

## SUPPORTING INFORMATION

### **Structural and Kinetic Changes to Small-Pore Cu-Zeolites After Hydrothermal Aging Treatments and Selective Catalytic Reduction of NO<sub>x</sub> with Ammonia**

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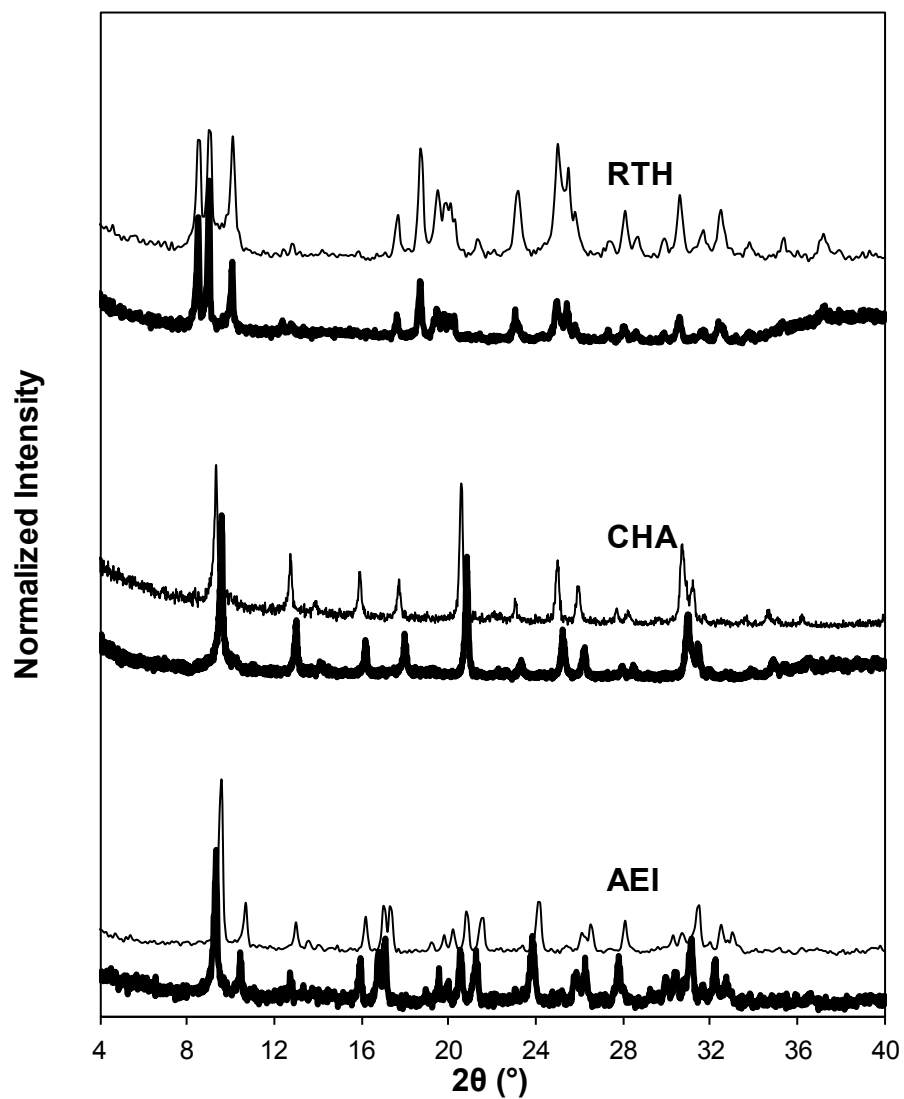
