

Supporting Information

Tuning Brønsted Acid Strength by Altering Site Proximity in CHA Framework Zeolites

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S1. DPE, DHE and NH₃ adsorption for site-pairs in CHA

Below are additional graphical representations for relative E_0 and acid strength metrics for both states of the second site for configurations explored in this study.

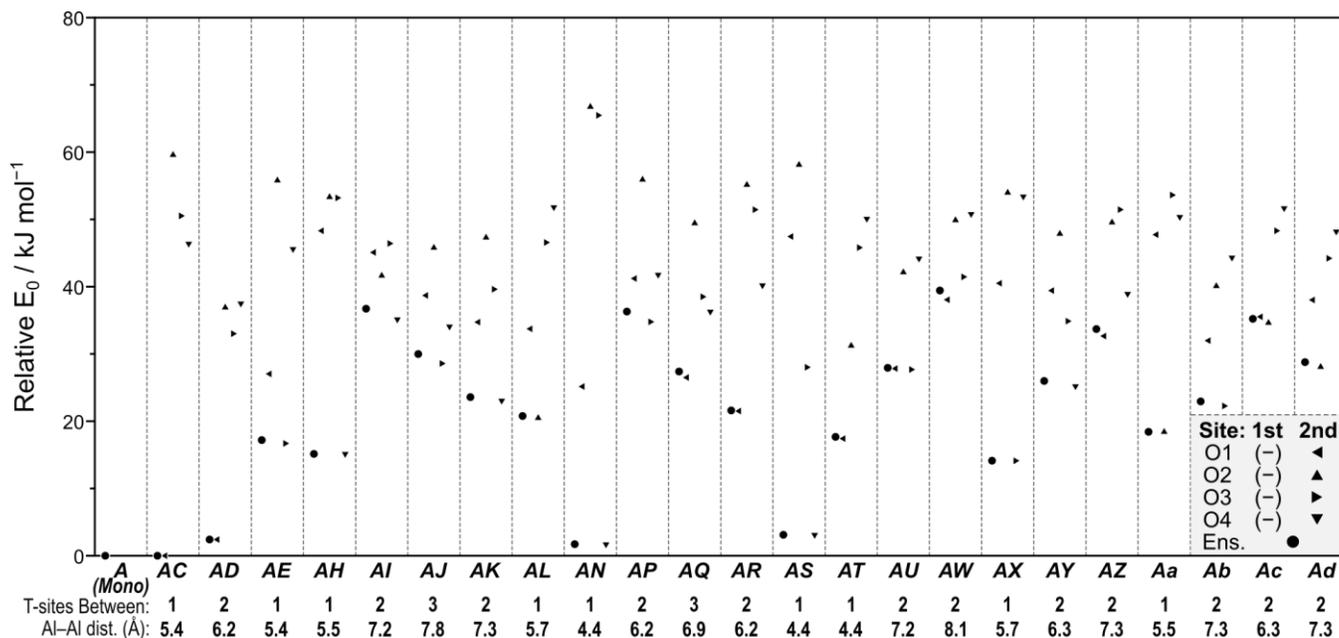


Figure S1. The relative E_0 for the isolated acid site (for which there is only one structure) and all site-pairs where the second site is protonated, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average E_0 for each site-pair, and triangles mark individual E_0 . The direction of the triangle indicates the location of the H on the second site: O1 (◄), O2 (▲), O3 (►), and O4 (▼).

