

Structure and Mechanism of Silicon Cluster Formation in Y Zeolite from ^1H -Enhanced ^{29}Si – ^{27}Al REAPDOR NMR Spectroscopy

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The aluminosilicates represent an extremely important class of materials that are used in a variety of industrial and scientific endeavors.¹ Often such materials, either crystalline or amorphous, require a number of characterization techniques for adequate definition as they lack the long-range order required for study by diffraction, the prime characterization method for crystalline solids. Therefore, the development of new approaches for the solution of structural problems involving aluminosilicates is of essential importance. In this Communication, we adapt a recently developed NMR experiment to the solution of structural problems in aluminosilicate chemistry and illustrate its use by answering some outstanding questions in the chemistry of encapsulated silicon nanoclusters in Y zeolite.

Size-controlled and spatially organized silicon nanoclusters have received a great deal of attention in recent years because of their photoluminescent properties and, therefore, their potential applications in silicon-compatible optoelectronic devices.^{2–6} Zeolites possess spatially well-organized cavities and have been explored extensively as nanoreactors for synthesizing three-dimensional arrays of size-controlled semiconductor clusters.^{7–11} The silicon nanoclusters synthesized in Y zeolites by thermal treatment of disilanes were intensively characterized in our previous publication.¹¹ However, what is still lacking is detailed information on the geometric structure and the nature of the attachment of the adsorbed disilanes to the cage walls. Some, if not all, of this information becomes available if we can assign the ^{29}Si NMR spectrum of the reaction products and intermediates in detail. Thus, we need new approaches to determine short-range interactions inside zeolites, especially those leading to information on connectivity.

The magnetically active framework nucleus ^{27}Al is closely associated with the Brønsted acid sites, responsible for molecular adsorption, and we may expect that the spatial correlation of ^{27}Al with another nucleus in the adsorbed molecules will provide the desired structural information. Since ^{27}Al is a quadrupolar nucleus, the recently developed REAPDOR (rotational echo, adiabatic passage, double resonance)^{12–14} technique is likely to be of use. Thus, as a first example of the ^{29}Si – ^{27}Al REAPDOR NMR experiment, the characterization of the silicon nanocluster and

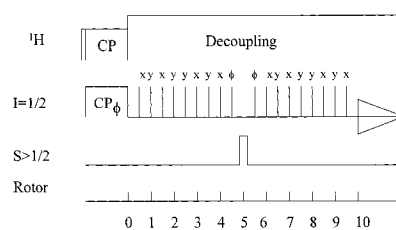


Figure 1. ^{29}Si – ^{27}Al REAPDOR NMR experiment.

the mechanism of the silicon nanocluster formation in Y zeolite will be reported in this Communication.

The REAPDOR NMR experiment, shown in Figure 1, was designed to probe internuclear distances by detecting the dipolar dephasing of a spin- $1/2$ nucleus (^{29}Si) caused by a nearby quadrupolar nucleus with spin $> 1/2$ (^{27}Al , $S = 5/2$). Two signals need to be acquired in this experiment. The first, without dipolar dephasing, requires pairs of π pulses applied to the transverse magnetization of the spin- $1/2$ nuclei in the middle and at the end of the MAS rotor period (T_r) for $2n$ rotor cycles, except at the end of the n th rotor period. The other experiment, with dipolar dephasing, has, besides the π pulses mentioned above, an adiabatic rf pulse of length $T_r/3$ applied to the channel of the quadrupolar nucleus located at the end of the n th rotor period.¹³ The dipolar dephasing time is determined by $2nT_r$. The REAPDOR fraction is defined as $[S_0(2nT_r) - S(2nT_r)]/S_0(2nT_r)$, where $S_0(2nT_r)$ and $S(2nT_r)$ represent the signal intensities without and with dipolar dephasing, respectively. The REAPDOR fraction describes the extent of the dipolar dephasing related to both the reciprocal cube of the internuclear distances and the relative orientation of the internuclear vectors. Therefore, the local molecular geometry can be derived by analysis of the variation of the REAPDOR fractions as a function of dipolar dephasing time (REAPDOR fraction curve).

