Supporting Information

On the formation of cyclotriazane (N_3H_3) from ammonia in contact with a silver-exchanged A zeolite: a reliable synthesis pathway?

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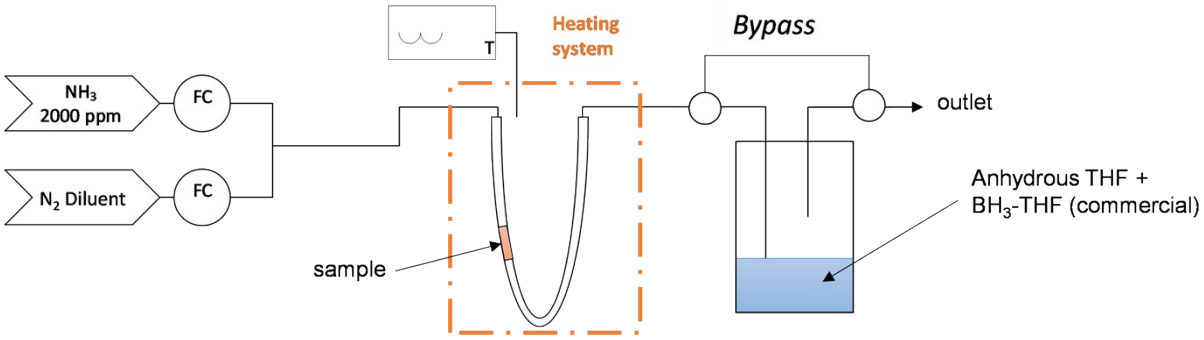

Figure S1. Experimental setup for trapping nitrogen species after treatment of samples with ammonia.

Zeolite characterization

Table S1. Elemental composition of the silver-exchanged zeolite determined by X-ray fluorescence.

Element	Al	Si	Ag	Na
% wt	12.8	13.5	49.6	<0.1
Concentration (mol/g)	4.75E-03	4.81E-03	4.6E-03	-

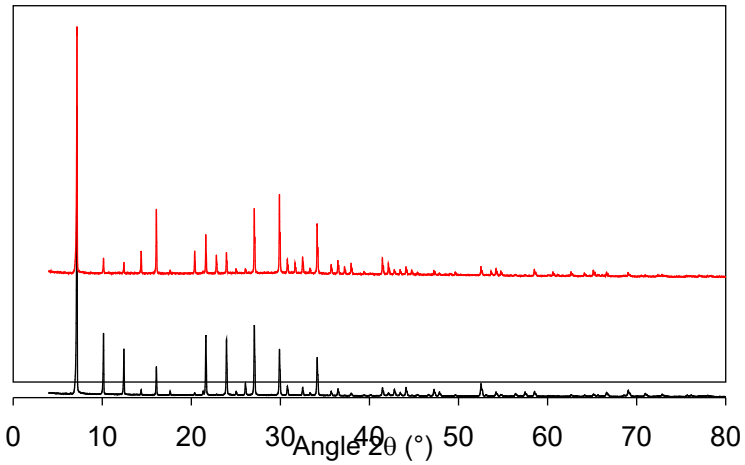

Figure S2. Diffractograms of commercial zeolite NaA (black) and Ag-LTA (red) after exchange and drying.