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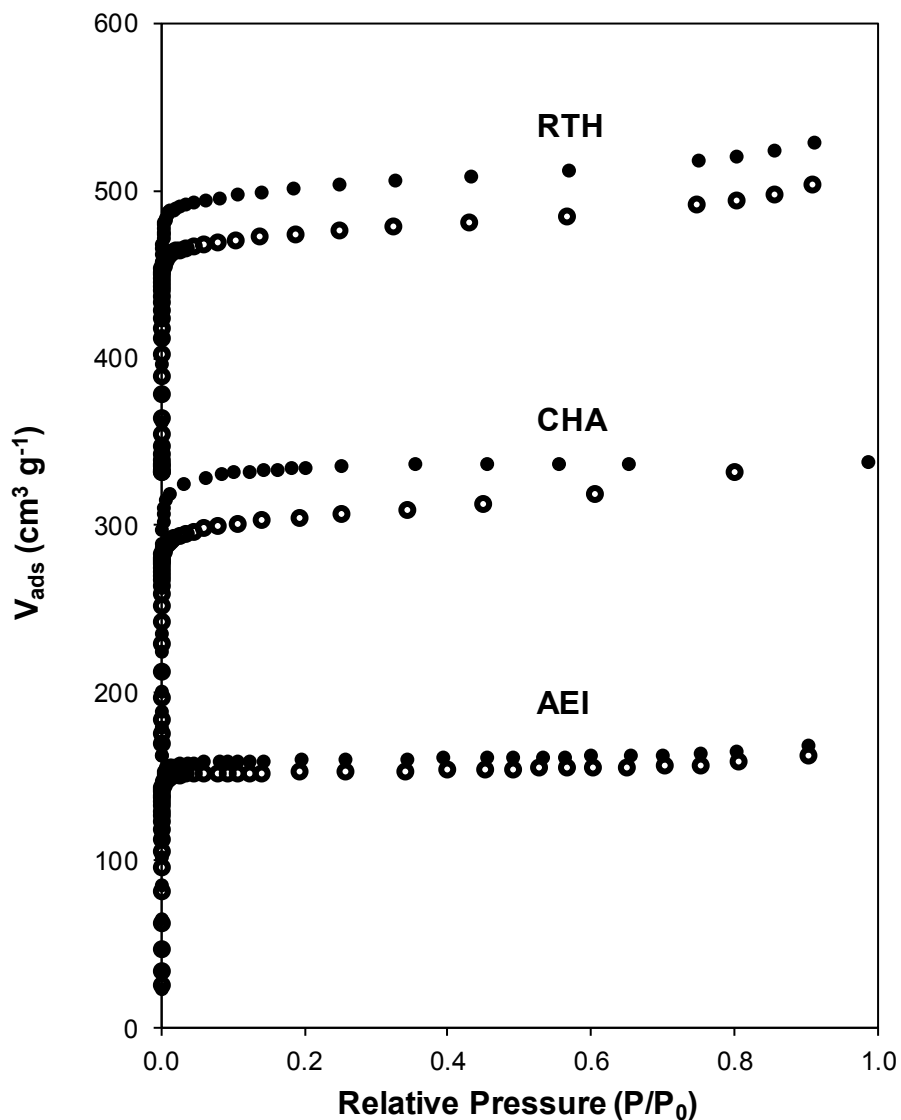
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Section S.1. Powder X-ray diffraction patterns on H- and Cu-zeolites



