

# Influence of oxygen and nitrogen on ${}^7\text{Li}$ MAS NMR spectra of zeolite LiX-1.0

M. Feuerstein and R. F. Lobo\*†

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

Nitrogen and oxygen were adsorbed in dehydrated samples of zeolite LiX-1.0  $[(\text{SiAlO}_4)_9\text{Li}_{196}]$ ; the  ${}^7\text{Li}$  MAS NMR spectra of these samples were compared with the spectrum of a sample studied in vacuum; it has been shown that the line assigned to Li cations at position SIII ( $\delta_{\text{iso}} = -0.7$ ) is influenced by the different gases, whereas lines belonging to Li cations in front of six-rings do not change (SI' line  $\delta_{\text{iso}} = 0.4$ , SII line  $\delta_{\text{iso}} = -0.3$ ).

Characterization of the acid and adsorption sites of porous materials is a key issue for understanding the adsorption process and its technical applications. LiX zeolites are commercially useful adsorbents for the production of nitrogen from air in the PSA (pressure swing adsorption) process.<sup>1</sup> Adsorption experiments have shown that the capacity of nitrogen adsorption correlates with the amount of the Li extraframework cations in these zeolites.<sup>2</sup> Recently, Plevret and coworkers<sup>3</sup> investigated zeolite LiX-1.0 by neutron diffraction and located Li cations in four crystallographic sites (SI', SII, SIII and SIII'). Li cations in zeolite LiX were also studied using a combination of  ${}^6\text{Li}$  and  ${}^7\text{Li}$  MAS NMR spectroscopy and neutron diffraction by Feuerstein and Lobo.<sup>4</sup>  ${}^6\text{Li}$  and  ${}^7\text{Li}$  MAS NMR spectra of dehydrated LiX-1.0 show three lines belonging to Li cations in sites SI' ( $\delta_{\text{iso}} = 0.4$ ), SII ( $\delta_{\text{iso}} = -0.3$ ), and SIII ( $\delta_{\text{iso}} = -0.7$ ). Variable temperature  ${}^7\text{Li}$  MAS NMR spectra have shown that the cations at SIII have to be considered mobile. In this earlier study zeolite samples were dehydrated in MAS NMR glass inserts and the inserts sealed while under vacuum. Here we discuss the changes in the  ${}^7\text{Li}$  MAS NMR spectra caused by the presence of nitrogen and oxygen on LiX-1.0.

NaKX-1.0 zeolite was prepared following a method similar to the one published by Kuehl<sup>5</sup> and the as-synthesized form was exchanged to the Li form by several ion exchanges (see ref. 4). The LiX-1.0 zeolites were dehydrated at 673 K and  $10^{-1}$  Pa. The integrity of the faujasite structure was confirmed by X-ray powder diffraction.  ${}^{29}\text{Si}$  MAS NMR spectra show an Si/Al ratio of 1.0 and  ${}^{27}\text{Al}$  MAS NMR spectra show only the existence of tetrahedral coordinated aluminium.  ${}^7\text{Li}$  MAS NMR spectra were recorded at a resonance frequency of 116.6 MHz using a Bruker MSL-300 spectrometer and a 4 mm double bearing Bruker probe. The sample studied in vacuum was prepared in MAS glass inserts. For the oxygen adsorption a sample was dehydrated in a MAS glass insert and sealed after filling the tube with dry oxygen (79.1 kPa). Studies of adsorption of nitrogen were performed by packing the MAS NMR rotor in a nitrogen atmosphere using a glove box.

Fig. 1 shows the  ${}^7\text{Li}$  MAS NMR spectra of zeolite LiX under three different sets of conditions: at vacuum, and after the adsorption of nitrogen and oxygen. The lines belonging to the Li cations in front of the six-ring windows [SI' ( $\delta_{\text{iso}} = 0.4$ ), and SII ( $\delta_{\text{iso}} = -0.3$ )] do not change after the adsorption of the different gases. Cations at SI' do not interact with the gas molecules because the van der Waals radii of  $\text{N}_2$  and  $\text{O}_2$  are too large to enter the  $\beta$ -cages and interact with this site. On the other hand, it is known from the refinements of the neutron diffraction data of LiX-1.0 that Li cations at SII are located inside the six-ring.<sup>3,4</sup> Therefore, the SII cations are effectively shielded by the

framework atoms and do not interact with molecules in the supercages.

The line observed at  $\delta_{\text{iso}} = -0.7$  in the  ${}^7\text{Li}$  MAS NMR spectrum of the sample studied in vacuum and attributed to the SIII cations shifts slightly to a lower frequency after the adsorption of nitrogen. This observation is explained by the preferred interaction of the nitrogen molecules with the Li cations at SIII. Interestingly,  ${}^{23}\text{Na}$  and  ${}^7\text{Li}$  MAS NMR experiments of LiNaX zeolites having different Li exchange levels had shown that the site population of Li cations at SIII correlate directly with its nitrogen adsorption capacity.<sup>6</sup> The presence of oxygen causes a down-field shift of the SIII line. The shift to higher frequency is explained by the paramagnetism of the oxygen molecules. Several authors have observed shorter spin-lattice relaxation times ( $T_1$ ) caused by the adsorption of oxygen.<sup>7</sup> Recently, Norby *et al.*<sup>8</sup> also observed a down-field shift of lines in  ${}^{133}\text{Cs}$  MAS NMR spectra (recorded at variable temperature) of a CsNaY zeolite. The down-field shift was explained by the paramagnetic interaction between the unpaired electrons of the oxygen molecules and the Cs nucleus. Variable temperature  ${}^7\text{Li}$  MAS NMR spectra of zeolite LiX-1.0 loaded with oxygen are depicted in Fig. 2. It can be observed that as a function of temperature, (i) the lines belonging to the six-ring cations show a small high-field shift, (ii) the line at high field belonging to the cations at SIII shows a down-field shift with decreasing temperature, (iii) the line width of the SIII line is increasing with decreasing temperature.