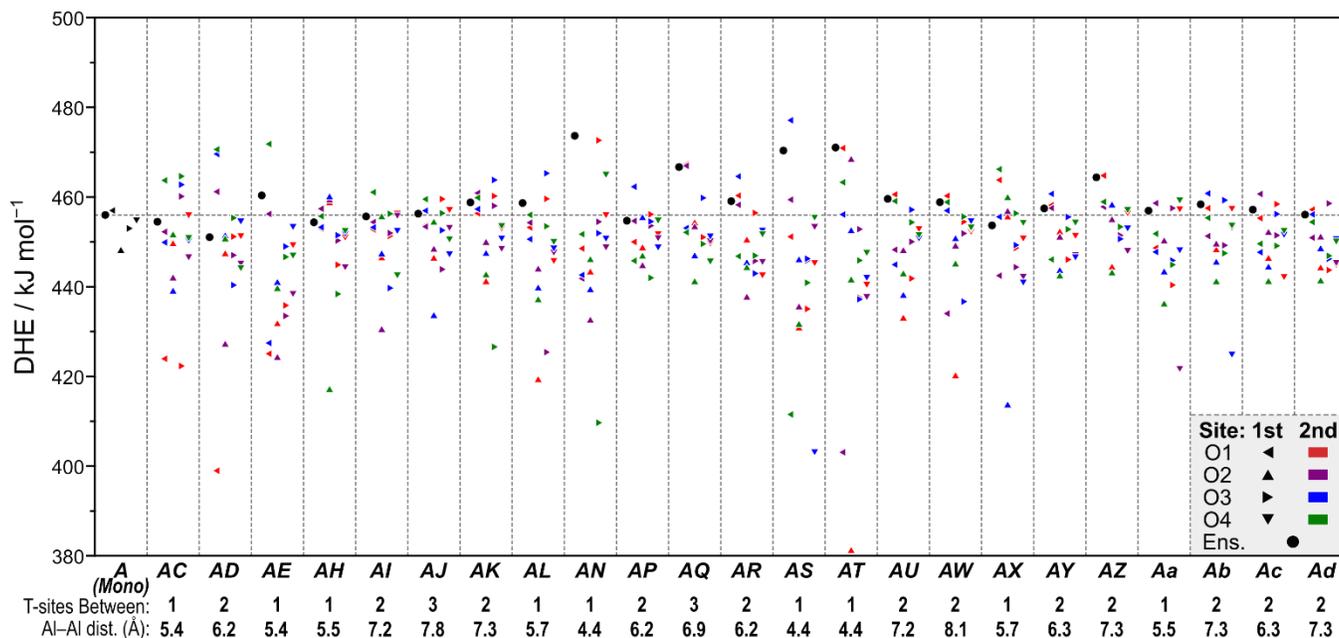


Figure S2. The DHE for the isolated acid site and all site-pairs where the second site is protonated, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average DHE for each site-pair. The dashed line marks the ensemble average DHE of

the isolated site and triangles mark individual DHE for each configuration. The direction of each triangle indicates the O atom from which the H was removed: O1 (\blacktriangleleft), O2 (\blacktriangle), O3 (\blacktriangleright), and O4 (\blacktriangledown). The color of each triangle denotes the location of the remaining H on the second site: O1 (red), O2 (purple), O3 (blue), and O4 (green). The configuration of the most acidic protons for each site combination by DHE is marked near its representative point, and the dehydrogenated O atom on the A site is underlined.

