SUPPORTING INFORMATION

Structural and Kinetic Changes to Small-Pore Cu-Zeolites After Hydrothermal Aging Treatments and Selective Catalytic Reduction of NOx with Ammonia

Jonatan D. Albarracin-Caballero[1,†], Ishant Khurana[1,†], John R. Di Iorio[1], Arthur J. Shih[1], Joel E. Schmidt[2], Michiel Dusselier[2,3], Mark E. Davis[2], Aleksey Yezerets[4], Jeffrey T. Miller[1], Fabio H. Ribeiro[1,*], Rajamani Gounder[1,*]

[1]*Charles D. Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA*

[2]*Chemical Engineering, California Institute of Technology, 1200 E. California Boulevard, MC 210-41, Pasadena, CA 91125, USA*

[3]*Center for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium*

[4]*Cummins Inc., 1900 McKinley Ave., MC 50183, Columbus, IN 47201, USA*

*Corresponding authors. E-mail: rgounder@purdue.edu, fabio@purdue.edu

[†]J.D.A.-C. and I.K. contributed equally to this work.

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

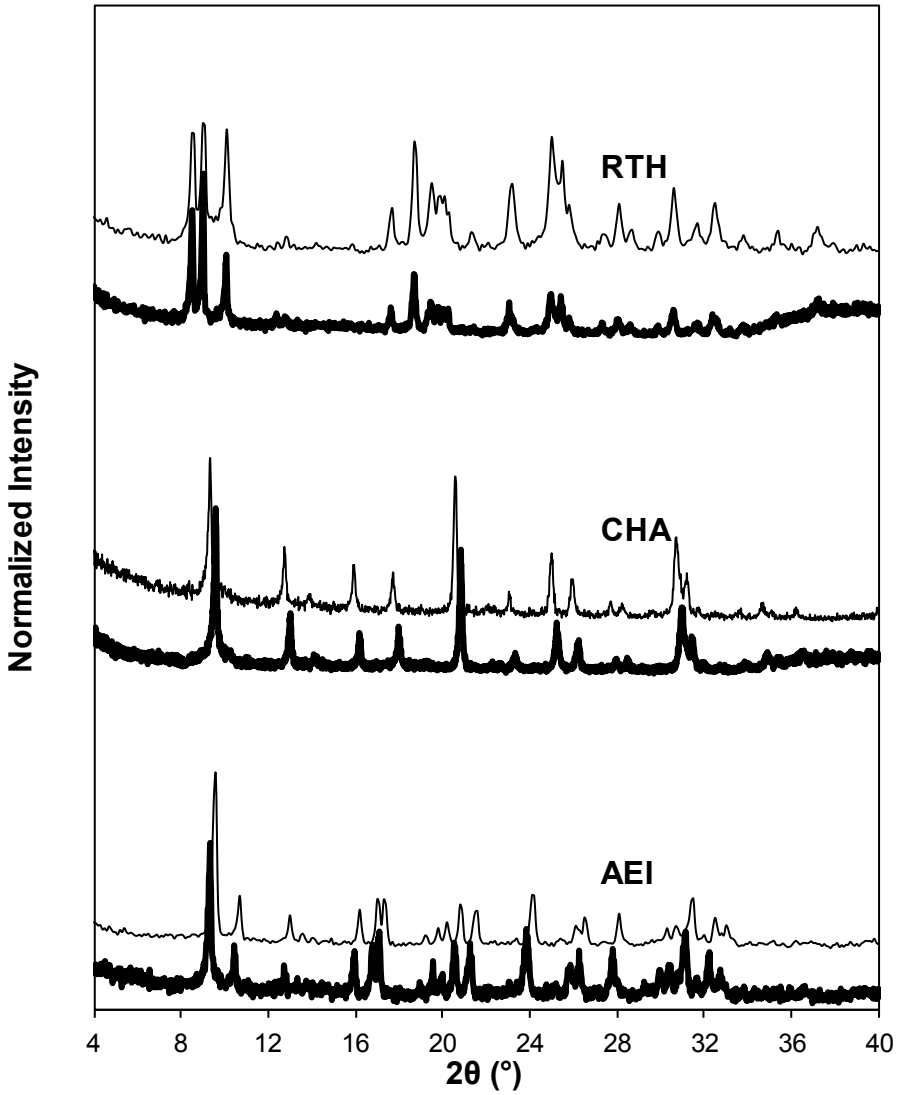

Figure S.1. XRD patterns of H-form (dark) and Cu-form (light) AEI, CHA, and RTH zeolites. Diffraction patterns are normalized so that the maximum peak intensity in each pattern is unity.

