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REAPDOR NMR Spectroscopy and Location of Cations in Molecular Sieves

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Crystalline molecular sieves consist of regular interconnecting pore or channel structures with sizes of the order of atomic dimensions.[1,2] Introducing aluminum or other heteroatoms (e.g., titanium) results in a negatively charged framework, which requires cations to counterbalance the charge. The cation exchange ability, in conjunction with framework topology, offers unique shape-selective properties of these materials and has led to many of their applications in chemical industry.

The determination of cation (e.g., Na, K, Ce, La, etc.) location in molecular sieves is of considerable structural importance since their precise locations in the channel systems of a topologically ordered framework is the key to an understanding of the unique catalytic properties exhibited by these materials. X-ray diffraction techniques are somewhat restrictive, since it is not always easy to grow diffraction quality crystals and cation mobility, when present, masks their detection. It is therefore desirable to explore experimental alternatives for the precise location of charge-balancing cations.

Recently, Fyfe et al.[3] have introduced INEPT MAS NMR experiments for zeolites to monitor the bond connectivity through $J_{\mathrm{Si-Na}}$ couplings. Similarly, the possibility of detecting through-space dipolar couplings between the cations such as sodium and the framework silicon, in the vicinity of these charge bearing heteroatoms, offers new opportunities for their location in molecular sieves. For nonspinning solids, these dipolar couplings can be measured experimentally using spin-echo double resonance (SEDOR).[4,5] MAS-based methods are superior since one can resolve chemically and crystallographically distinct tetrahedral silicons in the ^{29}Si MAS spectra and study the dipolar interactions with the cations at specific framework sites.[6] The heteronuclear dipolar couplings, averaged to zero by MAS, can be reintroduced by the basic rotational echo and transfer of populations in double resonance (REDOR and TRAPDOR)[7,8] experiments and their various extensions.[9−12] They have been successfully used to study ^{29}Si−^{27}Al,[10] ^{31}P−^{27}Al,[12] and ^{1}H−^{27}Al [13] interactions in zeolites.

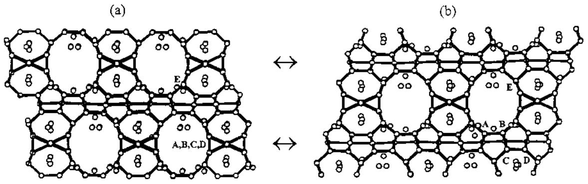

Figure 1. Framework structure of ETS-10 (polymorph B) showing the tetrahedral Si and octahedral Ti connectivities. The arrows indicate the titanium chains running in two mutually orthogonal directions to give the twelve- and seven-membered rings. The sodium cation locations, derived from molecular modeling and REAPDOR analysis, are represented by unconnected atoms (○). The Q4 [Si(3Si,1Ti)] and Q4 [Si(4Si,0Ti)] types of silicon are labeled A−D and E. Two perpendicular views (a,b) along the Ti−O−Ti chains are shown to indicate that the sodium cations are located exclusively within the seven-membered ring channels.

For the detection of dipolar interaction between a framework ^{29}Si nucleus and a cation nucleus bearing a half-integer quadrupolar spin (e.g., ^{23}Na, $I = {}^{3}/_{2}$), the REAPDOR experiment[14] is very suitable.

REAPDOR is a combination of the REDOR[7] and TRAPDOR[8] MAS experiments when applied on heteronuclear *IS* spin pairs. Following the rf excitation of the spin $^{1}/_{2}$ nucleus *I*, pairs of π-pulses are applied synchronously with sample spinning at the middle and end of the rotor period $(n/2)T_{\mathrm{R}}$, using *XY*−*n* phase cycling schemes.[15] A rf pulse of duration $\sim T_{\mathrm{R}}/2$, applied to the half-integer *S* spin, replaces the *I* spin π-pulse in the middle of the sequence, causing a partial adiabatic population inversion.[9,13] In a polycrystalline sample, this sequence results in a net dipolar dephasing of the *I* spin signal $S(nT_{\mathrm{R}})$, which in the absence of the *S* pulse yields a control signal $S_0(nT_{\mathrm{R}})$. Further, since the *S* pulse reintroduces only the dipolar interaction among *IS* spin pairs, the REAPDOR fraction $\{S_0(nT_{\mathrm{R}})\text{-}S(nT_{\mathrm{R}})\}/S_0(nT_{\mathrm{R}})$ is a true measure of the cation−silicon dipolar dephasing when applied to molecular sieves. The observed REAPDOR dephasing curves can be analyzed to derive structural information, via *I*−*S* distances, for the precise location of cations in a given molecular sieve.

