Silicon Cluster Formation Studied by REAPDOR NMR

Yong Ba
Department of Chemistry and Biochemistry, California State University
Los Angeles

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

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
  - $^{29}\text{Si} \text{ CP MAS}$
  - $^{29}\text{Si-}^{27}\text{Al REAPDOR}$
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
  - $\gamma = 6.9706 \times 10^{-7}$ 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

$^{29}$Si CP MAS Spectra

Precursor: disilanes anchored in the $\alpha$-cages of the HY zeolite

The HY zeolitic-inclusive silicon nano-clustered material
Problems and Solutions

- Assignment of the $^{29}\text{Si}$ spectra
- Disilane anchoring site and mode
- Structure of the silicon nano-clusters
- Formation mechanism of the silicon nano-clusters
- Probing Si-Al internuclear displacement
$^{29}\text{Si-}^{27}\text{Al REAPDOR Result}$

$r_{\text{Si-Al}} = 3.13 \, \text{Å} \ & \ D = 201.63 \, \text{Hz}$
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 $-\text{SiH}_3$

$^{29}\text{Si}$ 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.
The lower REAPDOR curve: -SiH₃ 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

Silicon molecular clusters

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


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