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

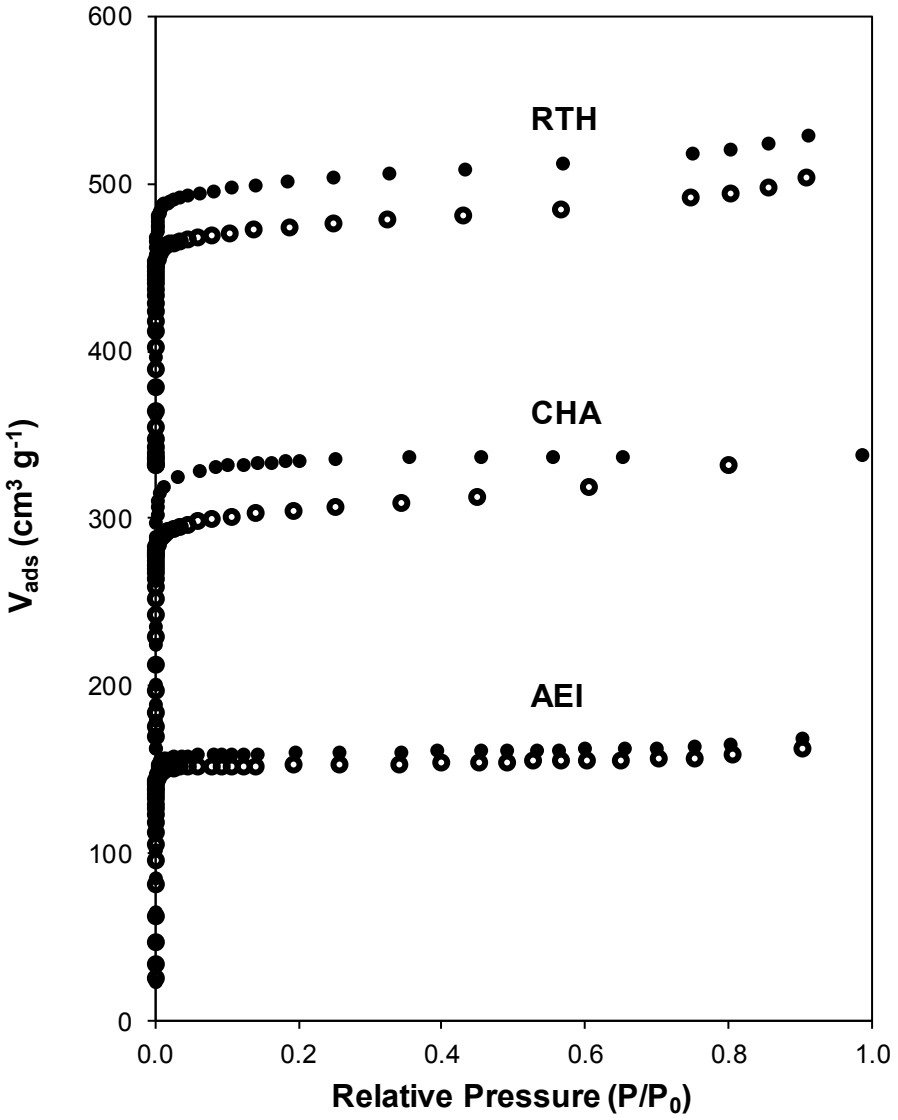

Figure S.2. Ar adsorption isotherms (87 K) on H-form (filled) and Cu-form (open) RTH, CHA and AEI zeolites. Adsorption isotherms are vertically offset (CHA: 160 cm^3 g^{-1}, RTH: 320 cm^3 g^{-1}) for clarity.

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

^{27}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 (Al_f) and extra-framework (Al_{ex}) Al species. NMR lines centered at 60 ppm were present for tetrahedral Al for RTH, and a small shoulder for penta-coordinated 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 Al_f species, although we recognize difficulties in quantifying Al_f content from NMR spectra, because some species can reversibly change between tetrahedral and octahedral coordination depending on the conditions of the measurement[3–5], and some extraframework alumina may also contain tetrahedrally-coordinated Al.[1,6] The Al NMR lines centered at 0 ppm for octahedral Al were taken to reflect Al_{ex} species. Spectra of H- and Cu- form zeolites show Al incorporated predominantly into tetrahedral framework positions, with Al_f/Al_{tot} values given in Table 2 of the main text.