**Figure S.1.** XRD patterns of H-form (dark) and Cu-form (light) AEI, CHA, and RTH zeolites. Diffraction patterns are normalized so that the maximum peak intensity in each pattern is unity.

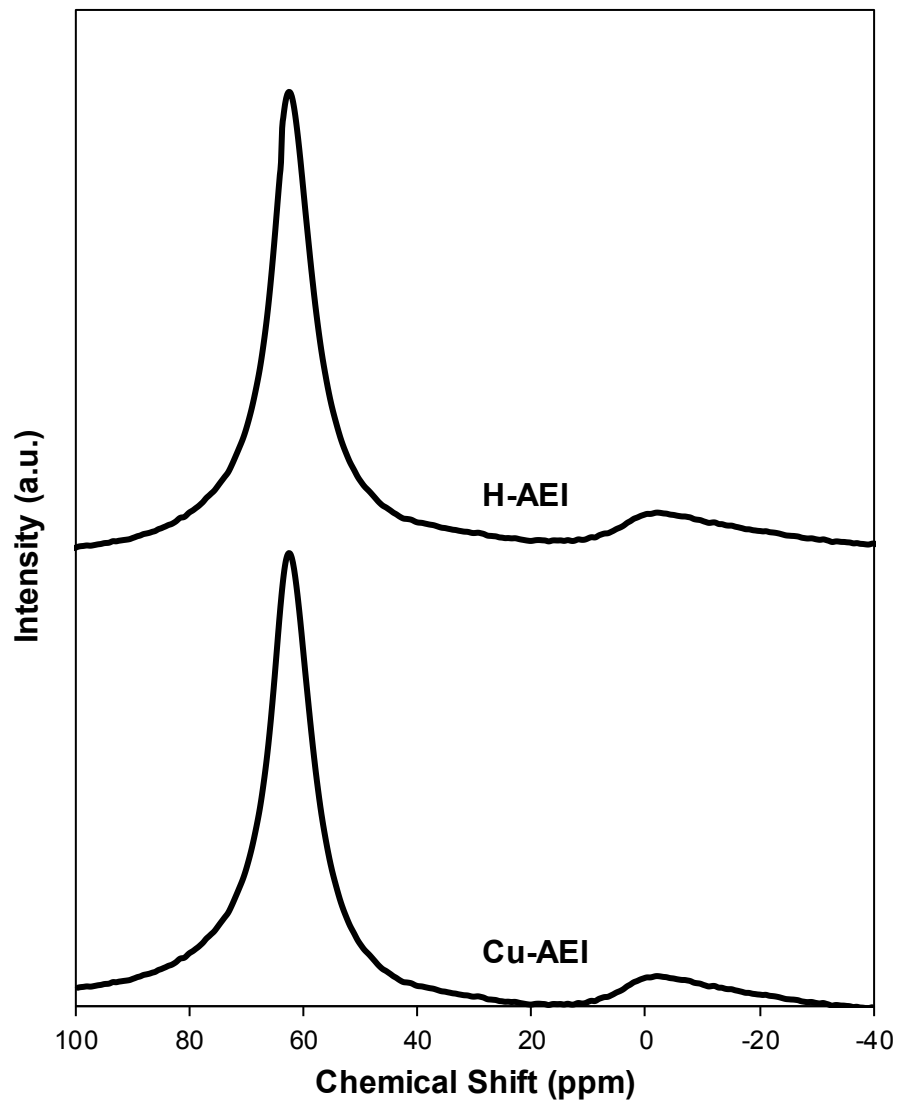
Section S.2. Argon adsorption isotherms on H- and Cu-zeolites