The NMR experiments¹⁵ were carried out on the photoluminescent silicon cluster material prepared as described previously.¹¹ Figure 2A shows the CP MAS ^{29}Si NMR spectrum of the precursor. The ^{29}Si chemical shifts arising from the HY zeolite framework occur at ~ -100 ppm, and thus the two peaks at -4.8 and -21.6 ppm are from the anchored disilanes, which are thought to bind to the Brønsted-acid-site oxygens in the α cages of Y zeolites.¹¹ We will examine this assumption with ^{29}Si – ^{27}Al REAPDOR, as the Si–Al internuclear distance will reflect this model. Furthermore, REAPDOR will enable us to assign the latter two peaks. Figure 2B shows the ^{29}Si CP MAS NMR spectrum of the silicon nanoclustered material. The peaks at -4.8 and -21.6 ppm in Figure 2A have disappeared, and the broad peak apparent at ~ -79.0 ppm is assigned to the silicon clusters.¹¹ Whether the peak truly represents silicon clusters formed in the α cages of HY zeolite also will be determined by ^{29}Si – ^{27}Al REAPDOR.

The REAPDOR fraction curves for the two peaks at -4.8 (Δ) and -21.6 ppm (∇) are shown in Figure 3. The similarity of the two curves indicates that the distance from the corresponding silicon atoms to the Brønsted-acid-site aluminums is the same, thus excluding the possibility of the two peaks arising from the two different silicons in one Al–O–SiH₂–SiH₃ group.

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(15) Experiments were carried out on a Bruker AVANCE-400 spectrometer equipped with a triple-resonance probe tuned to the resonance frequencies of ^1H , ^{29}Si , and ^{27}Al . The samples were handled in a glovebox under dry Argon gas and sealed in 7-mm rotors with airtight O-ring caps. A MAS frequency of 4 kHz was used for the experiments. The π pulse length for ^{29}Si was 6 μs . The ^{27}Al rf field strength was 26.3 kHz, as measured for an $\text{Al}(\text{H}_2\text{O})_6^{3+}$ aqueous solution, and the rf offset was -5.9 kHz relative to the resonance of the liquid. The spin-echo sequence in the REAPDOR experiment was preceded by ^1H – ^{29}Si cross polarization with a 10-ms contact time.

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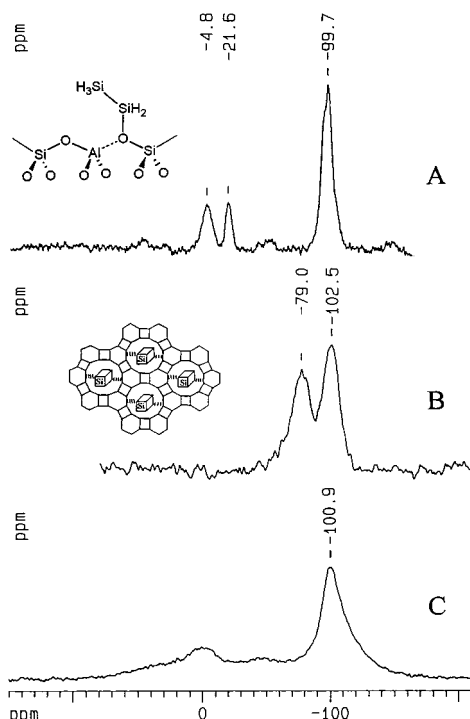


Figure 2. CP MAS ^{29}Si NMR spectra of the precursor (A) and the silicon nanoclustered material (B), and CP static ^{29}Si NMR spectrum of the precursor (C).

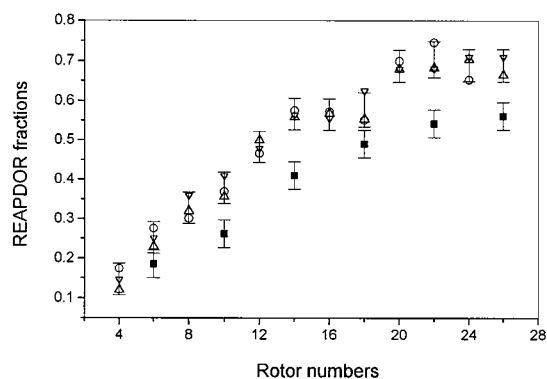


Figure 3. Experimental REAPDOR fraction curves for the two peaks at -4.8 (Δ) and -21.6 ppm (∇) in Figure 2A, for the ^{29}Si coordinated to one aluminum in a NaHY zeolite (\circ), and for the peak at ~ -79.0 ppm in Figure 2B (\blacksquare).