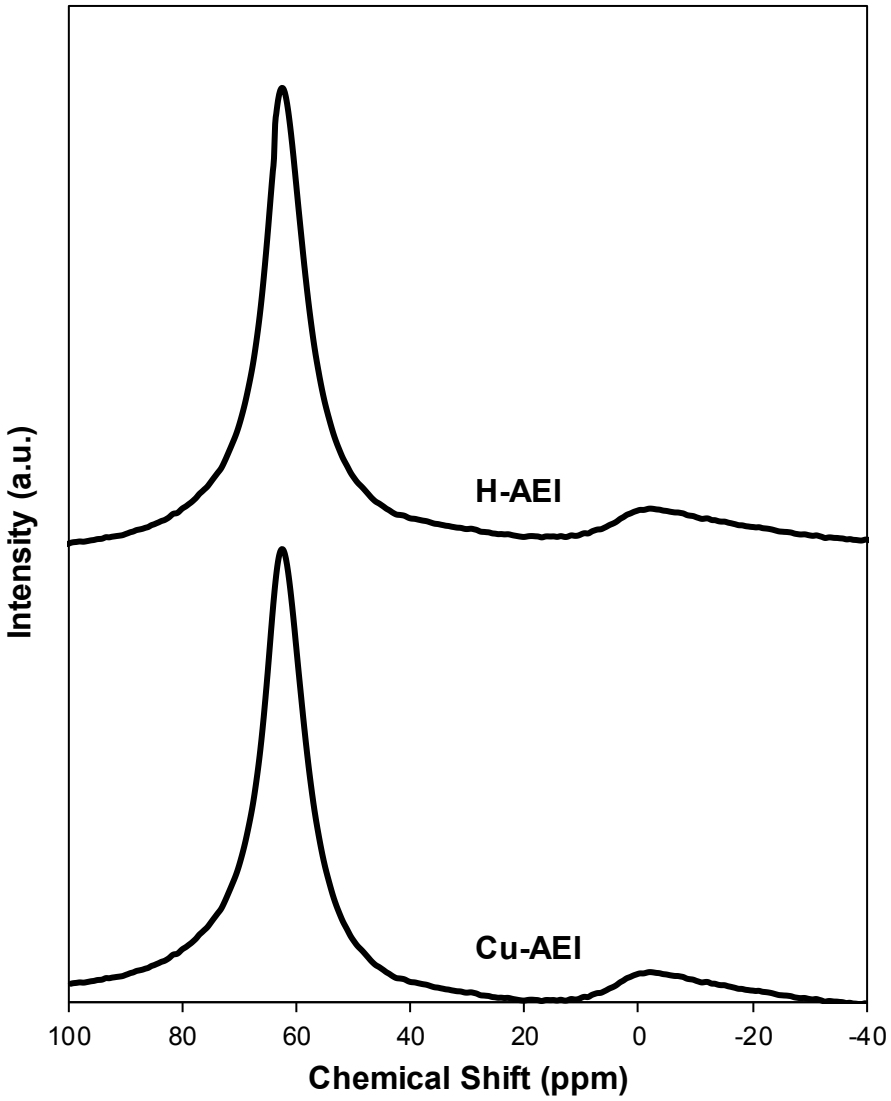

Figure S.3.1. ^{27}Al MAS NMR spectra of H-AEI and Cu-AEI.