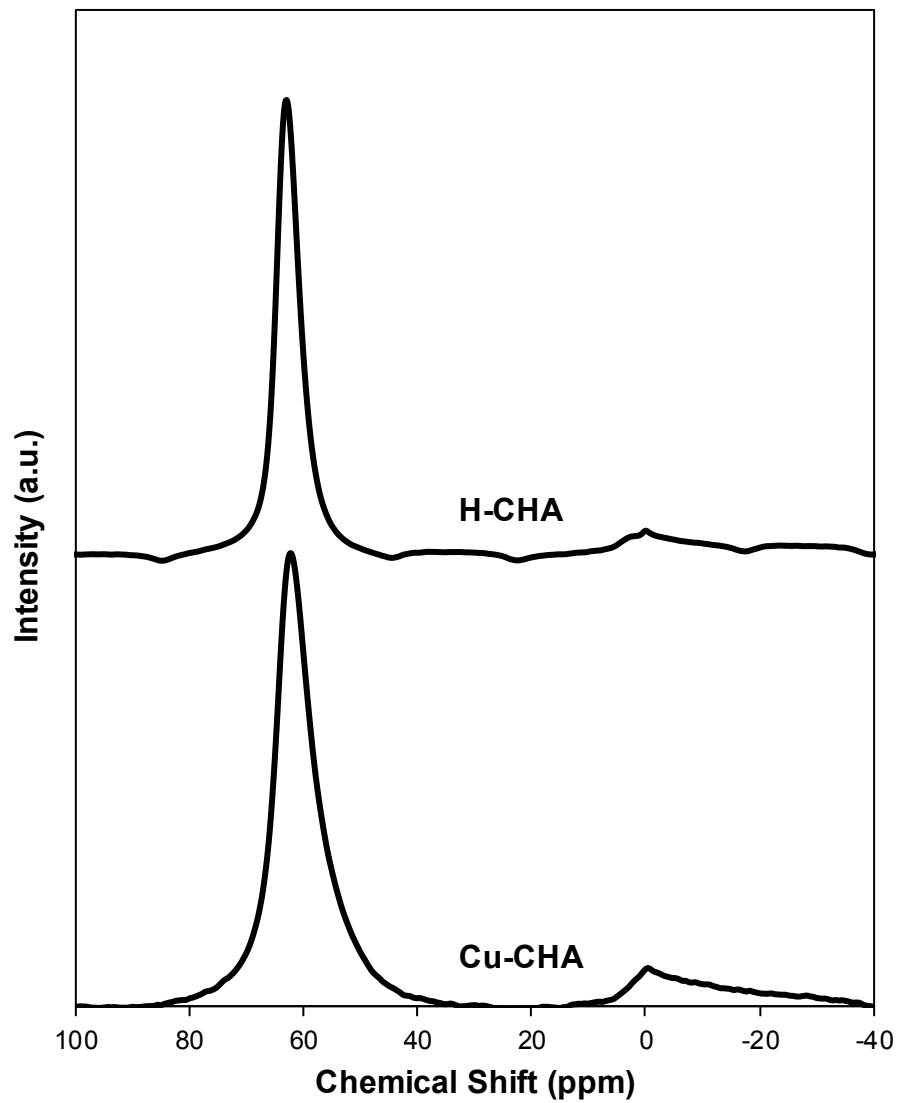
**Figure S.2.** Ar adsorption isotherms (87 K) on H-form (filled) and Cu-form (open) RTH, CHA and AEI zeolites. Adsorption isotherms are vertically offset (CHA:  $160 \text{ cm}^3 \text{ g}^{-1}$ , RTH:  $320 \text{ cm}^3 \text{ g}^{-1}$ ) for clarity.

