# The Search for Microporous, Strongly Basic Catalysts: Experimental and Calculated $^{29}$Si NMR Spectra of Heavily Nitrogen-Doped Y Zeolites

# Supplementary Information

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Table S1: Thermochemical data for intact zeolite clusters from Table 2 of the main text. Energies are those of the reaction zeolite + $n$NH$_3$ = N-zeolite + $n$H$_2$O. Symbols: $V$, electronic energy; $H$, enthalpy; $S$, entropy; $G$, Gibbs free energy. Standard conditions are the ideal gas state at 298.15 K and 1 atm. Calculated at B3LYP/6-311G(d,p).

| Label | Description | $\Delta V$ (kJ/mol) | $\Delta H°$ (kJ/mol) | $\Delta S°$ (J/mol K) | $\Delta G°$ (kJ/mol) |
|---|---|---|---|---|---|
| 2 | ≡Si–NH–Si≡ | 90.26 | 87.90 | 2.81 | 87.06 |
| 6 | ≡Si–NH$_2$–Al≡ | 30.38 | 31.70 | −2.95 | 32.58 |
| 18 | ≡Al–OH–Si–NH$_2$–Al≡ | 34.53 | 35.78 | −3.10 | 36.70 |
| 20 | =Si(–NH$_2$–Al≡)$_2$ | 66.93 | 66.06 | −20.61 | 72.21 |

Table S2: Selected chemical shifts and quadrupolar coupling constants for $^{27}$Al and $^{14/15}$N nuclei in the structures of Table 2 of the main text. Calculated at B3LYP/cc-pVTZ. Note that shielding constants are independent of isotope unless vibrational corrections are applied.

| **Label** | $\delta_{\mathbf{N}}$ **(ppm)**[a] | $C_Q^{\mathbf{14N}}$ **(MHz)** | $\eta_Q^{\mathbf{14N}}$ | $\delta_{\mathbf{Al}}$ **(ppm)**[b] | $C_Q^{\mathbf{27Al}}$ **(MHz)** | $\eta_Q^{\mathbf{27Al}}$ |
|---|---|---|---|---|---|---|
| 2 | −352 | 3.42 | 0.41 | | | |
| 3 | −341, −349 | 3.12, 2.96 | 0.16, 0.39 | | | |
| 4 | −333, −338, −348 | 2.71, 2.91, 2.80 | 0.00, 0.41, 0.13 | | | |
| 5 | −335, −338, −339, −344 | 2.52, 2.04, 2.36, 3.04 | 0.01, 0.33, 0.95, 0.25 | | | |
| 6 | | | | 65.6 | −16.2 | 0.49 |
| 8 | −350 | 2.09 | 0.87 | 74.9 | −12.3 | 0.52 |
| 12 | −348, −345 | 3.18, 2.25 | 0.32, 0.77 | 75.5 | −11.9 | 0.41 |
| 13 | −340, −349 | 2.74, 3.08 | 0.10, 0.48 | 69.6 | −18.5 | 0.33 |
| 14 | −339, −343, −340 | 2.97, 2.12, −2.32 | 0.27, 0.43, 0.74 | 70.1 | -19.71 | 0.34 |
| 15 | −346, −343, −331 | 3.19, 2.25, 3.12 | 0.30, 0.78, 0.11 | 75.5 | −11.76 | 0.40 |
| 18 | −348 | 2.06 | 0.80 | 75.2, 68.7 | −14.4, 9.0 | 0.42, 0.023 |
| 20 | −348, −345 | −1.40, 2.14 | 0.35, 0.77 | 75.0, 75.4 | −13.7, 5.87 | 0.42, 0.03 |
| 26 | | | | 65.1, 71.8, 73.2 | −21.38, 9.97, −23.49 | 0.56, 0.06, 0.21 |
| 27 | −350 | −1.23 | 0.96 | 60.5, 70.2, 79.3 | −19.3, 8.9, −18.9 | 0.37, 0.11, 0.22 |
| 29 | −345, −347 | −1.10, −1.31 | 0.64, 0.87 | 60.6, 75.3, 79.0 | −19.7, 7.67, −18.2 | 0.35, 0.12, 0.18 |
| 30 | −343 (2), −345 | −1.00, 1.92, 2.24 | 0.59, 0.48, 0.41 | 68.7, 75.8, 76.1 | −16.7, −15.6, 8.9 | 0.5, 0.3, 0.0 |
| 38 | −343, −339, −349, −345 | −1.44, −1.73, 1.94, 1.31 | 0.69, 0.86, 0.11, 0.69 | 80.8, 77.1, 65.5, 81.4 | −13.6, 9.35, −19.3, −21.3 | 0.51, 0.38, 0.18, 0.39 |
| 40 | −375 | −1.41 | 0.0014 | | | |
| 42 | −380 | −1.83 | 0.49 | | | |
| 43 | −374, −374 | −1.31, 2.17 | 0.23 | | | |