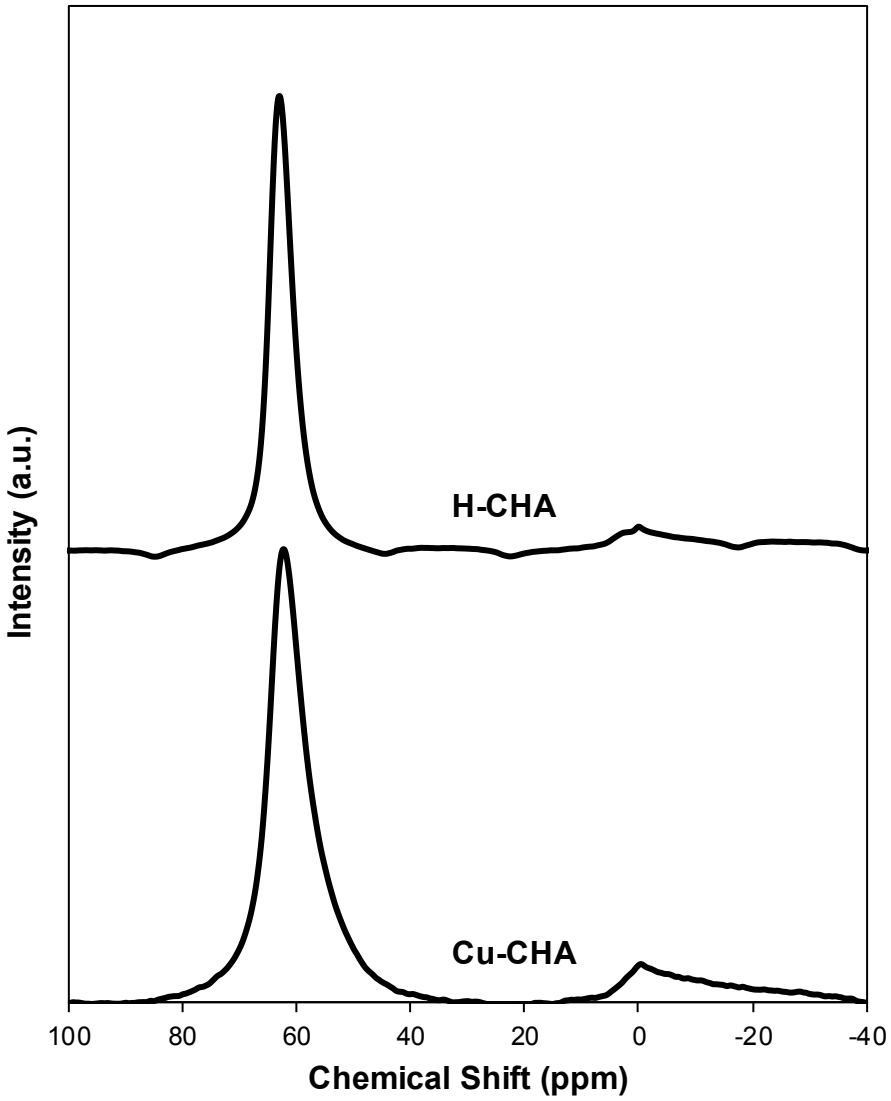

Figure S.3.2. ^{27}Al MAS NMR spectra of H-CHA and Cu-CHA.