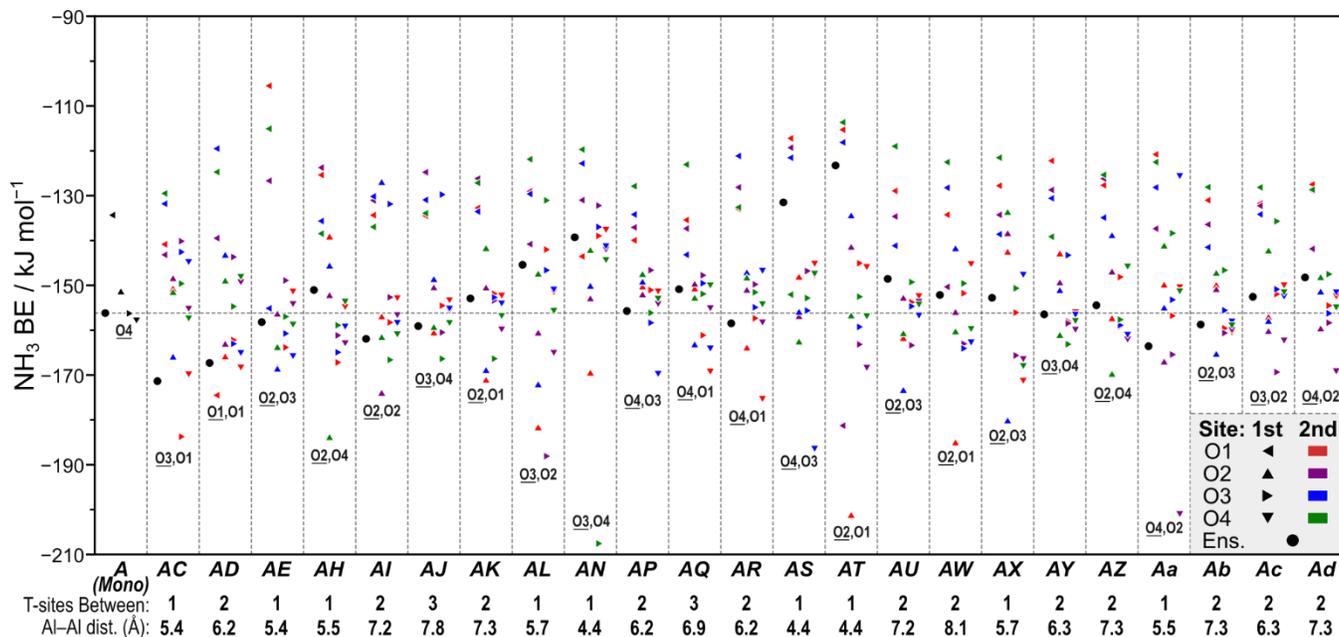


Figure S3. The NH_3 BE for the isolated acid site and all site-pairs where the second site is protonated, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average NH_3 BE for each site-pair. The dashed line marks the ensemble average NH_3 BE of the isolated site and triangles mark individual NH_3 BE for each configuration. The direction of each triangle indicates the O atom from which the H was removed: O1 (\blacktriangleleft), O2 (\blacktriangle), O3 (\blacktriangleright), and O4 (\blacktriangledown). The color of each triangle denotes the location of the remaining H on the second site: O1 (red), O2 (purple), O3 (blue), and O4 (green). The configuration of the most acidic protons for each site combination by NH_3 BE is marked near its representative point, and the deprotonated O atom on the A site is underlined.