[a] Nitrogen chemical shifts are reported relative to neat liquid nitromethane. This shift is computed relative to gaseous ammonia ($\sigma$ = 266.0387 ppm), which in turn has an experimental chemical shift of −400.34 ppm from nitromethane.[1]

[b] For lack of a better gas-phase reference molecule, aluminum chemical shifts are reported relative to solvated $Al^{3+}$ ion, which is defined to have a chemical shift of zero parts per million.[2] Solvated aluminum ion is represented by $[Al(H_2O)_6]^{3+}$ inside a polarized continuum.

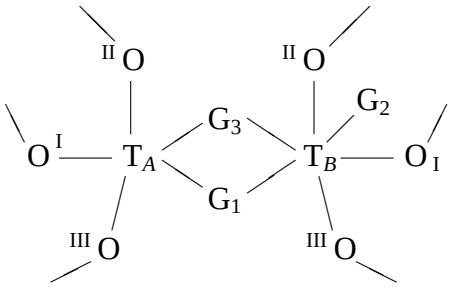


Figure S1: Schematic of cluster used to represent intermediate structures of the addition reaction zeolite + $NH_3$ = $NH_3$-zeolite. The two atoms $T_A$ and $T_B$ are tetrahedral atoms; one is silicon, the other aluminum. The groups $G_1$, $G_2$, and $G_3$ can be any of $NH_2$, $NH_3$, OH, or $OH_2$ as indicated in Table S3. Their constituency is subject to the constraint $G_1 + G_2 + G_3 = NOH_n$, where $n = 3$ for $T_A = T_B = Si$, and $n = 4$ for $T_A = Al$ or $T_B = Al$. Group $G_2$ protrudes into the hexagonal prism connecting two sodalite cages (see Figure S2 for examples). Roman numerals indicate the crystallographically distinct oxygen atoms of the intact zeolite according to the numbering scheme of Klein et al.[3]

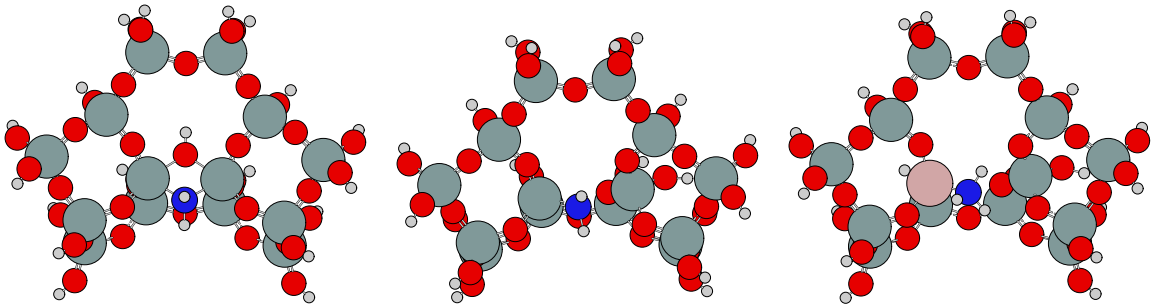

Figure S2: Structures S1, S2, and S7, possible reaction intermediates in the addition of ammonia to HY zeolite. Other possible intermediates are listed in Table S3.