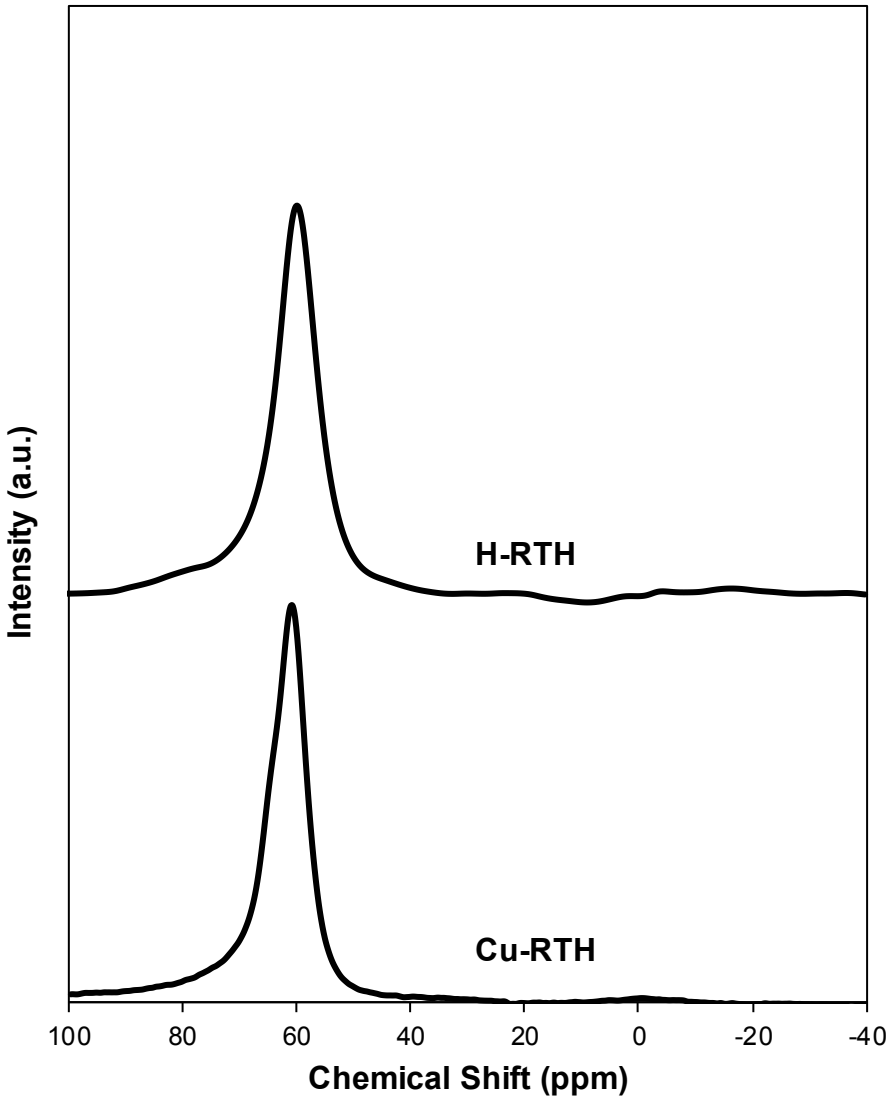

Figure S.3.3. ^{27}Al MAS NMR spectra of H-RTH and Cu-RTH.

Section S.4. IR Spectra of H-RTH Before and After NH_3 Exposure

In situ IR experiments were performed to monitor interactions of H^+ sites in H-RTH (Si/Al = 15) with NH_3. 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.[7] The sample was heated to 723 K and held for 2 h under 50 mL min^{-1} of 10% O_2 (99.5%, Indiana Oxygen) and balance N_2 (99.999% UHP, Indiana Oxygen), and then cooled to 433 K under flow (10% O_2 and balance N_2) 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_3 (350 ppm, 3 h, 433 K), to give the spectra (light traces) in Figure S.4. After NH_3 saturation, Brønsted OH bands disappeared completely, and new IR bands for NH_4^+ bending vibrations at 1425 cm^{-1} appeared concomitantly. These data indicate that all H^+ sites in H-RTH were titrated by NH_3, and that the H^+/Al_f value of 0.61 measured in NH_3 TPD experiments does not reflect a fraction of H^+ sites that were inaccessible to NH_3.