In this paper, we show that through-space dipolar interactions between charge-bearing sodium cations and lattice silicons can indeed be detected by REAPDOR NMR and interpreted in terms of silicon−sodium distances. This is demonstrated on the molecular sieve ETS-10, a prominent member of the recently discovered microporous titanosilicate family,[16] the building blocks of which comprise corner-sharing SiO_4^{4-} tetrahedra and TiO_6^{8-} octahedra linked through bridging oxygens to form twelve- and seven-membered ring channel systems[17] as shown in Figure 1. The incorporation of titanium in the silicate framework requires sodium or potassium cations to neutralize the negative (2−) charge. Their locations are not known a priori, although the framework atoms have been located to a good degree of atomic accuracy for the two ordered polymorphs, A and B,[18] which lead to a stacking disorder in this otherwise highly crystalline material.

We show in Figure 2 the ^{29}Si MAS NMR spectrum of ETS-10 in which the three well-resolved resonances are readily assigned to the titanium-rich [Q4(3Si,1Ti)], (A,B; −94.1 ppm) and (C,D; −96.2 ppm) and the silicious [Q4(4Si,0Ti)] (E; −103.3 ppm) environments according to the A−E labeling[17] indicated in Figure 1. REAPDOR curves of these three ^{29}Si lines were measured on

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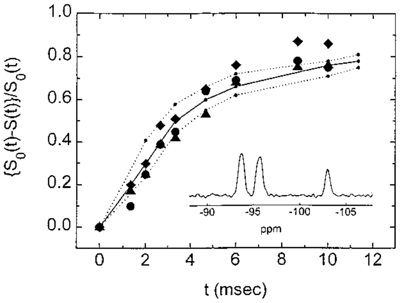

Figure 2. The REAPDOR fraction $\{S_0(t)-S(t)\}/S_0(t)$ for the three distinct ^{29}Si resonances as a function of the dephasing time *t* for ETS-10. The experimental data are indicated for ^{29}Si resonances at −94.1 ppm (◆), −96.2 ppm (○), and −103.3 ppm (▲). The solid line represents the calculated REAPDOR dephasing as discussed in the text. The two dotted lines represent the REAPDOR responses obtained by varying all distances going into the calculation by ±0.3 Å. The insert shows the ^{29}Si MAS NMR spectrum of ETS-10.

a hydrated ETS-10 sample by applying the population inversion pulse at the ^{23}Na Larmor frequency. The experimental results are shown in Figure 2.

The REAPDOR response at each resolved ^{29}Si line is adequately described by considering more than one Na neighbor in the vicinity of each observed silicon, since for this titanium rich material (Si/Ti = 5.0) a single Si−Na interaction alone is unlikely to determine the observed REAPDOR behavior. Considering that sodium ordering within the cages must necessarily satisfy an underlining charge-balancing criteria imposed by the framework titaniums, Si−Na distances were estimated by molecular modeling using the InsightII software package (Biosym Technologies Inc.). For these calculations, sodium cations were considered to be immobile. Such an assumption is also validated by triple quantum ^{23}Na MAS experiments.[19] These distances were subsequently used to calculate the REAPDOR response at each crystallographically nonequivalent Si site.[20] This was done using a straightforward time-dependent density matrix calculation, taking into account all experimental parameters, such as pulse lengths, delays, and intensities, nuclear quadrupole parameters of the *S* spin, and lengths and directions of the internuclear distance vectors. For *S* spin pulses on the order of half the rotor period, the curves are insensitive to moderate changes in the quadrupole couplings.[21] For more than one S spin neighbor, REAPDOR curves are calculated taking into account all necessary $I-S$ interactions.