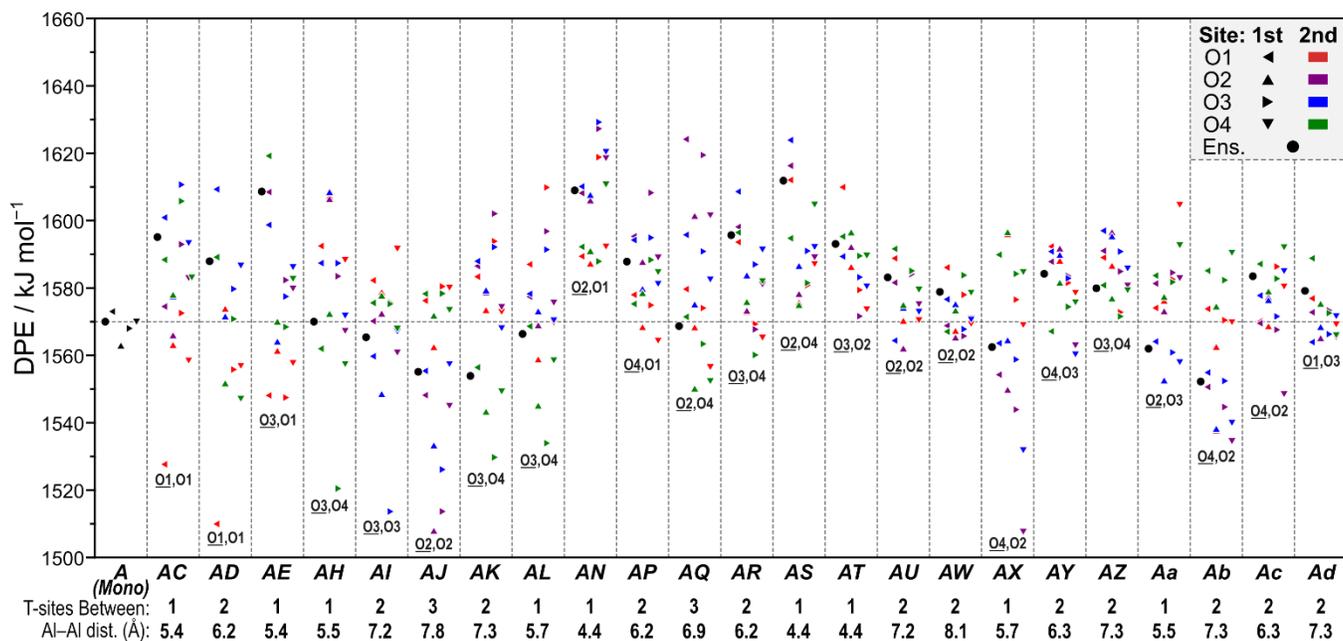


Figure S4. The DPE for the isolated acid site and all site-pairs where the second site has NH_3 adsorbed, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average DPE for each site-pair. The dashed line marks the ensemble average DPE of the isolated site and triangles mark individual DPE for each configuration. The direction of each triangle indicates the O atom from which the H was removed: O1 (\blacktriangleleft), O2 (\blacktriangle), O3 (\blacktriangleright), and O4 (\blacktriangledown). The color of each triangle denotes the location of the NH_3 on the second site: O1 (red), O2 (purple), O3 (blue), and O4 (green). The configuration of the most acidic protons for each site combination by DPE is marked near its representative point, and the deprotonated O atom on the A site is underlined.