### Section S.3. $^{27}\text{Al}$ MAS NMR spectra on H- and Cu-zeolites

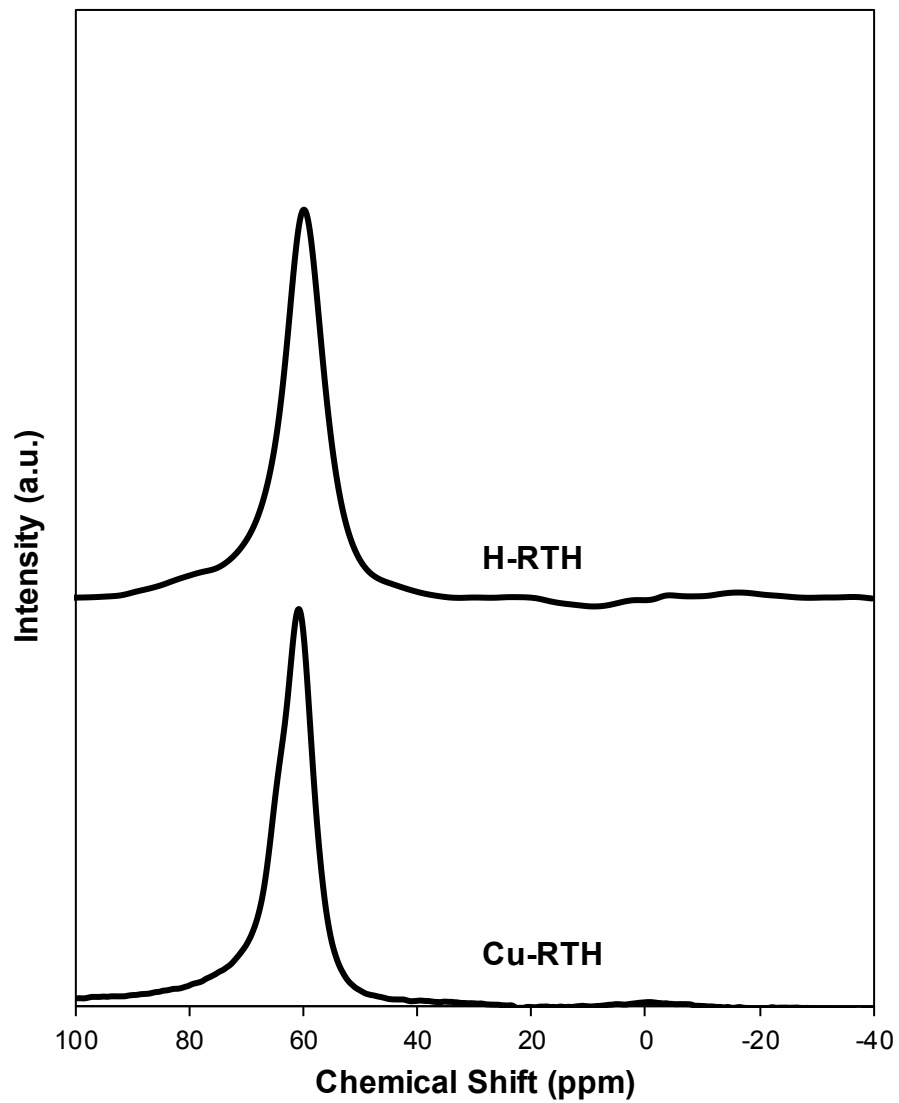
$^{27}\text{Al}$  MAS NMR spectra were measured on the H- and Cu-forms of the three zeolites in this study, AEI (Figure S.3.1), CHA (Figure S.3.2) and RTH (Figure S.3.3), in order to estimate the distribution of framework ( $\text{Al}_f$ ) and extra-framework ( $\text{Al}_{\text{ex}}$ ) Al species. NMR lines centered at 60 ppm were present for tetrahedral Al for RTH, and a small shoulder for penta-coordinated  $\text{Al}^{1,2}$  was present for CHA and AEI. The tetrahedral along with distorted tetrahedral and penta-coordinated Al NMR lines were integrated together to estimate the total number of  $\text{Al}_f$  species, although we recognize difficulties in quantifying  $\text{Al}_f$  content from NMR spectra, because some species can reversibly change between tetrahedral and octahedral coordination depending on the conditions of the measurement<sup>3-5</sup>, and some extraframework alumina may also contain tetrahedrally-coordinated Al.<sup>1,6</sup> The Al NMR lines centered at 0 ppm for octahedral Al were taken to reflect  $\text{Al}_{\text{ex}}$  species. Spectra of H- and Cu- form zeolites show Al incorporated predominantly into tetrahedral framework positions, with  $\text{Al}_f/\text{Al}_{\text{tot}}$  values given in Table 2 of the main text.



