

Correction to “Quantitatively Probing the Al Distribution in Zeolites”

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Pages 8303–8304. The NMR analysis results reported in Table 2 are incorrect due to errors in referencing the NMR spectra displayed in Figures 9 and 10, as a result of significant and continuous main field drift during the course of the NMR measurement that, unfortunately, was not realized at the time of data analysis. In the original article, the HBEA150 and HBEA25 spectra must be shifted by -2 and $+0.5$ ppm, respectively. The corrected spectra are shown here in the revised Figures 9 and 10. While these corrections do not affect the values of the octahedral Al³⁺ fractions listed in Table 2, a reassignment of the NMR T-site distribution is required. The distribution is determined by fitting the peaks in the measured spectra to chemical shifts derived from the DFT calculations for the nine T-sites.

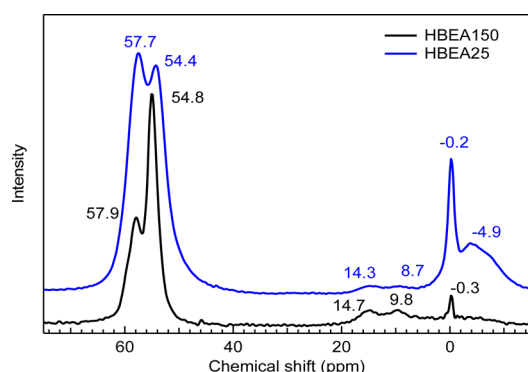


Figure 9. ²⁷Al MAS NMR spectra measured for HBEA150 (black) and HBEA25 (blue). The intensity of HBEA25 spectrum was scaled (0.33) for better visualization.

The resultant least-squares fit (global minimum) to the HBEA150 spectrum (Figure 10a) is obtained using T-sites 1, 2, 7, and 9 in a ratio of 57:21:10:12 (error ~5%). To compare with the EXAFS linear combination fit analysis, the above T-site distribution equates to 78% Set A (T1, T2, T5, and T6) and 22% Set C (T7, T8, and T9), whereas the EXAFS analysis gives 79% Set A and 21% Set B (T3 and T4) rather than Set C.

A comprehensive re-evaluation of the reported EXAFS uncertainties showed that the fit quality is not substantially improved by inclusion of the Set B or Set C standards, since the reduced χ^2_v is not decreased by including Set B and/or C in the fit. This implies that lesser populations of Sets B and C are indeterminable by EXAFS analysis alone. Three other unique fits (with higher χ^2) to the HBEA150 NMR spectrum could be obtained by off-setting the chemical shifts of the T-sites by a few ppm around the minimum value. However, these local minima all exclude Set A T-sites as major constituents, and thus were deemed less probable given the EXAFS results that Set A sites are dominant in the HBEA150 sample.

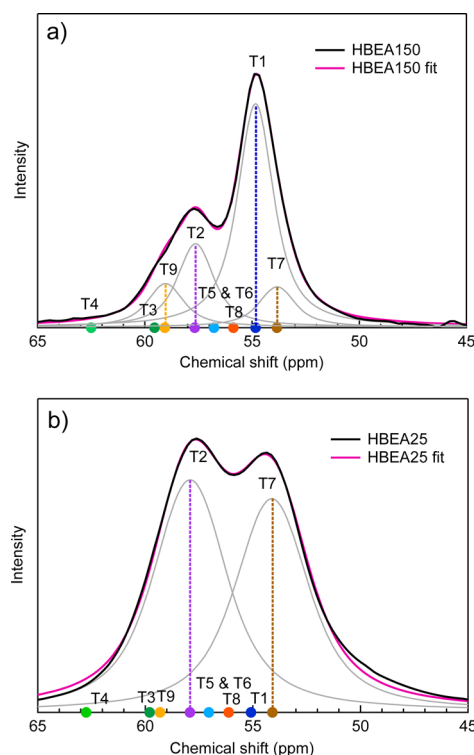


Figure 10. Calculated ²⁷Al MAS NMR chemical shifts for the tetrahedral Al based on the DFT optimized T-site structures for the measured HBEA150 (a) and HBEA25 (b). Fitted NMR peaks are shown in gray; the fit spectrum is shown in magenta. Note: the T5 and T6 signals overlap.

The corresponding fit to the corrected HBEA25 NMR spectrum (Figure 10b) gives T2 and T7 present in a ratio of 52:48 (error ~5%), although we note that forcing a small offset (0.2 ppm) in the chemical shifts causes minor amounts (~10%) of T1 and T9 sites to be included in the distribution. This distribution is consistent with the EXAFS analysis, which gives a 53:47 ratio of Set A to Set C.

In the original article, we speculated that dealumination of HBEA may lead to selective removal of the T2 and T7 sites, whereas the T5 and T6 sites remain mostly intact. The above analysis now suggests that instead the T1 sites remain mostly intact.

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