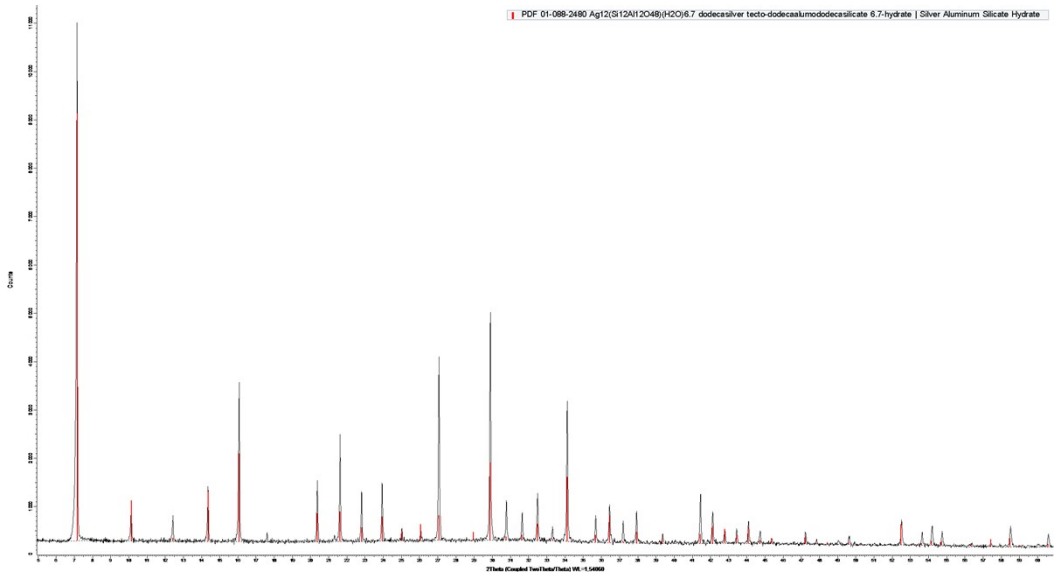

Figure S3. Diffractogram of Ag-LTA after ion exchange (black); diffraction peaks of $Ag_{12}Si_{12}Al_{12}O_{48}(H_2O)_{6.7}$ (red) [phase identified using EVA crystallographic software integrated with 2021 Powder Diffraction File (PDF) database].

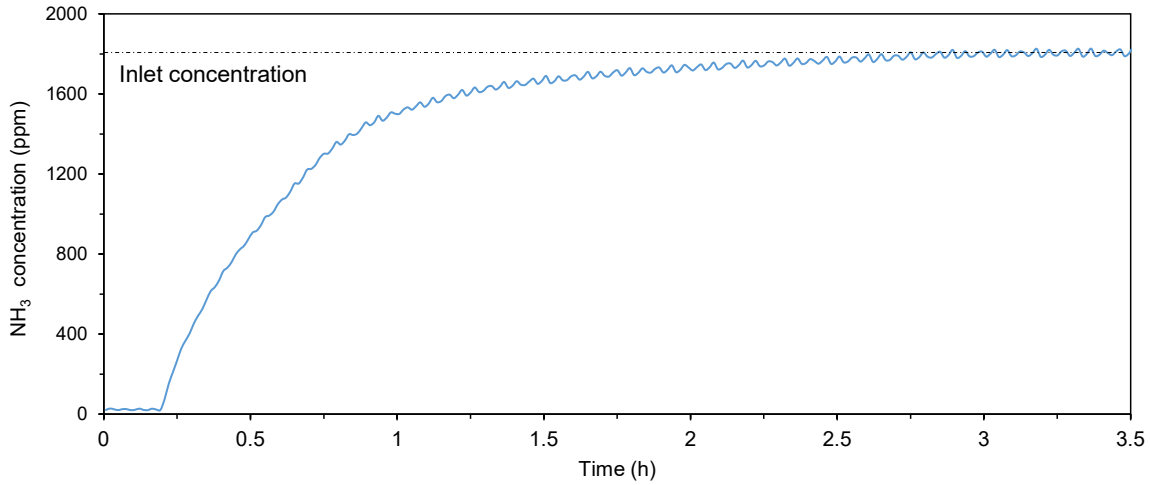

Figure S4. Breakthrough curve of ammonia on Ag-LTA monitored by FT-IR.