**Figure S.3.1.**  $^{27}\text{Al}$  MAS NMR spectra of H-AEI and Cu-AEI.



**Figure S.3.2.**  $^{27}\text{Al}$  MAS NMR spectra of H-CHA and Cu-CHA.

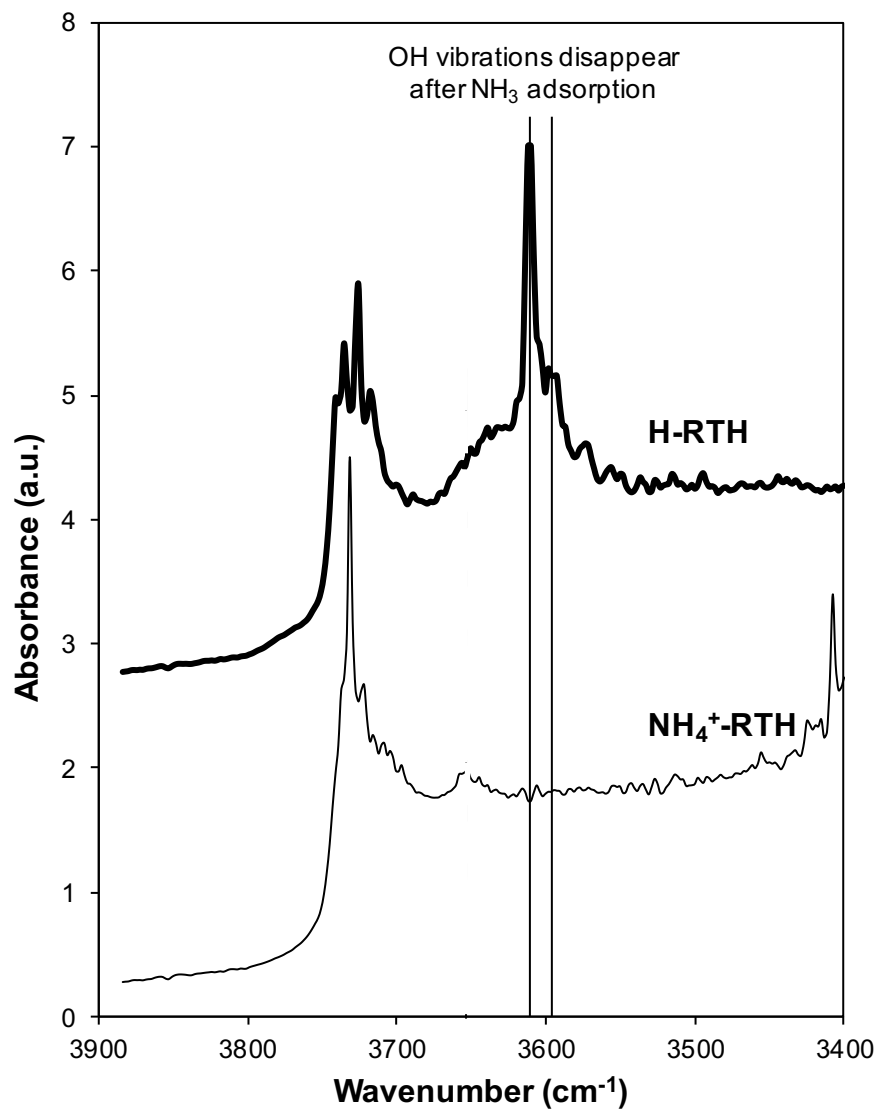


**Figure S.3.3.**  $^{27}\text{Al}$  MAS NMR spectra of H-RTH and Cu-RTH.

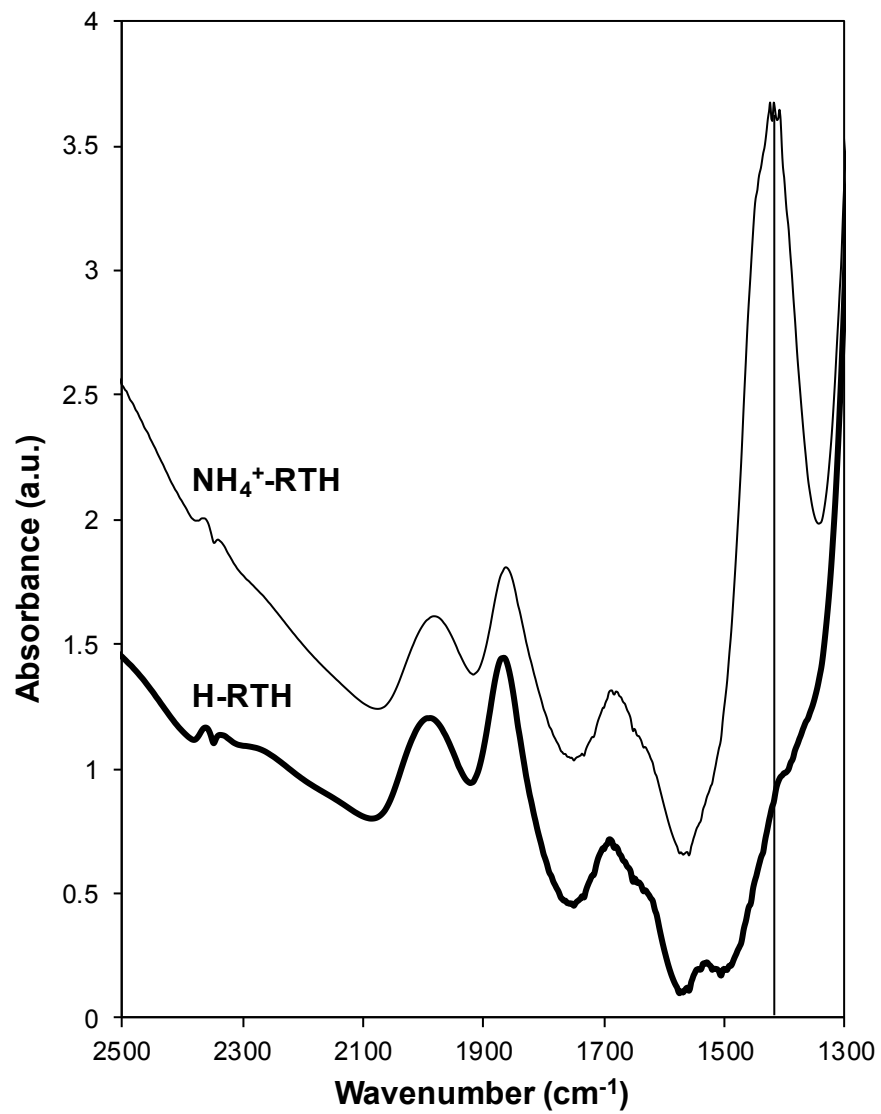
## Section S.4. IR Spectra of H-RTH Before and After NH<sub>3</sub> Exposure

*In situ* IR experiments were performed to monitor interactions of H<sup>+</sup> sites in H-RTH (Si/Al = 15) with NH<sub>3</sub>. H-RTH was pressed into a self-supporting wafer (~0.40 g) and placed within an *operando* FTIR cell, using a procedure that has been described elsewhere.<sup>7</sup> The sample was heated to 723 K and held for 2 h under 50 mL min<sup>-1</sup> of 10% O<sub>2</sub> (99.5%, Indiana Oxygen) and balance N<sub>2</sub> (99.999% UHP, Indiana Oxygen), and then cooled to 433 K under flow (10% O<sub>2</sub> and balance N<sub>2</sub>) to give the spectra (dark traces) in Figure S.4 (OH stretching region shown in Fig. S.4.1, NH bending region shown in Fig. S.4.2). The H-RTH wafer was then saturated in flowing NH<sub>3</sub> (350 ppm, 3 h, 433 K), to give the spectra (light traces) in Figure S.4. After NH<sub>3</sub> saturation, Brønsted OH bands disappeared completely, and new IR bands for NH<sub>4</sub><sup>+</sup> bending vibrations at 1425 cm<sup>-1</sup> appeared concomitantly. These data indicate that all H<sup>+</sup> sites in H-RTH were titrated by NH<sub>3</sub>, and that the H<sup>+</sup>/Al<sub>f</sub> value of 0.61 measured in NH<sub>3</sub> TPD experiments does not reflect a fraction of H<sup>+</sup> sites that were inaccessible to NH<sub>3</sub>.



