Kinetic and structural data reaffirm the importance of the buried negative charge adjacent to His 57,[11,12] but suggest that its absolute position is critical only for the highly efficient catalysis of the wild-type enzyme. Therefore, in spite of the observation that the active sites of the structurally unrelated enzymes of the trypsin and subtilisin families have converged to geometries with less than a 0.2-Å root mean square deviation,[13] designed proteins which are meant to incorporate serine protease-like activity can utilize an alternate orientation for the carboxylate. The flexibility inherent in these alternate motifs may facilitate the introduction of efficient catalytic triads into other scaffolds without disruption of preexisting substrate binding or catalysis.

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Extraframework Sodium Cation Sites in Sodium Zeolite Y Probed by ^{23}Na Double-Rotation NMR

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The most commonly encountered "inorganic" charge-balancing cation found in as-synthesized zeolites is Na$^+$. Extraframework Na$^+$ cations play an important role in determining the adsorption, chemical, catalytic, and solid-state properties of zeolites with respect to a wide range of guests.[1,2] ^{23}Na NMR spectra, however, usually exhibit large quadrupolar broadening even upon magic angle spinning (MAS), which renders the interpretation of the experimental data difficult.[3] The newly developed double-rotation (DOR) technique removes the anisotropic broadening of quadrupolar nuclei, thereby facilitating significantly improved spectral resolution.[4] We report here for the first time high-resolution ^{23}Na DOR spectra of dehydrated sodium zeolite Y, Na$_{56}$Y, and its Tl$^+$ exchanged derivatives, Tl$_n$Na$_{56-n}$Y.[5] By interchanging Tl$^+$ and Na$^+$ cations at particular locations within the unit cell of Na$_{56}$Y,[6] we are able to identify distinct ^{23}Na DOR signals which correspond to Na$^+$ cations at specific sites, as well as deduce some information concerning the ion-exchange pathway.

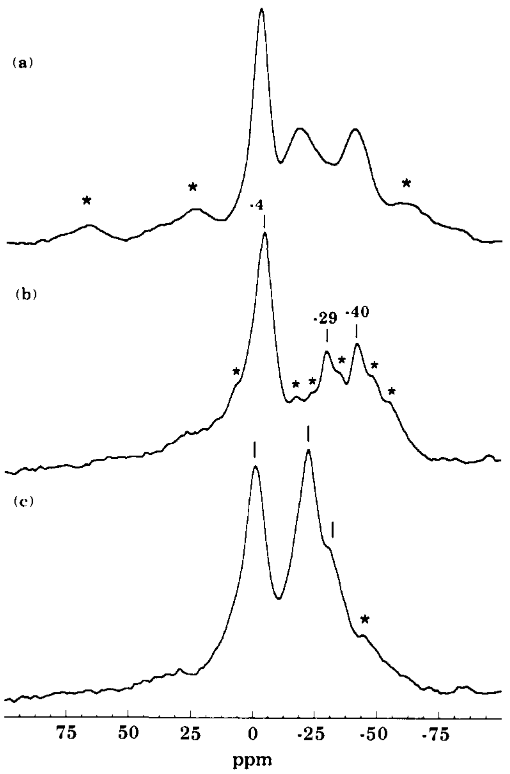

Figure 1. ^{23}Na NMR spectra of Na$_{56}$Y zeolite: (a) MAS spectrum of dehydrated Na$_{56}$Y; (b) DOR spectrum of dehydrated Na$_{56}$Y; (c) DOR spectrum of 16{W(CO)$_6$}-Na$_{56}$Y. * indicates spinning side bands.

^{23}Na NMR spectra of dehydrated Na$_{56}$Y are shown in Figure 1. The MAS spectrum, Figure 1a, displays a peak around −4 ppm, while features upfield are composed of quadrupolar broadened peaks and overlapping spinning side bands. The DOR spectrum, shown in Figure 1b, yields higher resolution. The anisotropic quadrupolar broadening is averaged out in the DOR experiment, and three distinct peaks emerge: a prominent Gaussian around −4 ppm and two weaker peaks, on top of a broad background signal and a side band manifold, at −29 ppm and −40 ppm, respectively.

In order to assign the ^{23}Na DOR signals to specific Na$^+$ sites within the zeolite lattice, we first examined the spectrum of 16{W(CO)$_6$}-Na$_{56}$Y, shown as Figure 1c. An intense resonance is observed around −26 ppm. This peak is assigned to Na$^+$ cations at site II in the α-cage, since previous studies have determined that an α-cage-encapsulated W(CO)$_6$ molecule is anchored to two site II Na$^+$ cations.[8]

XRD and ND measurements[9] establish that about 7-8% of the Na$^+$ cations in dehydrated Na$_{56}$Y occupy site I, 24-33% are located inside the β-cage at site I′, 53-57% are inside the α-cage at site II, and the remainder are either in the α-cage at site III or unlocated. The distribution of Na$^+$ cations seems different from that which we observe in the DOR experiment. The relatively small intensity of the ^{23}Na DOR resonance from site II Na$^+$ in the virgin dehydrated Na$_{56}$Y, at around −30 ppm (Figure 1b), might originate from a distribution of chemical environments of Na$^+$ at this site, which could also explain the broad background ^{23}Na signal. This distribution might be brought about through motion, on the time scale of the NMR experiment, of the site II

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(5) NMR experiments were recorded in a 11.7 T magnetic field on a Chemagnetics CMX-500 spectrometer. The DOR experiments were carried out with a home-built DOR probe whose features have been described elsewhere.[7] A total of 3000-5000 acquisitions were accumulated, using short radio frequency pulses with 0.5-s delays. The external reference used was 0.1 M NaCl.