^{11}B and ^{14}N NMR spectra of the trapping solution

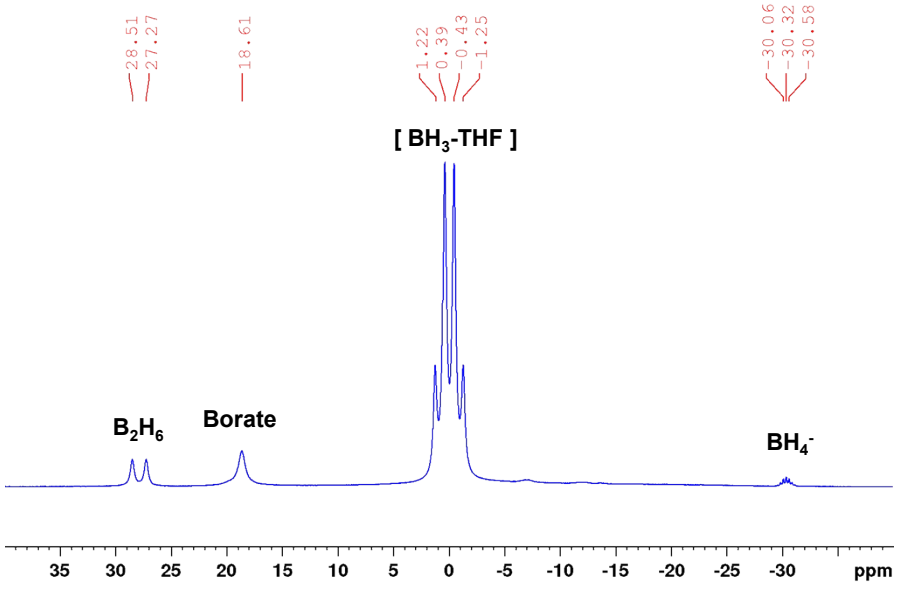

Figure S5. ^{11}B spectrum of the trapping solution before the start of the experiment.

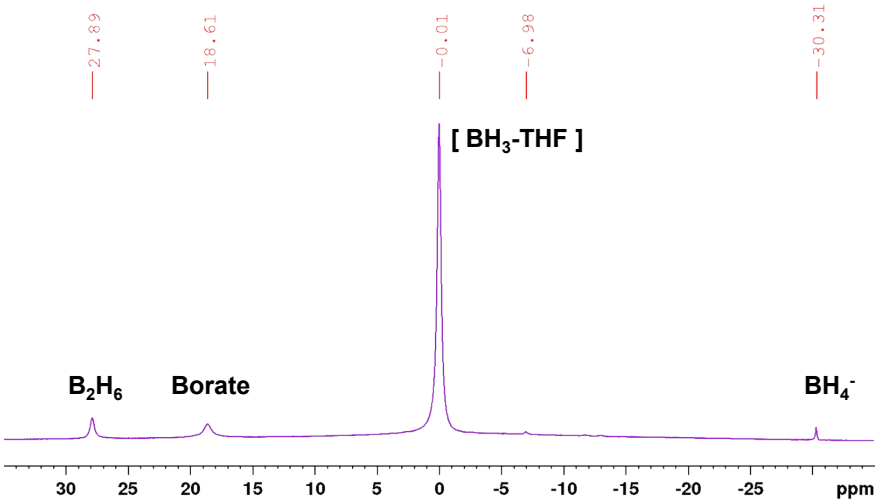

Figure S6. ^{1}H-decoupled ^{11}B spectrum of the trapping solution before the start of the experiment.