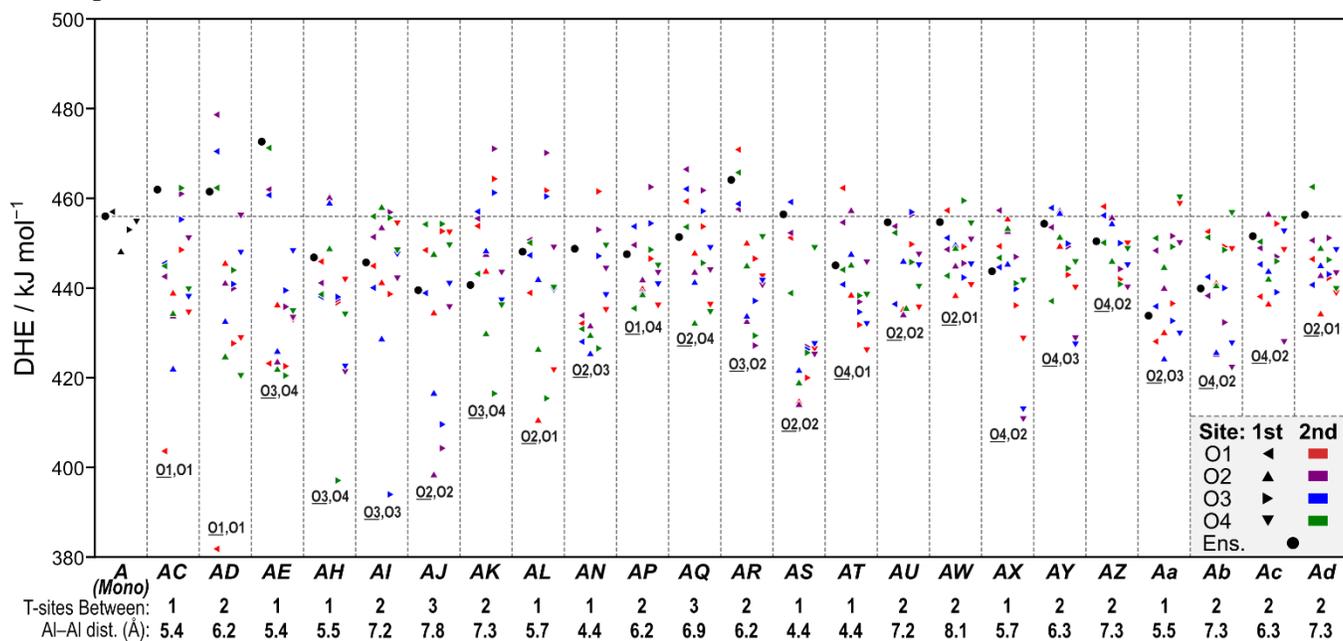


Figure S5. The DHE for the isolated acid site and all site-pairs where the second site has NH_3 adsorbed, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average DHE for each site-pair. The dashed line marks the ensemble average DHE of the isolated site and triangles mark individual DHE for each configuration. The direction of each triangle indicates

the O atom from which the H was removed: O1 (\blacktriangleleft), O2 (\blacktriangle), O3 (\blacktriangleright), and O4 (\blacktriangledown). The color of each triangle denotes the location of the NH₃ on the second site: O1 (red), O2 (purple), O3 (blue), and O4 (green). The configuration of the most acidic protons for each site combination by DHE is marked near its representative point, and the deprotonated O atom on the A site is underlined.

