Supplementary Information

for

Solid-State NMR Study of Various Mono- and Divalent Cation Forms of the Natural Zeolite Natrolite

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Figure Captions

**Fig. S1** Powder XRD patterns of the hydrated form of various mono- and divalent cation-exchanged natrolite zeolites.

**Fig. S2** TGA/DTA traces of the hydrated form of mono- and divalent cation-exchanged natrolite zeolites.

**Fig. S3** Powder XRD patterns of the hydrated form of different mono- and divalent cation-exchanged natrolites measured during in situ heating under vacuum to a residual pressure of $5 \times 10^{-3}$ Torr. The top traces denoted as RT(air) are the patterns measured at room temperature after temperature-programmed XRD experiments up to 800 °C followed by exposure to ambient air for 0.5 h. The asterisk denotes X-ray peaks from the Pt sample holder.

**Fig. S4** Experimentally observed $^{29}$Si MAS NMR chemical shifts of the dehydrated form of monovalent cation-exchanged NAT materials vs the shifts calculated using eq. 1 (see text). Si$_2$(3Al) and Si$_1$(2Al) species are designated by ■ and ●, respectively.

**Fig. S5** $^{27}$Al MQMAS NMR spectra of the hydrated form of various mono- and divalent cation-exchanged natrolite zeolites.

**Fig. S6** Decomposition of the $^{27}$Al MAS NMR spectra of dehydrated Na-NAT (left) and K-NAT (right) obtained at 300 (bottom) and 400 MHz (top) MAS NMR spectrometers.

**Fig. S7** $^{27}$Al MQMAS NMR spectra of the hydrated form of divalent cation-exchanged natrolites.

**Fig. S8** Powder XRD patterns of hydrated Ca-NAT (left) and scolecite (right) before (bottom) and after (top) stirring twice in 2.0 KNO$_3$ solutions (1.0 g solid/100 mL solutions) at 80 °C for 6 h. The arrow denotes the most intense X-ray peak corresponding to the (220) reflection of hydrated K-NAT.
Fig. S1
Fig. S2
Fig. S3
Fig. S4
Fig. S5
<table>
<thead>
<tr>
<th>Material</th>
<th>Structural unit</th>
<th>$\delta_{CS}$, ppm (300 / 400 MHz)</th>
<th>$C_Q$, MHz</th>
<th>$\eta$</th>
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<tbody>
<tr>
<td>Na-NAT</td>
<td>$\text{Al}_1(4\text{Si})$</td>
<td>68.4 / 68.9</td>
<td>2.0</td>
<td>0.9</td>
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<tr>
<td></td>
<td>$\text{Al}_2(4\text{Si})$</td>
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<td>6.7</td>
<td>0.4</td>
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<tr>
<td></td>
<td>$\text{Al}_3(4\text{Si})$</td>
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<td>0.9</td>
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<tr>
<td>K-NAT</td>
<td>$\text{Al}_1(4\text{Si})$</td>
<td>67.5 / 67.4</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>$\text{Al}_3(4\text{Si})$</td>
<td>65.7 / 65.3</td>
<td>2.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Fig. S6**
Fig. S7
Fig. S8