

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).

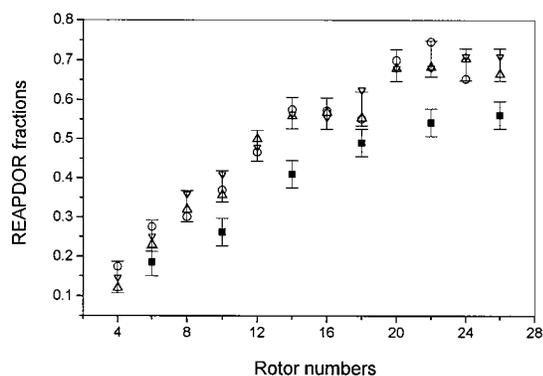


Figure 3. Experimental REAPDOR fraction curves for the two peaks at -4.8 (Δ) and -21.6 ppm (∇) in Figure 2A, for the ^{29}Si coordinated to one aluminum in a NaHY zeolite (\circ), and for the peak at ~ -79.0 ppm in Figure 2B (\blacksquare).

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., $-^*\text{Si}$ –Si–O–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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