# S1 Alternate clusters

## S1.1 Broken and intermediate structures

While the intact clusters of Tables 2 and 3 in the main text are a good fit to the experimental spectra, using them exclusively avoids the question of whether the zeolite remains intact during the reaction. We investigate this possibility by calculating the structure and chemical shift of several different zeolite structures where the addition of ammonia has either broken the framework structure or forms an intermediate structure where both amine and hydroxyl groups are present. A schematic of these structures is shown in Figure S1, and their chemical shifts and relative energies are given in Table S3. We have shown a few of these structures in Figure S2 to clarify the diagram in Figure S1. From the chemical shifts and energies of each of these intermediate structures, we can safely assume that none of these structures is present in sufficient quantity that we need to be concerned with its presence.

Table S3: Possible reaction intermediates in the reaction of a zeolite with ammonia. See Fig. S1 for an explanation of the symbols.

| **Label** | $\mathbf{T}_A$ | $\mathbf{T}_B$ | $G_1$ | $G_2$ | $G_3$ | $\delta_{\mathrm{Si}}$ **(ppm)** | $\Delta V$ **(kJ/mol)** |
|---|---|---|---|---|---|---|---|
| S1 | Si | Si | $NH_2$ | | OH | −141.5 | 173.0 |
| | | | | | | −141.5 | |
| S2 | Si | Si | $NH_2$ | OH | | −81.9 | 159.9 |
| | | | | | | −100.6 | |
| S3 | Si | Al | OH | $NH_3$ | | (unstable; ammonia desorbs) | |
| S4 | Si | Al | $NH_3$ | OH | | −96.0 | 122.13 |
| S5 | Si | Al | $OH_2$ | $NH_2$ | | −99.0 | 185.08 |
| S6 | Si | Al | $NH_2$ | $OH_2$ | | (unstable; water desorbs) | |
| S7 | Al | Si | $NH_3$ | OH | | −79.7 | 42.05 |
| S8 | Al | Si | OH | $NH_3$ | | (unstable; ammonia desorbs) | |
| S9 | Al | Si | $NH_2$ | $OH_2$ | | (unstable; water desorbs) | |
| S10 | Al | Si | $OH_2$ | $NH_2$ | | −63.9 | 135.15 |
| S11 | Si | Al | $NH_2$ | | $OH_2$ | (unstable; water desorbs) | |

## S1.2 Extraframework aluminum

Another possible place for nitrogen to substitute is near aluminum atoms that exist outside the zeolite framework. This extra-framework aluminum, or EFAl, is present on the surfaces of HY zeolites that have been de-aluminated with steam at high temperatures. This is how Y zeolites with Si/Al ratios higher than about 3 are often prepared. Most EFAl is usually dissolved away with a strong acid after the dealumination procedure, but some invariably remains.[4] It is also possible that more EFAl *forms* during the nitrogen treatment procedure: ammonia could have a similar effect as water at elevated temperatures; that is, ammoniolysis.

We have prepared six different kinds of EFAl models based on the work of Mota and coworkers.[5,6] These structures are shown in Figure S3, and are designed after those in Figure 2 of Reference 5. The chemical shifts we calculate for these structures are shown in Table S4.

The $^{29}$Si chemical shifts of extraframework aluminum species as shown in Table S4 are much the same for substituted and unsubstituted sites. This alone disqualifies them from producing *new* peaks in the silicon NMR spectrum, and therefore the silicon NMR spectrum is of little use in determining whether extra-framework aluminum is present in substituted zeolites.

