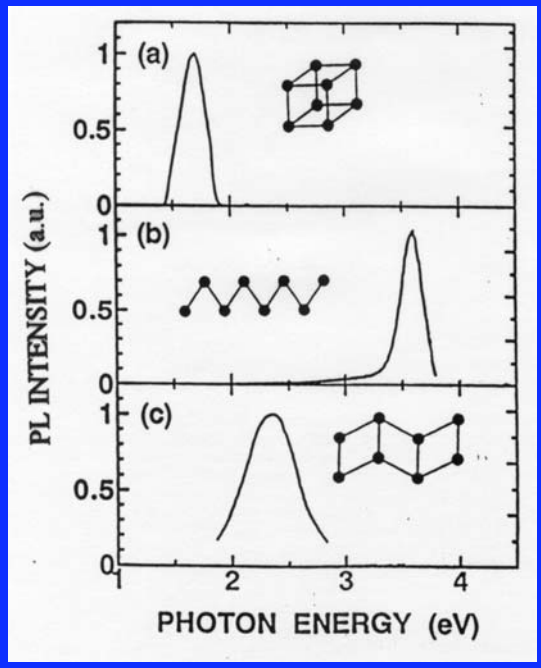
HY inclusive silicon nano-clustered material



The dangling bonds are terminated by the -H and -O

J. He, Y. Ba, C. I.Ratcliffe, J. A. Ripmeester, D. D. Klug, J. S. Tse, K. F. Preston, *J. Am. Chem. Soc.* **120** (1998) 10697.

Silicon molecular clusters



The dangling bonds are terminated by the isopropyl Groups in (c)

Y. Kanenitsu and K. Suzuki, *Phys. Rev.* 51 B (1995) 10666.