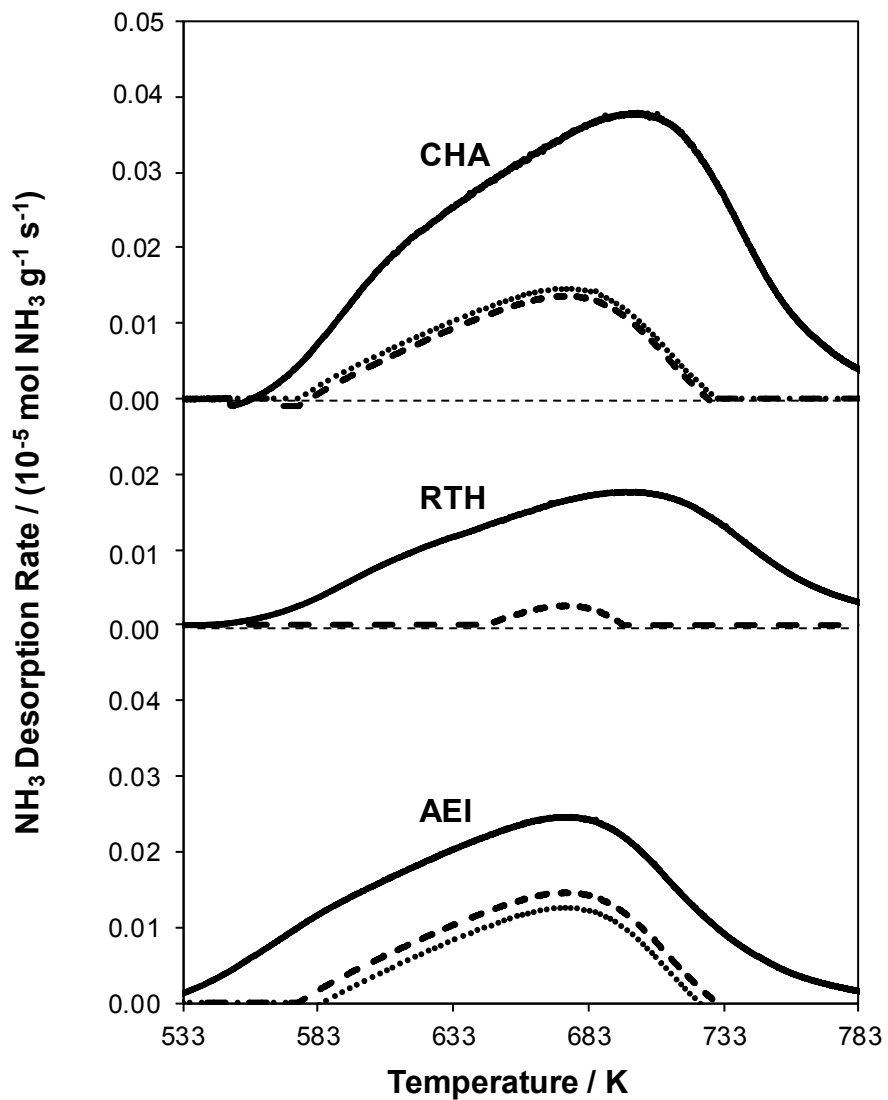


**Figure S.4.1.** IR spectra (OH stretching region: 3400-3900 cm<sup>-1</sup>) of H-RTH at 433 K before (dark) and after (light) NH<sub>3</sub> saturation.



**Figure S.4.2.** IR spectra (N-H bending region: 1300-2500 cm<sup>-1</sup>) of H-RTH at 433 K before (dark) and after (light) NH<sub>3</sub> saturation.

Section S.5. NH<sub>3</sub> TPD on Cu-zeolites



**Figure S.5.** NH<sub>3</sub> desorption rates as a function of temperature on fresh Cu-form after SCR (solid), aged Cu-form before SCR (dashed) and aged Cu-form after SCR (dotted) on CHA, RTH, and AEI zeolites.

## Section S.6. References

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