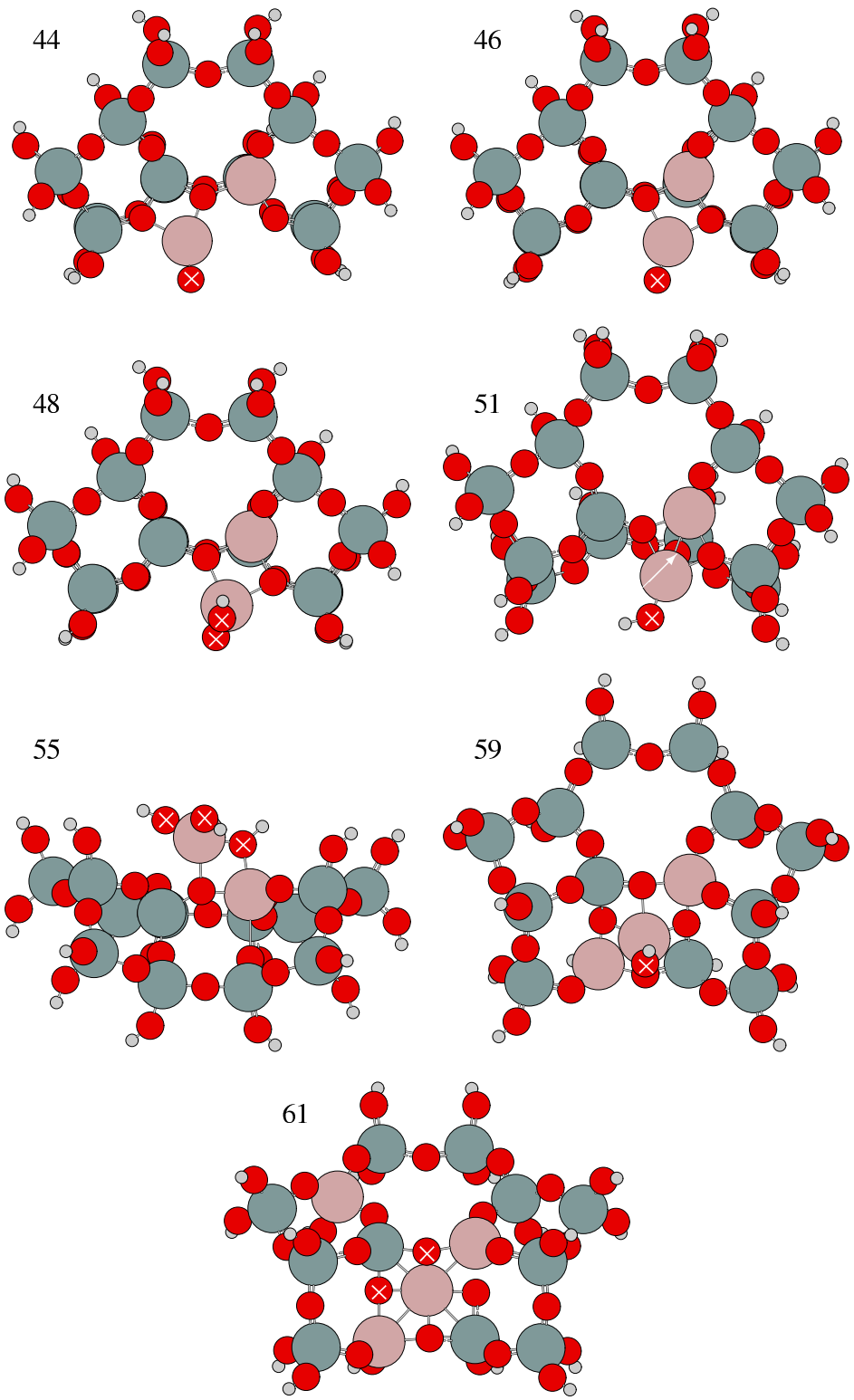


Figure S3: Structure of extraframework aluminum species. From top left: $AlO^+$ ion, Si side (Structure S12); $AlO^+$ ion, Al side (Structure S14); $Al(OH)_2^+$ (Structure S16); AlOOH (Structure S19); $Al(OH)_3$ (Structure S23); $Al(OH)^{2+}$ (Structure S27); $Al^{3+}$ (Structure S29). White arrows and crosses denote oxygen atoms that are substituted for nitrogen in some clusters in Table S4.