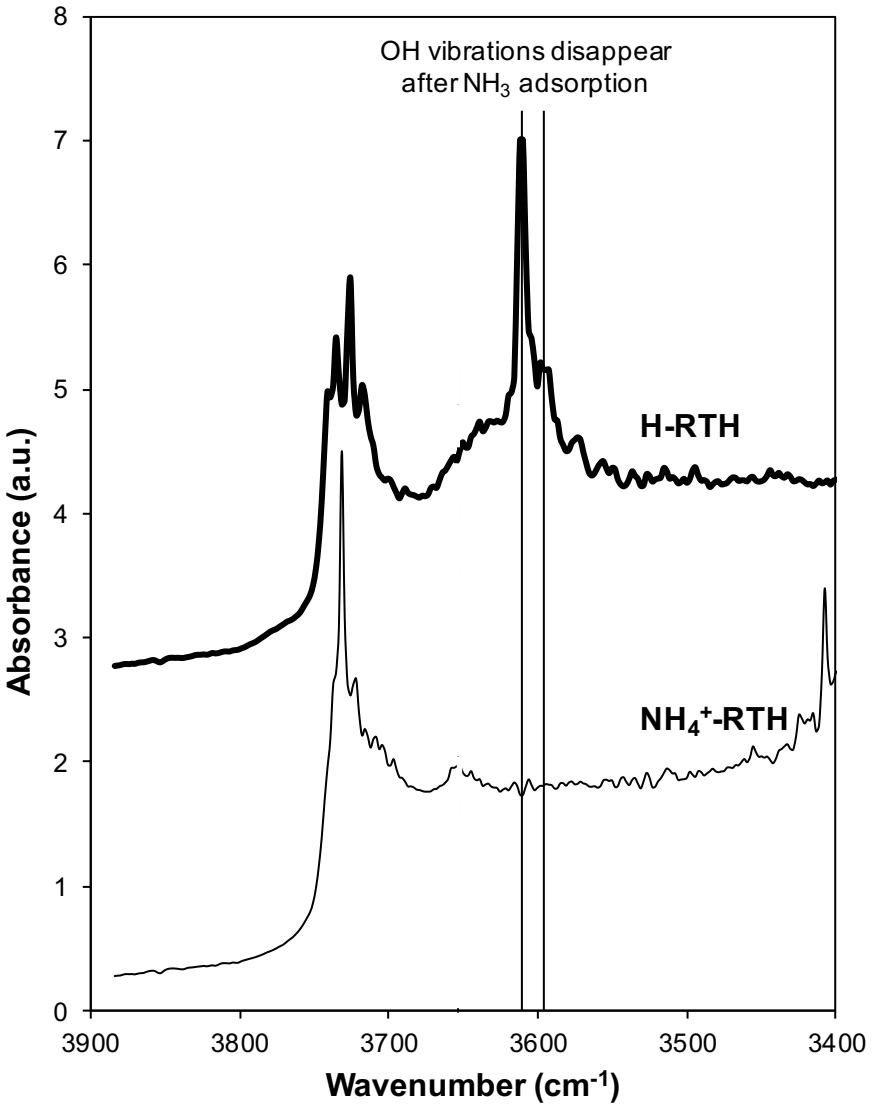

Figure S.4.1. IR spectra (OH stretching region: 3400-3900 cm^{-1}) of H-RTH at 433 K before (dark) and after (light) NH_3 saturation.