Instead of extensive modeling calculations, an experimental ^{29}Si – ^{27}Al REAPDOR fraction calibration curve was established for a dehydrated NaHY zeolite. The resulting curve for a framework ^{29}Si coordinated to a single aluminum atom is indicated by \circ in Figure 3. This REAPDOR fraction curve falls in the same range as the two from the anchored disilanes described above. Direct comparisons are reasonable in view of the insensitivity of REAPDOR curves to different quadrupolar parameters.¹⁴ This result indicates that the geometry of the anchored silicons in the disilanes relative to the closest framework aluminums is the same as that of the framework silicons relative to the closest framework aluminums in NaHY, as indicated in the inset in Figure 2A. This constitutes proof that the anchored silicons form covalent bonds with the Brønsted-acid-site oxygens; i.e., it is a Si–O–Al linkage. The chemical shifts of -4.8 and -21.6 ppm must, therefore, correspond to disilanes anchored at Brønsted acid sites in the α cage in two structurally different modes. One possibility is that two kinds of disilane bound through a single silicon atom coexist in the α cages. Another is that there are disilanes bound through two silicon atoms to two near-neighbor Brønsted acid sites in a single α cage, although this results in a five-membered ring, which

may not be a preferred geometry. The exact structures, however, still need to be confirmed.

We are now left with assigning the $-^*\text{SiH}_3$ chemical shift for the single-silicon-bonded disilanes. The silicons in this group have much stronger dipolar interactions with protons as compared to framework ^{29}Si 's, and therefore the use of short CP contact time should allow the selection of the anchored disilanes. Besides the two peaks at -4.8 and -21.6 ppm, a broad peak at ~ -100 ppm was observed in the CP MAS experiments with shorter contact time. This peak is likely from the $-^*\text{SiH}_3$ group. However, there still is some ambiguity, as this peak position overlaps the chemical shift range of the framework silicons. Because of rotation about the Si–Si bond, the ^{29}Si chemical shift anisotropy of $-^*\text{SiH}_3$ is expected to be much smaller than those arising from framework silicons. Thus, static CP experiments with short contact time were performed; the result with 1-ms contact time is shown in Figure 2C. Besides the lines with a large chemical shift anisotropy arising from $-\text{SiH}_2-$ groups, a relatively narrow line with a much smaller anisotropy was observed at ~ -100 ppm. For comparison, static CP experiments were carried out on a sample of HY zeolite. The peak at ~ -100 ppm in Figure 2C does not appear in the spectrum, and the signals arising from the framework silicons are as broad as ~ 95 ppm. The variable contact time CP experiment on the precursor shows that the intensity of the -100 ppm peak grows more slowly than the others because of modulation of the ^1H – ^{29}Si dipolar interaction by the Si–Si bond rotation. We can conclude that the peak at ~ -100 ppm in Figure 2C, indeed, should be assigned to $-^*\text{SiH}_3$ groups.

After deconvolution was used to remove the other peaks in the spectrum of the nanoclustered product (Figure 2B), the experimental REAPDOR fraction curve for the peak at ~ -79.0 ppm is shown in Figure 3 as \blacksquare . This REAPDOR fraction curve grew more slowly and leveled off at a lower value than the others. This indicates that there are silicons associated with the peak at ~ -79.0 ppm that have longer distances to the closest Brønsted-acid-site aluminums than those that bind directly to the Brønsted-acid-site oxygens. The explanation for this is that the silicons which were present as $-^*\text{SiH}_3$ groups in the precursor now are part of the silicon cluster cores in the HY α cages, i.e., $-^*\text{Si}-\text{Si}-\text{O}-\text{Al}$. On forming the silicon clusters, the component of the line at ~ -100 ppm associated with the chemical shift of $-^*\text{SiH}_3$ disappears. This change is also confirmed by the different character of the REAPDOR curves (not shown) for the peaks at ~ -100 ppm in Figure 2A,B.

Previous work showed that the number of H atoms in each α cage is reduced dramatically upon thermal treatment of the cluster precursors.¹¹ On considering this reduction and the above REAPDOR results, the former $-^*\text{SiH}_3$ group silicons must now be attached to other Si atoms in the silicon clusters. Previous XPS and Si K-edge XANES spectra showed the existence of non-oxidized Si_n , as well as partly oxidized Si.¹¹ The above REAPDOR analysis confirms that they are, indeed, from the silicon clusters encapsulated in the α cages of the Y zeolites, as schematically shown by the inset of Figure 2B.

In conclusion, the following specific structural information was obtained by analyzing the ^{29}Si – ^{27}Al REAPDOR curves: (1) disilane molecules are bonded directly to the Brønsted-acid-site oxygens; (2) two different bonded disilanes in an α cage are observed; and (3) Si atoms present as $-^*\text{SiH}_3$ groups in the precursor are incorporated into the core of the silicon clusters.

The research presented here shows that ^{29}Si – ^{27}Al REAPDOR NMR experiments can be used in complex spectral assignment problems and promise broader applications to elucidate the structures of aluminosilicates, including the details of reaction products and mechanisms.

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