Table S4: Chemical shifts of the silicon nucleus labeled in Figure 1 of the main text and associated extraframework aluminum nuclei for intact structures and possible products of their reaction with ammonia. The unreacted clusters are depicted in Figure S3.

| **Label** | **Description** | $\delta_{Si}$ **(ppm)** | $\delta_{Al}$ **(ppm)** | $C_Q^{^{27}Al}$ **(MHz)** | $\Delta V$ **(kJ/mol)** |
|---|---|---|---|---|---|
| S12 | $AlO^+$ (Si-side) | −100.9 | 76.23 | 30.6 | -0- |
| S13 | $AlNH^+$ (Si-side) (#S12 with extraframework oxygen replaced by NH) | −100.8 | 95.92 | 30.2 | 102.4 |
| S14 | $AlO^+$ (Al-side) (Like Ref. 5, #1a) | −102.5 | 82.02 | 20.4 | -0- |
| S15 | $AlNH^+$ (#S14 with extraframework oxygen replaced by NH) | −102.2 | 101.64 | 19.8 | 96.5 |
| S16 | $Al(OH)_2^+$ (Like Ref. 5, #2) | −101.3 | 65.89 | −16.01 | -0- |
| S17 | $AlOHNH_2^+$ (#S16 with one extraframework OH replaced by $NH_2$) | −101.4 | 86.48 | −16.0 | 59.3 |
| S18 | $Al(NH_2)_2^+$ (#S16 with two extraframework OH's replaced by $NH_2$) | −101.3 | 106.17 | −18.3 | 121.7 |
| S19 | AlOOH (Like Ref. 5, #3) | −101.1 | 68.55 | 16.4 | -0- |
| S20 | AlNHOH (Like #S19 with the O replaced by NH) | −102.0 | 94.53 | 28.8 | 170.5 |
| S21 | $AlONH_2$ (Like #S19 with the OH replaced by $NH_2$) | −101.1 | 93.10 | 14.1 | 57.6 |
| S22 | $AlNHNH_2$ (Like #S19 with O and OH replaced by NH and $NH_2$) | −102.2 | 115.47 | 33.54 | 231.7 |
| S23 | $Al(OH)_3$ (Like Ref. 5, #4) | −100.3 | 76.52 | −11.1 | -0- |
| S24 | $AlNH_2(OH)_2$ (Like #S23) | −101.0 | 109.23 | 11.9 | 60.9 |
| S25 | $Al(NH_2)_2OH$ (Like #S23) | −101.3 | 92.91 | 13.8 | 125.5 |
| S26 | $Al(NH_2)_3$ (Like #S23) | −102.8 | 118.93 | −14.8 | 180.8 |
| S27 | $Al(OH)^{2+}$ (Like Ref. 5, #5a) | −96.4 | 49.16 | −8.9 | -0- |
| S28 | $Al(NH_2)^{2+}$ (Like #S27) | −96.6 | 66.63 | −9.4 | 52.5 |
| S29 | $Al^{3+}$ (Like Ref. 5, #6) | −92.7 | 91.15 | 26.5 | -0- |
| S30 | $Al^{3+}$, 1NH (Like #S29, but with one O adjacent to the $Al^{3+}$ ion replaced by NH) | −87.3 | 102.95 | −10.2 | 71.1 |
| S31 | $Al^{3+}$, 2NH (Like #S29, but with two O's adjacent to the $Al^{3+}$ ion replaced by NH) | −77.6 | 113.12 | 25.47 | 168.3 |

# Supplementary References


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