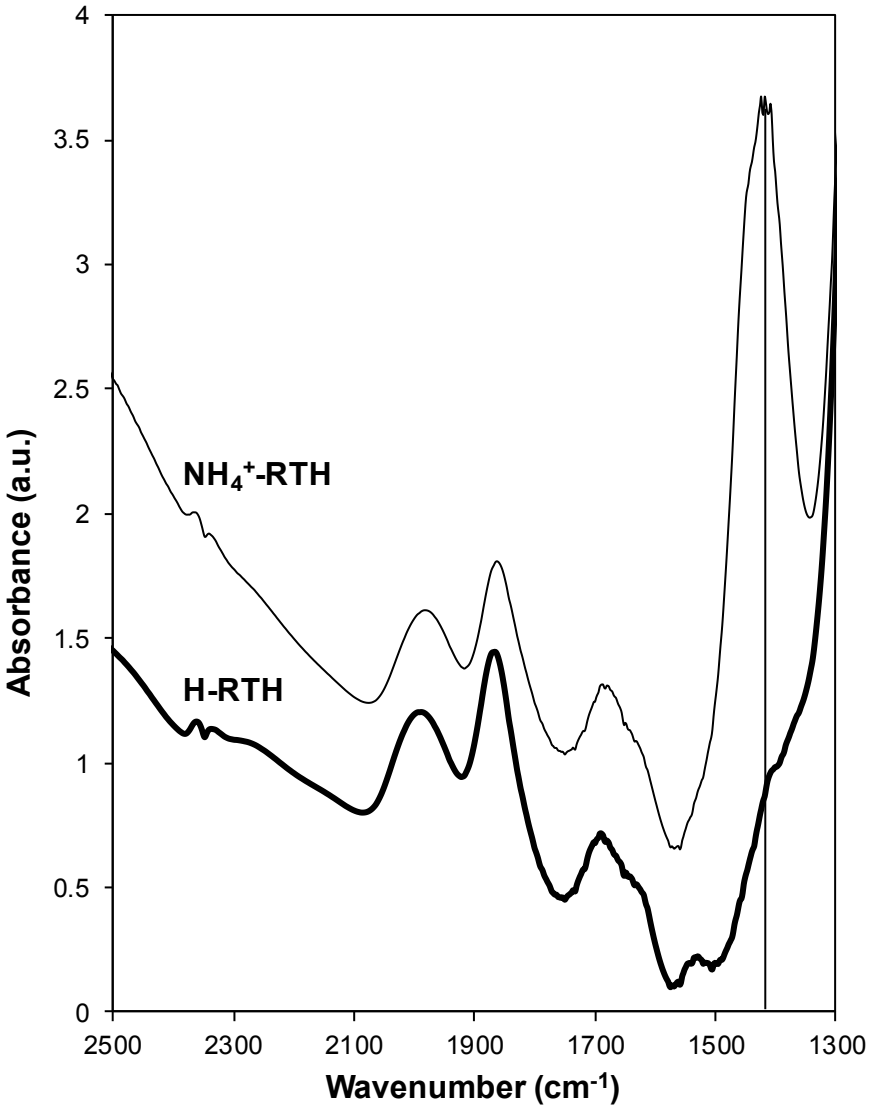

Figure S.4.2. IR spectra (N-H bending region: 1300-2500 cm^{-1}) of H-RTH at 433 K before (dark) and after (light) NH_3 saturation.

Section S.5. NH_3 TPD on Cu-zeolites

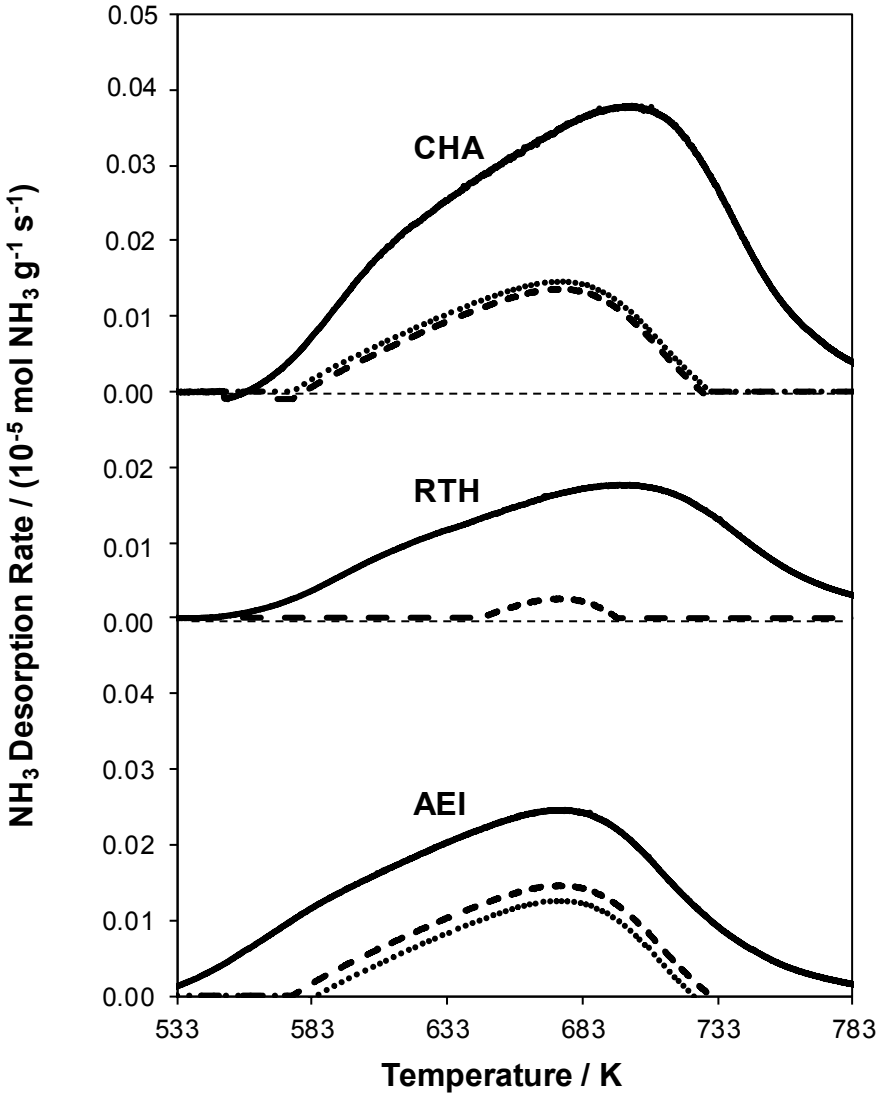

Figure S.5. NH_3 desorption rates as a function of temperature on fresh Cu-form after SCR (solid), aged Cu-form before SCR (dashed) and aged Cu-form after SCR (dotted) on CHA, RTH, and AEI zeolites.

Section S.6. References

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