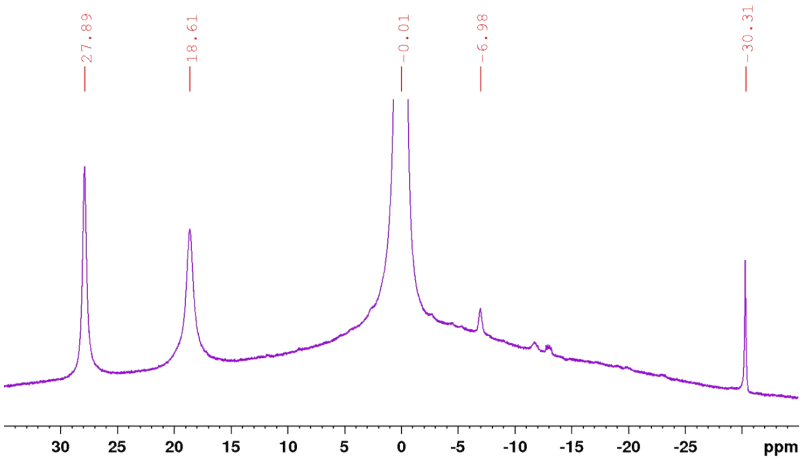

Figure S7. ^{1}H-decoupled ^{11}B spectrum of the trapping solution (zoom of Figure S6).

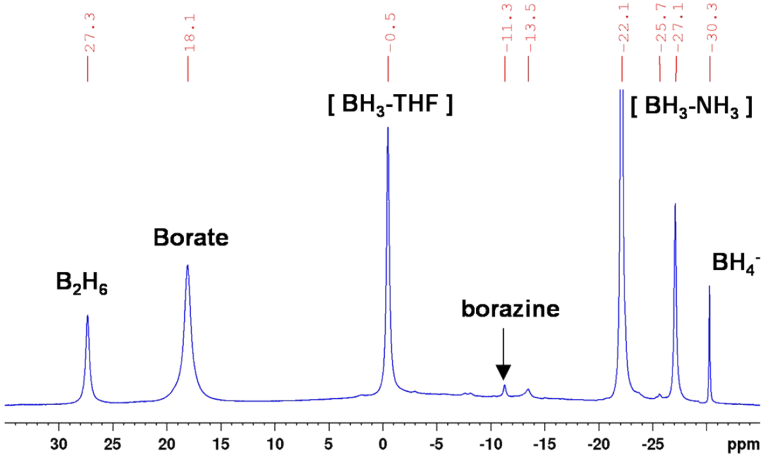

Figure S8. ^{1}H-decoupled ^{11}B spectrum of the trapping solution after adsorption/desorption of ammonia on Ag-LTA .

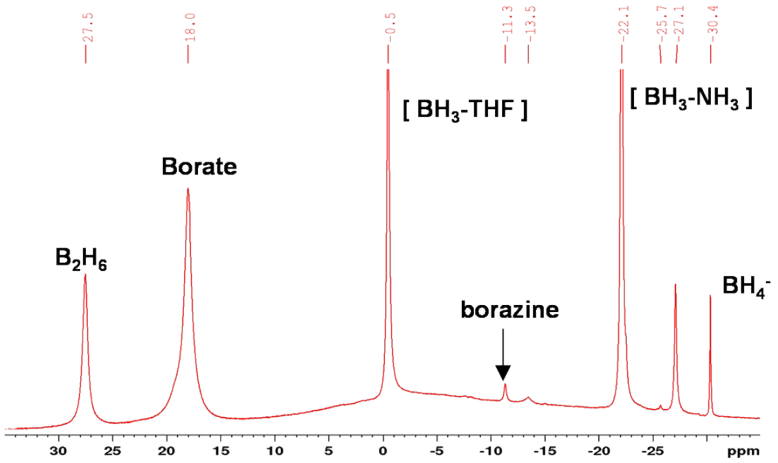

Figure S9. [1]H-decoupled [11]B spectrum of the trapping solution after a blank test (flow of ammonia with no sample in the reactor).