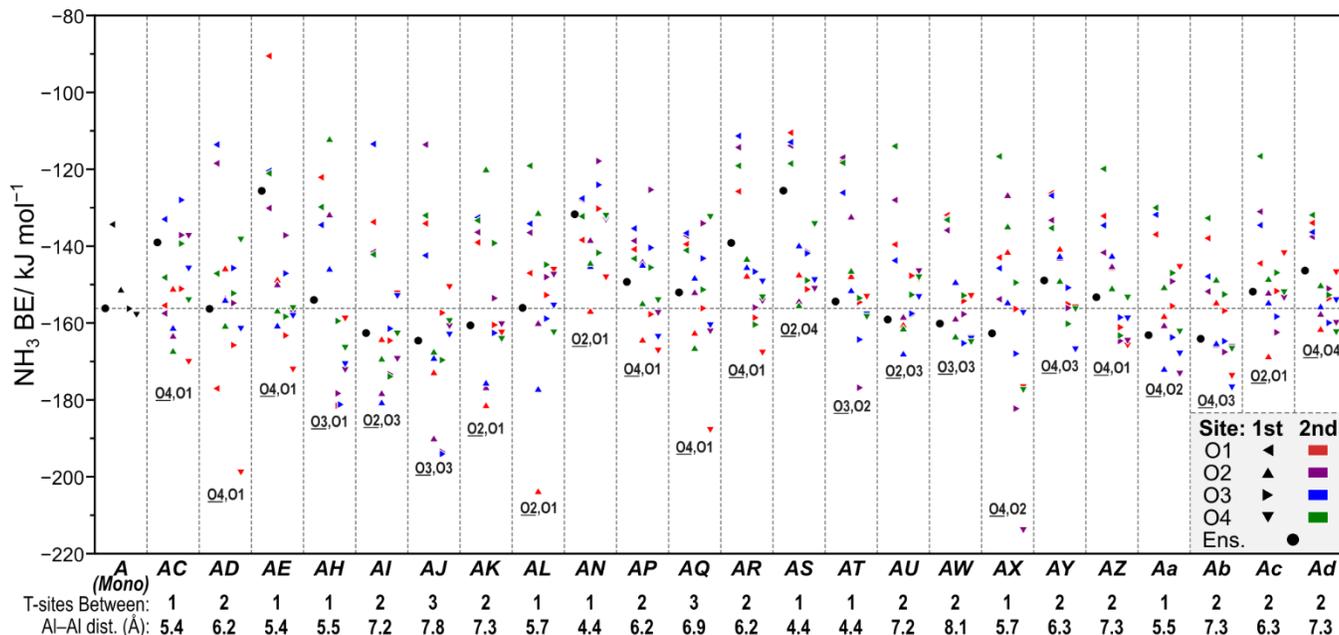


Figure S6. The NH₃ BE for the isolated acid site and all site-pairs where the second site has NH₃ adsorbed, with the number of Si linkers between each site and the distance in Å between the T-atoms of each site shown below. Circles represent ensemble average NH₃ BE for each site-pair. The dashed line marks the ensemble average NH₃ BE of the isolated site and triangles mark individual NH₃ BE for each configuration. The direction of each triangle indicates the O atom from which the H was removed: O1 (\blacktriangleleft), O2 (\blacktriangle), O3 (\blacktriangleright), and O4 (\blacktriangledown). The color of each triangle denotes the location of the NH₃ on the second site: O1 (red), O2 (purple), O3 (blue), and O4 (green). The configuration of the most acidic protons for each site combination by NH₃ BE is marked near its representative point, and the deprotonated O atom on the A site is underlined.

S2. Comparison between the RPBE-D3BJ, PBE-D3BJ, and BEEF functionals

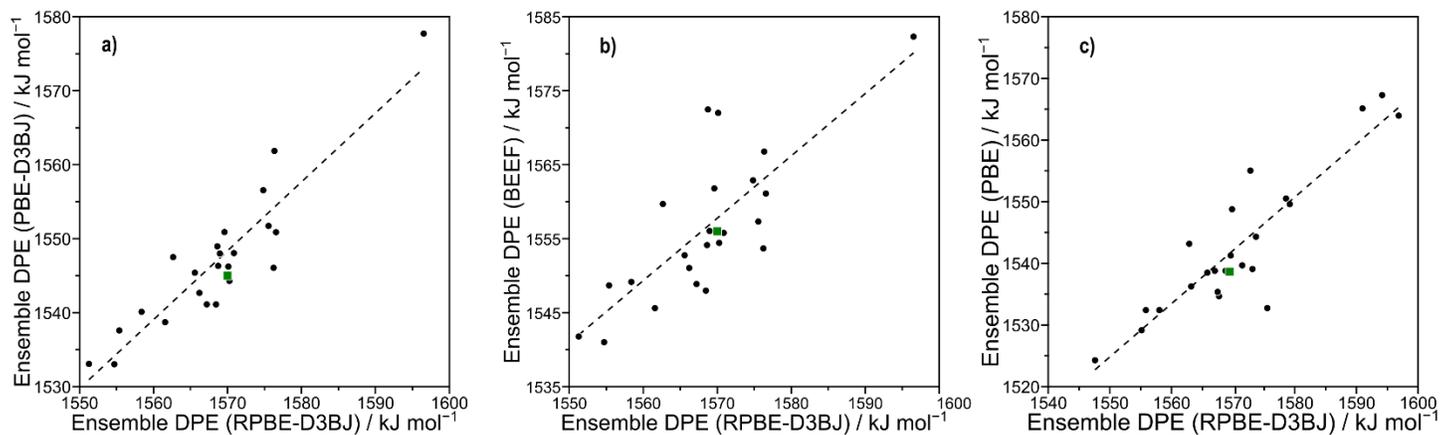


Figure S7. Comparison of the DPE values between RPBE-D3BJ and **a)** PBE-D3BJ, **b)** BEEF-vdW, and **c)** PBE (without dispersion correction) functionals. The green dot represents ensemble DPE values of the isolated site. The values in part **c)** were optimized such that forces on each atom were less than $0.05 \text{ eV } \text{\AA}^{-1}$, while those in parts **a)** and **b)** were optimized such that the forces on each atom were less than $0.01 \text{ eV } \text{\AA}^{-1}$.