The high-field shift of the SI' and SII components was also observed in  ${}^7\text{Li}$  MAS NMR spectra of LiX-1.0 recorded at variable temperature with samples studied under vacuum in a MAS glass insert. Neutron diffraction experiments have shown that in LiX-1.0 a phase transition occurs at  $T = 220\text{--}230$  K.<sup>4</sup> The symmetry changes from the cubic space group  $Fd\bar{3}$  to the orthorhombic space group  $Fddd$ . This phase transition might cause a slightly different environment of the Li cations and accounts for the change in the chemical shifts of the SI' and SII lines. This point, however, is not completely understood and needs additional study. The down-field shift of the SIII line at lower temperatures is due to the temperature dependence of the

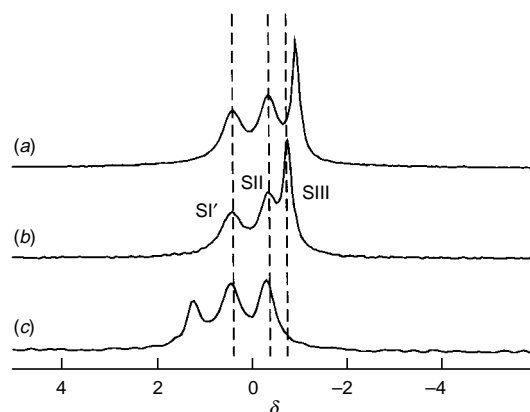
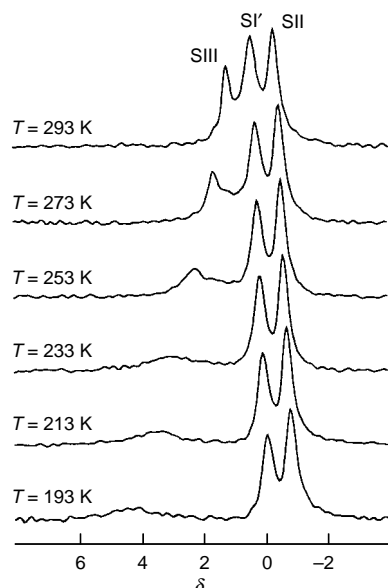


Fig. 1  ${}^7\text{Li}$  MAS NMR spectra of LiX-1.0, (a) after adsorption of nitrogen, (b) in vacuum, and (c) after adsorption of oxygen



**Fig. 2** Variable temperature  ${}^7\text{Li}$  MAS NMR spectra of zeolite LiX after adsorption of oxygen

paramagnetic shift  $\Delta\nu \approx 1/T$ . The increase of the line broadening at lower temperatures is caused by two effects: a line broadening of the SIII line was previously observed in a study of  ${}^7\text{Li}$  MAS NMR spectra of LiX in vacuum in the temperature range 233–253 K.<sup>4</sup> This effect is related to motion of the SIII cations and the line narrowing by the MAS NMR experiment. However, at temperatures below 233 K a narrow SIII line was again observed in the sample studied in vacuum. The  ${}^7\text{Li}$  MAS NMR spectra shown in Fig. 2 differ in this point and the SIII line broadens further at temperatures below 233 K.

The source of the other broadening is the paramagnetic shift due to the anisotropic interaction of the nuclear spin with the electron spin.<sup>9</sup>

The adsorption of oxygen can be easily used to test for accessibility of a cation site in microporous materials in general. The present work shows clearly the advantage of using  ${}^7\text{Li}$  MAS NMR spectroscopy to study the adsorption sites in zeolite LiX, namely the Li cations at site SIII. We will discuss this topic in more detail in the future and compare the  ${}^7\text{Li}$  MAS NMR spectra of different zeolites recorded under vacuum and after adsorption of nitrogen and oxygen.

Note added at proof: Plevert *et al.*<sup>10</sup> very recently reported a study of the paramagnetic shift of  ${}^6\text{Li}$  in zeolite Li-X. Their results are fully consistent with the results presented here for  ${}^7\text{Li}$  in zeolite Li-X.

## Notes and References

† E-mail: lobo@che.udel.edu

- 1 C. C. Chao, *U.S. Pat.* 4 859 217, 1989.
- 2 J. F. Kirner, *U.S. Pat.* 5 268 023, 1993.
- 3 J. Plevert, F. Di Renzo, F. Fajula and G. Chiari, *J. Phys. Chem. B*, 1997, **101**, 10 340.
- 4 M. Feuerstein and R. F. Lobo, *Chem. Mater.*, in press.
- 5 G. H. Kuehl, *Zeolites*, 1987, **7**, 451.
- 6 M. Feuerstein, G. Engelhardt, P. L. McDaniel, J. E. MacDougall and T. D. Gaffney, submitted.
- 7 (a) R. H. Meinhold and D. M. Bibby, *Zeolites*, 1990, **10**, 74; (b) D. J. Cookson and B. E. Smith, *J. Magn. Reson.*, 1985, **63**, 217; (c) J. Klinowski, T. A. Carpenter and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1986, 956.
- 8 P. Norby, F. I. Poshni, A. F. Gualtiere, J. C. Hanson and C. P. Grey, *J. Phys. Chem. B*, 1998, **102**, 839.
- 9 A. Nayeem and J. P. Yesinowski, *J. Chem. Phys.*, 1988, **89**, 4600.
- 10 J. Plevert, L. C. de Menorval, F. Di Renzo and F. Fajula, *J. Phys. Chem. B*, 1998, **102**, 3412.

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