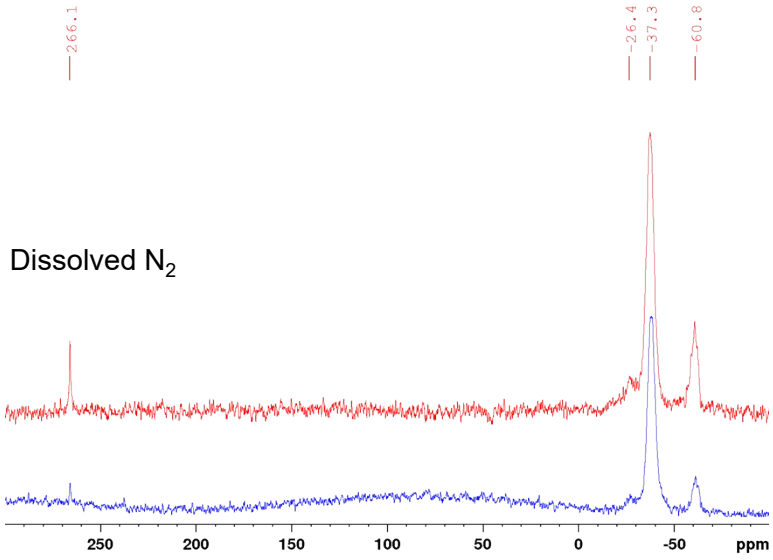

Figure S10. [14]N NMR spectra of the trapping solution after adsorption/desorption of ammonia on Ag-LTA (blue) and after a blank test (red).

HR mass spectroscopy

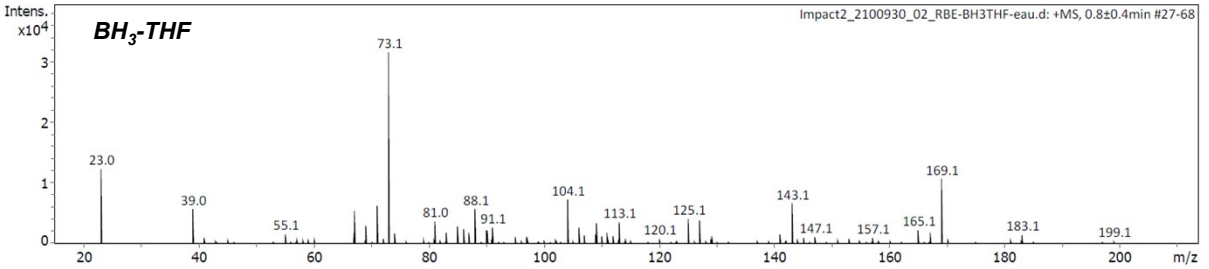

Figure S11. HR ESI mass spectrum of the BH_3 solution in THF.

Operando FT-IR results

The DRIFT spectra of the adsorbed species Na-LTA upon 2,000 ppm of ammonia adsorption are shown as a function of time (Figure S12) and converted into a kinetic plot (Figure S13). Ammonia adsorbs quickly onto the surface until it reaches a pseudo-plateau from 1.5 h under flow, and then the amount of adsorbed ammonia increases slightly until it becomes stable after 16 h under flow. The DRIFT spectra of thermodesorption of NH_3 on Na-LTA are compiled in Figure S14. It should be noted that a large proportion of the initial ammonia has desorbed after treatment at 350°C. Desorption of NH_3 on Na-LTA is mostly reversible.