S3. Calculation of H and G for isolated DPE, DHE, and NH_3 BE

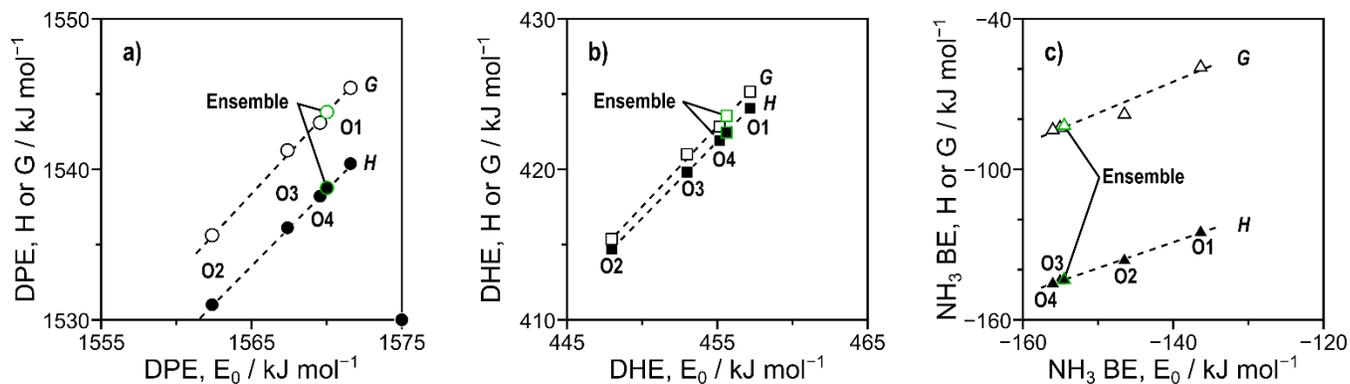


Figure S8. The linear relationship between **a)** electronic DPE and DPE enthalpies (filled) and free energies (hollow), **b)** electronic DHE and DHE enthalpies (filled) and free energies (hollow), and **c)** NH_3 BE and NH_3 BE enthalpies (filled) and free energies (hollow). Dashed lines represent linear fits and ensemble energies are represented by points outlined in green.

S4. Tests on boundary condition changes for isolated acid sites

The artifacts associated with periodic calculations of charged systems and the strong dipoles created by the presence of a charge-neutralizing background charge were explored through a series of calculations designed to understand what factors influence these artifacts. The effects of acid site and anion position were examined by forming a single Brønsted acid site at multiple crystallographically identical T-sites in CHA. These acids should give identical DPE values, but their DPE varied by 1.4 kJ mol^{-1} across the six T-sites (A through F, Fig. 1 in the main text) examined, with an average of $1568.2 \text{ kJ mol}^{-1}$ (Fig. S8). Next, we examined the effects of centering the anion within the unit cell for each of the six T-sites tested, which alters the composition and charge density at the unit cell boundary. These values should also be identical, but instead they varied by 1.3 kJ mol^{-1} and had a higher average value ($1569.0 \text{ kJ mol}^{-1}$) than the previous set, indicating that the position of the acid site and resulting anion have small impacts ($1\text{--}2 \text{ kJ mol}^{-1}$) on calculated DPE values. These calculations were first performed with convergence criteria where the maximum force on any atom was $< 0.05 \text{ eV \AA}^{-1}$ and repeated with lower convergence criteria ($< 0.01 \text{ eV \AA}^{-1}$) to compare the precision of the two calculations and the impact of boundary conditions on the results for both criteria. The spread of energies for these calculations significantly decreased from $\sim 1.3 \text{ kJ mol}^{-1}$ to $< 0.2 \text{ kJ mol}^{-1}$ with stricter convergence criteria and the average DPE values were close to 1570 kJ mol^{-1} (Fig. S8). While these tighter convergence criteria did reduce the effects of charge location artifacts and altered DPE values, the effects ($1\text{--}2 \text{ kJ mol}^{-1}$) were still significantly less than the errors inherent in DFT methods ($\sim 5\text{--}10 \text{ kJ mol}^{-1}$).