The observed REAPDOR dephasing is satisfactorily simulated when the crystallographically distinct silicons, in the ordered polymorphs of ETS-10, have two or three neighboring sodiums that are located at a distance smaller than 4 Å. According to the calculations, while in polymorph B the two closest sodiums to all silicons have distances between 3.0 and 3.5 Å and, while in polymorph A, some of the silicons have closest neighbors at 2.0 Å. Although the crystallographically identified silicons did not lead to unique sets of ^{23}Na−^{29}Si distances, the REAPDOR response could be simulated by considering two distinct sodium environments (with distances varying between 2.0 and 4.0 Å) for each silicon site A to E. The calculations for the three ^{29}Si lines showed that their REAPDOR curves are nearly identical over the measured dephasing time period. This curve is plotted in Figure 2. To estimate the accuracy of our data and the agreement between the experimental and theoretical results, two additional curves were evaluated, assuming a change of ±0.3 Å in all distances entering the calculation. Our experimental results are in good agreement with the theoretical calculations, whereby the sodium ions are found to be located exclusively in the smaller channels made up of seven-membered rings. Interestingly, the REAPDOR response for the ^{29}Si line at −94.1 ppm shows a significant deviation at long times and envisages possibly an increasing number of sodium atoms influencing the signal dephasing. Experiments performed on a dehydrated ETS-10 sample resulted in REAPDOR curves identical to the presented results, suggesting that the sodium environment is little influenced by the state of hydration. The ^{23}Na spectra were also found to be independent of the hydration state of ETS-10. The water is essentially zeolytic and presumably resides in the large 12-ring pores where they can experience high mobility.

The REAPDOR experiments were performed on a 4.7 T three-channel homebuilt spectrometer, using a triple-tuned probe housing a Doty spinner assembly. The ^{29}Si (39.7273 MHz) and ^{23}Na (52.9033 MHz) pulses were controlled at rf fields of 25.8 and 62.5 kHz, respectively, using a Tecmag data acquisition system and two ENI LPI-10 rf power transmitters. The spinning speed was regulated at 2994 Hz, using a homebuilt air-flow controller. The control $S_0(nT_R)$ and the dipolar dephased $S(nT_R)$ signals were accumulated and stored in separate memory locations in two contiguous experiments under identical spectrometer conditions.

In conclusion, we have shown that dipolar interaction between framework silicons and cations, possessing half-integer nuclear spins, in molecular sieves can be detected using REAPDOR MAS NMR spectroscopy. From our demonstration on the titanosilicate ETS-10, we have been able to show that distance constraints based on molecular modeling can be effectively used to calculate the observed REAPDOR response at distinct Si sites and locate sodium ions exclusively in the seven-membered ring channels of the framework structure. This technique complements other presently known approaches and provides valuable distance information that can be subsequently used in structural refinements.

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Supporting Information Available: Tables of positional coordinates, unit cell representations, and molecular modeling results (18 pages). See any curent masthead page for ordering information and Web access instructions.

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(20) The unit cell composition of ETS-10 is $Si_{80}Ti_{16}O_{208}$. The 16 titaniums require 32 cations (Na^+ and/or K^+) to balance the charge on the framework. In the synthesized material, the Na/K is 7:1 and the K cations are inactive in the REAPDOR experiment. On this basis, we estimate that 14% of the silicons with two nearest neighboring cations experience only one sodium and 10% of the silicons with three neighboring cations experience only two sodiums. These changes in the ^{23}Na occupation of the cationic sites do not change the overall REAPDOR response by an amount larger than the differences between the theoretical curves shown in Figure 2.

(21) For the actual calculations, ^{23}Na quadrupole interaction tensors reported by Anderson et al.[18] were found to simulate our observed ^{23}Na MAS spectrum of ETS-10. For the REAPDOR calculations, a single interaction tensor with a quadrupole coupling constant of 1.0 MHz and asymmetry parameter of 0.6 was used. The dependence of the REAPDOR response on the relative orientation of the internuclear distance vector in the principal axis system of the quadrupole nucleus was found to be minor in a polycrystalline sample, and hence, arbitrary orientations were used.