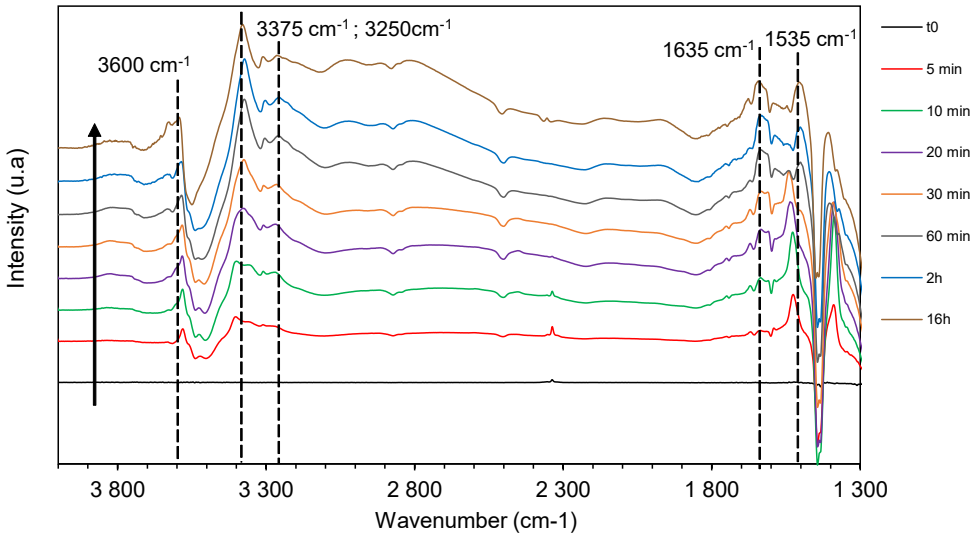

Figure S12. DRIFT spectra of Na-LTA at different times during NH_3 adsorption.

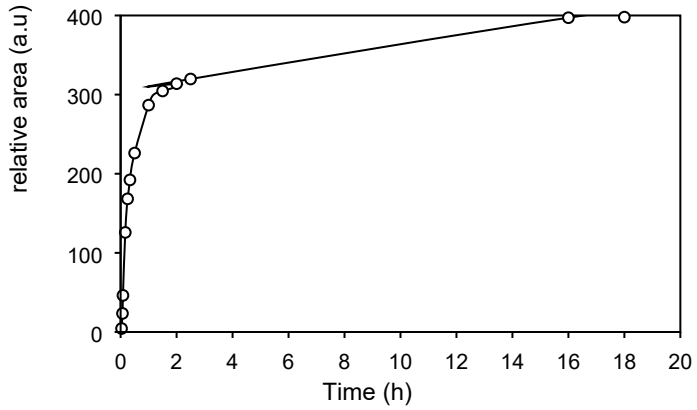

Figure S13. Kinetics of NH_3 adsorption on Na-LTA (area of the signal between 3400 and 1800 cm^{-1} on the IR spectra).

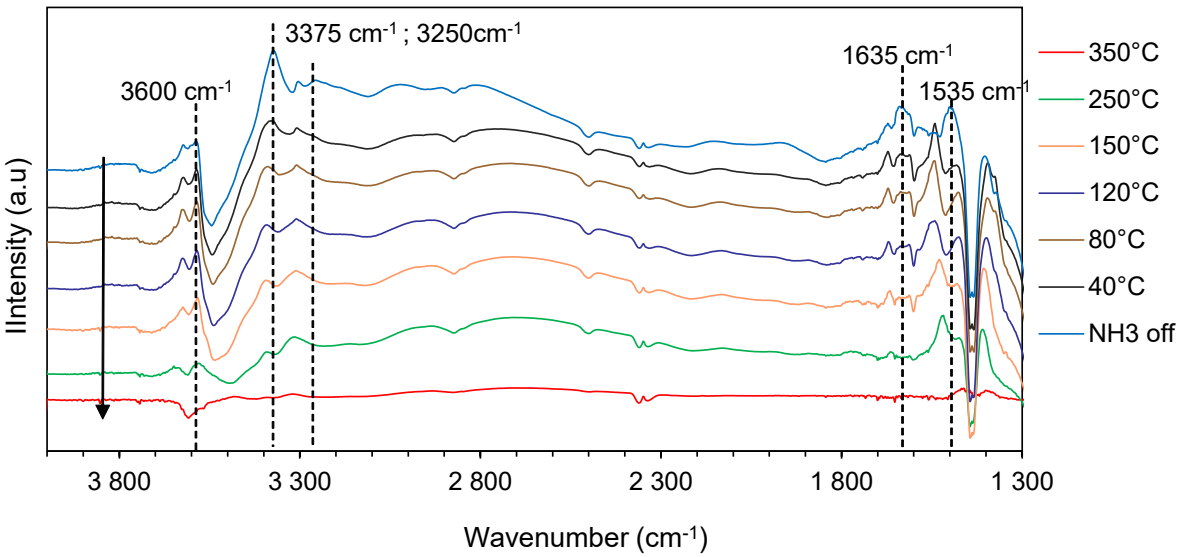

Figure S14. DRIFT spectra of Na-LTA as a function of NH_3 desorption temperature.