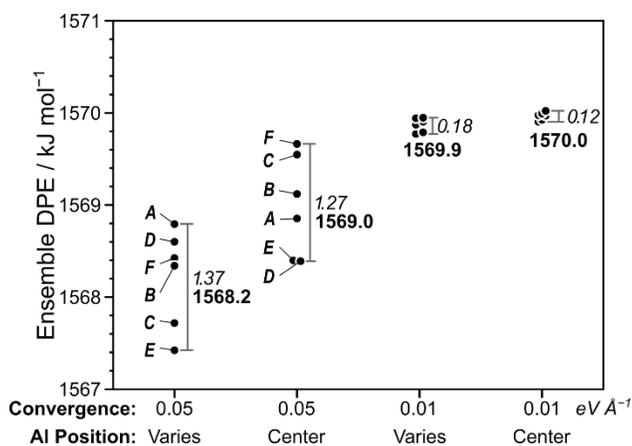


Figure S9. Effects of varying the location of the Al site in the CHA framework (sites A–F), the position of the framework relative to the unit cell (by shifting those sites to the center of the unit cell), and the convergence criteria for optimizations (both 0.05 and 0.01 eV \AA^{-1} were used as force maxima). The ensemble DPE values are calculated using Eq. 6 for the four O atom locations of the proton for each acid site.

S5. Correlation between DPE, DHE, and NH₃ BE when the second site has NH₃ adsorbed

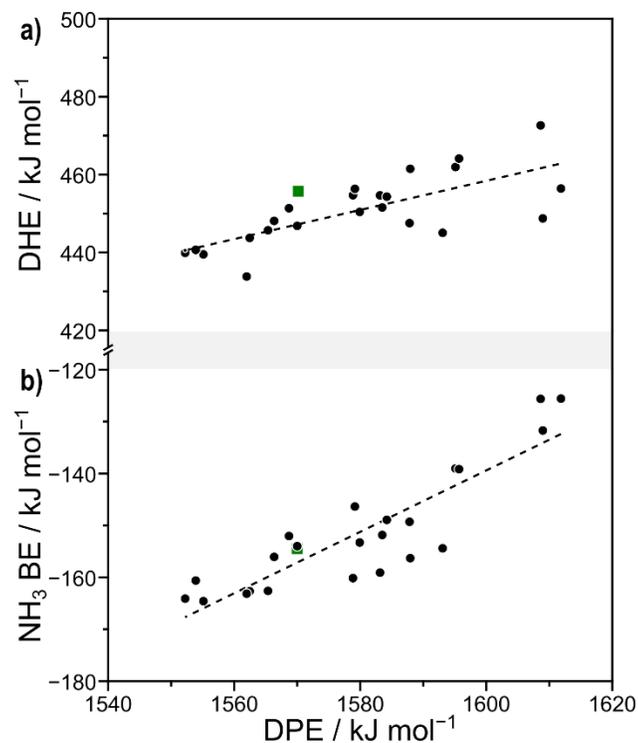


Figure S10. The relationship between a) DPE and DHE and b) DPE and NH₃ BE for all site-pairs where the second site has NH₃ adsorbed. Energies shown are ensemble averages for each measurement of acid strength in kJ mol⁻¹. Dashed lines represent linear fits.