

Electronic Supplementary Information

NMR Crystallography of Monovalent Cations in Inorganic Matrixes: Li⁺ Siting and Local Structure of Li⁺ Sites in Ferrierites

P. Klein,^{a,b} J. Dedecek,^a H. M. Thomas,^a S. R. Whittleton,^a V. Pashkova,^a J. Brus,^c L. Kobera^c and S. Sklenak^a

^a J. Heyrovský Institute of Physical Chemistry, The Czech Academy of Sciences, Dolejškova 3, CZ 182 23 Prague 8, Czech Republic.

^b Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Doubravice 41, Pardubice, CZ 532 10, Czech Republic.

^c Institute of Macromolecular Chemistry, The Czech Academy of Sciences, Heyrovsky sq. 2, CZ 162 06, Prague 6, Czech Republic.

Sample Preparation and Characterization

FER/20 (Si/Al 20, Li/Al 0.98 Unipetrol, a.s., CZ), FER/27 (Si/Al 27, Li/Al 1.01 laboratory synthesis), and FER/30 (Si/Al/30, Li/Al 0.97 Zeolyst International, Inc.) were investigated. The parent NH₄-FER samples were equilibrated with 1 M LiNO₃ three times for 24 h at 60 °C and carefully washed by distilled water. The dehydrated samples for the NMR experiments were prepared by “in situ” evacuation in a rotor for five hours under dynamic vacuum at 450 °C. Subsequently to the dehydration, the sample was cooled down and sealed under vacuum.

⁷Li NMR Experiments

⁷Li MAS and ⁷Li-⁷Li correlation MAS NMR spectra were collected by a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer using 3.2 mm o.d. ZrO₂ rotors with a spinning frequency of 20-22 kHz. The ⁷Li MAS NMR spectra were recorded using a single-pulse experiment with an optional ¹H decoupling during data acquisition. The length of 90° (⁷Li) pulse was 2.2 μs, repletion delay was 4 s and the number of scans 64. The ⁷Li-⁷Li correlation MAS NMR spectra were recorded using the NOESY-type three-pulse sequence. Duration of the spin-exchange period between the second and third pulse was 1 - 100 ms. Spectral width in both frequency dimensions was rotor-synchronized to be 20-22 kHz. The indirect detection period *t*₁ consisted of 320 increments each made of 8-16 scans. The ⁷Li chemical shifts were referenced to LiCl at -

1.04 ppm. Prior to the spectra measurement, the samples were dehydrated in the rotor under vacuum (10^{-3} Pa) at 450 °C for 4 h and sealed. Full dehydration of the samples was monitored by ^1H MAS NMR.

^7Li MAS NMR Spectra

^7Li MAS NMR spectra of the dehydrated FER/20, FER/27, and FER/30 samples (FER/A, FER/B, and FER/C, respectively, in Ref.¹) are shown in Fig. S1.

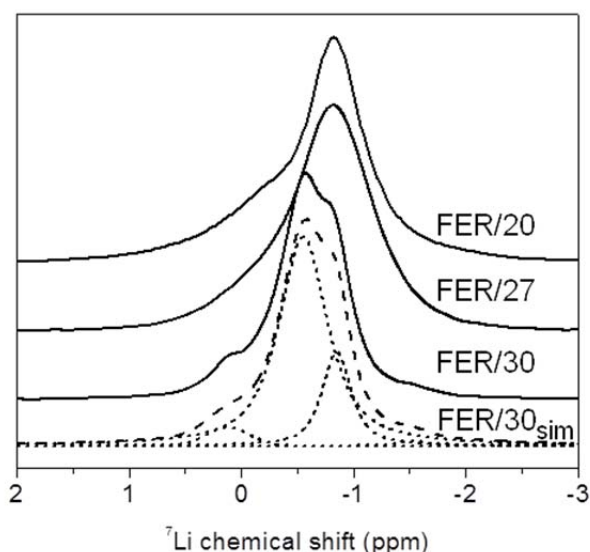


Fig. S1 ^7Li MAS NMR spectra of the dehydrated FER/20 - FER/30 samples together with the simulation of the spectrum of the FER/30 sample FER/30_{sim} (---) with individual components (...).

Computational Models and Methods

Structural Models

Five models, possessing the P1 symmetry, featuring one Al/Si substitution in the framework T1a,¹ T1b,¹ T2, T3, and T4 sites¹ and one Li^+ cation compensating the corresponding negative charge of AlO_4^- were employed. The models were composed of a super cell consisting of two unit cells (Si/Al 71) along the c dimension. The starting structure of the all-silica zeolite

framework (no Li^+) was downloaded from the zeolite structural database.² All possible symmetrically non-equivalent Li^+ sites with Li^+ ions coordinated to two oxygen atoms of one AlO_4^- tetrahedron (with the Li-O_{Al} distances of some 2 Å) for each of the five models were used as the starting structures.

Electronic Structure Calculations

The CP2K suite of software³ was employed using the BLYP functional,^{4, 5} GTH pseudopotentials,^{6, 7} and the TZV2P-GTH basis set. The energy cutoff of 1120 Ry was used.

Molecular Dynamics

Molecular dynamics (MD) simulations were performed as implemented in the QUICKSTEP program,⁸ a part of the CP2K suite of software.³ Born-Oppenheimer MD simulations of 3000 - 8000 fs durations were performed in the canonical ensemble, with a time step of 1.0 fs and a mean temperature of 400 K regulated using a chain of Nose-Hoover thermostats. The duration of the MD simulation depended on the number of steps needed to equilibrate the calculated system. When the calculated systems were equilibrated, the structures of ten distinct "snapshots" were collected from each molecular dynamics simulation and optimized. The most stable structures of all distinct Li^+ sites for all five models (i.e., Al in all the five framework T sites) were used for subsequent NMR computations.

Geometry Optimizations

The lattice parameters and the atomic positions were optimized employing conjugate-gradient algorithm minimization of energies and forces as implemented in the QUICKSTEP program,⁸ a part of the CP2K suite of software.³

Calculations of ^7Li NMR Shielding

Clusters of seven coordination shells around the Al atom ($\text{Al-O-Si-O-Si-O-Si-O-H}_{\text{link}}$) and the Li^+ ion were extracted from the optimized structures. Due to the presence of silicate rings in the framework of ferrierite, the created seven-shell clusters contained pairs of very close H_{link} atoms. Since the close H_{link} atoms represented the same Si atom, they were replaced by the

corresponding $\text{Si}(\text{OH}_{\text{link}})_2$ moiety. This was repeated until the cluster contained no such pairs. The ^7Li NMR shielding values were calculated by the gauge independent atomic orbital method (GIAO)⁹ using Gaussian09,¹⁰ the B3LYP functional,^{5, 11} and the pcS basis sets of Jensen,¹² pcS-4 for the Li and Al atoms and pcS-1 for all the other atoms. The calculated ^7Li NMR shielding values were converted to ^7Li chemical shifts using the calculated shielding of 90.16 ppm for $\text{Li}^+(\text{H}_2\text{O})_4$ (^7Li chemical shift is 0.00 ppm by definition).¹³ The geometry of $\text{Li}^+(\text{H}_2\text{O})_4$ was optimized at B3LYP/cc-pVQZ and subsequently the ^7Li NMR shielding of 90.16 ppm was obtained at the same level of theory.

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