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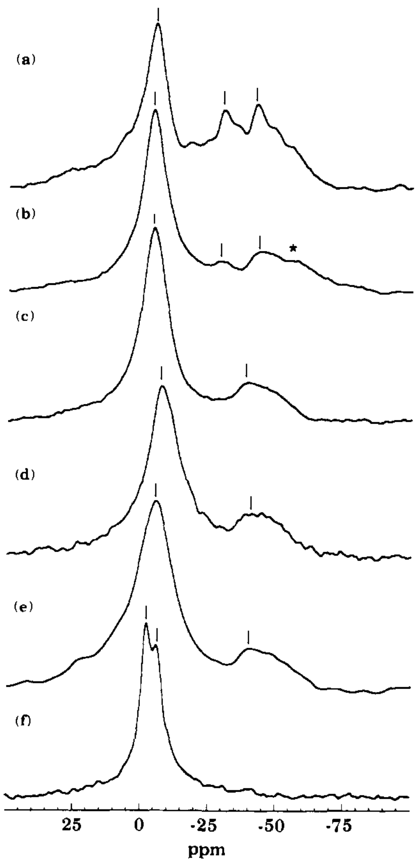

Figure 2. ^{23}Na DOR spectra of dehydrated Na$_{56}$Y at various stages of Tl$^+$ exchange: (a) Na$_{56}$Y; (b) Tl$_8$Na$_{48}$Y; (c) Tl$_{16}$Na$_{40}$Y; (d) Tl$_{32}$Na$_{24}$Y; (e) Tl$_{40}$Na$_{16}$Y; (f) Tl$_{48}$Na$_8$Y. * indicates spinning side bands. The intensity of the spectra was scaled according to the zeolite Y molar ratio in the sample.

Na$^+$ cations between accessible sites in the spacious α-cage. However, a more ordered array of "anchored" site II sodium cations is formed upon adsorption of W(CO)$_6$ into the α-cages of Na$_{56}$Y, thus restricting the Na$^+$ to a specific location, with the concomitant emergence of the narrow resonance at around −26 ppm.

^{23}Na DOR spectra of a series of Tl$^+$ exchanged Na$_{56}$Y are shown in Figure 2. The intensity of the ^{23}Na peak at −30 ppm decreases as around 15% of the Na$^+$ cations are exchanged (Figure 2b), and the overall background signal seems to diminish as well. When approximately 30% of the sodium cations are exchanged, the peak at around −30 ppm which is ascribed to the α-cage site II Na$^+$ is no longer apparent, as shown in Figure 2c. The upfield signal seems to shift to a lower field (Figure 2c), and its intensity decreases somewhat upon progressively loading more Tl$^+$ cations (Figure 2c–e).

The ^{23}Na DOR spectrum of Na$_8$Tl$_{48}$Y shown in Figure 2f displays a diminishingly small remnant of the signal around −40 ppm, while the prominent downfield resonance is split into two signals at −2 and −6 ppm, respectively. The disappearance of the peak at −40 ppm implies that this signal might be associated with site I′ Na$^+$ cations, as in the high Tl$^+$ loading, these cations may displace Na$^+$ in the sodalite cages. The Gaussian peak at around −5 ppm is therefore assigned to site I cations. The intense narrow line shape of the DOR resonance from Na$^+$ cations at site I, which is observed throughout the entire exchange series, is probably due to the essentially octahedral environment experienced by Na$^+$ at this site, located inside the hexagonal prism between two six-rings. Another factor might be the restricted Na$^+$ motion anticipated in this site. Thus, although the population of site I Na$^+$ cations is quite low compared to sites II and I′,[9] the small electric field gradient at the site, as well as the "pinning down" experienced by the Na$^+$ cations, leads to the relatively narrower peak and higher intensity of the ^{23}Na DOR resonance. The observation of a well-resolved splitting of the ^{23}Na signal in the spectrum of Tl$_{48}$Na$_8$Y indicates the existence of at least two distinct Na$^+$ site I local symmetries. Since at this stage Tl$^+$ cations located in the α-cages replace Na$^+$ in the sodalite cages, this splitting might be related to a nearest-neighbor effect of the Tl$^+$ cations present in cages adjacent to the hexagonal prisms. The nonobservation of a ^{23}Na signal from site III in our experiments could be due either to the very small Na$^+$ cation population at this site and/or motion and exchange effects.

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Registry No. Na, 7440-23-5; Tl, 7440-28-0; W(CO)$_6$, 14040-11-0.

Synthesis of Monodispersed High Molecular Weight Polymers and Isolation of an Organolanthanide(III) Intermediate Coordinated by a Penultimate Poly(MMA) Unit

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Synthesis of high molecular weight polymers ($M_n > 100 \times 10^3$) with extremely narrow polydispersity ($M_w/M_n < 1.05$) remains an important target in polymer chemistry, since such compositionally pure materials must serve as a bench mark for the accurate physical and chemical properties of other polymers. Although various living polymerization systems have been developed, no type of anionic[1,2] or cationic polymerization,[3] group-transfer polymerization,[4] or metal carbene initiated polymerization[5,6] has ever achieved this end. We now report here the first example of high molecular weight poly(methyl methacrylate) with unusually narrow polydispersity (molecular weight distribution), using by the unique catalytic function of (C$_5$R$_5$)$_2$LnR′ organolanthanide(III) complexes. The utility of organolanthanides has already been

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