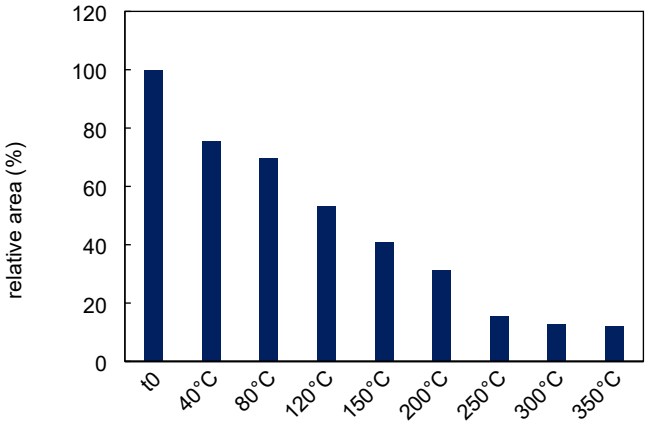

Figure S15. Relative area of the signal between 3400 and 1800 cm^{-1} as a function of desorption temperature of ammonia on Na-LTA.

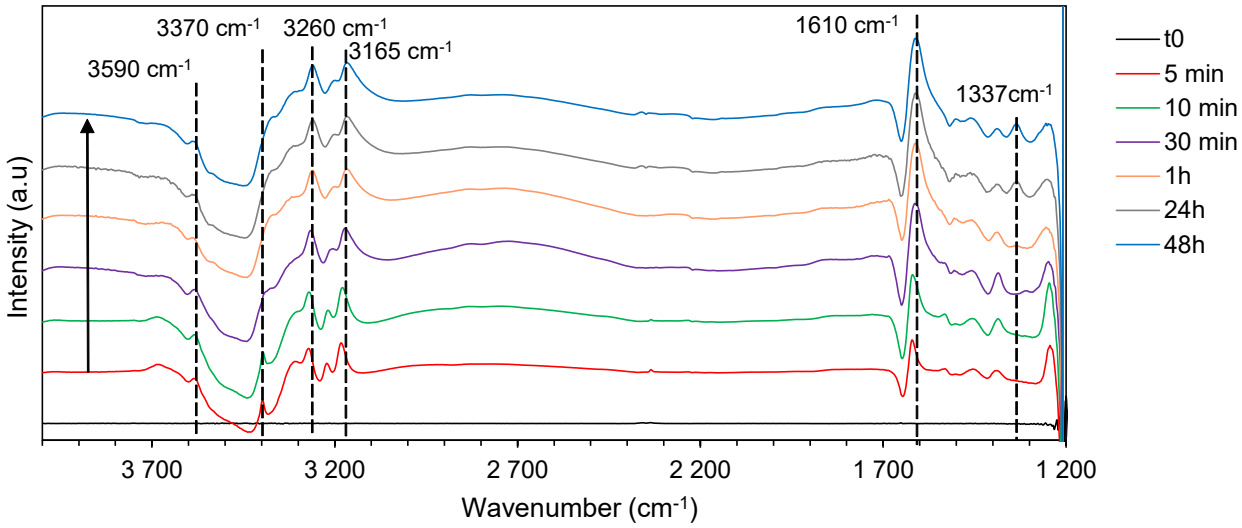

Figure S16. DRIFT spectra of Ag-LTA at different times during NH_3 adsorption.

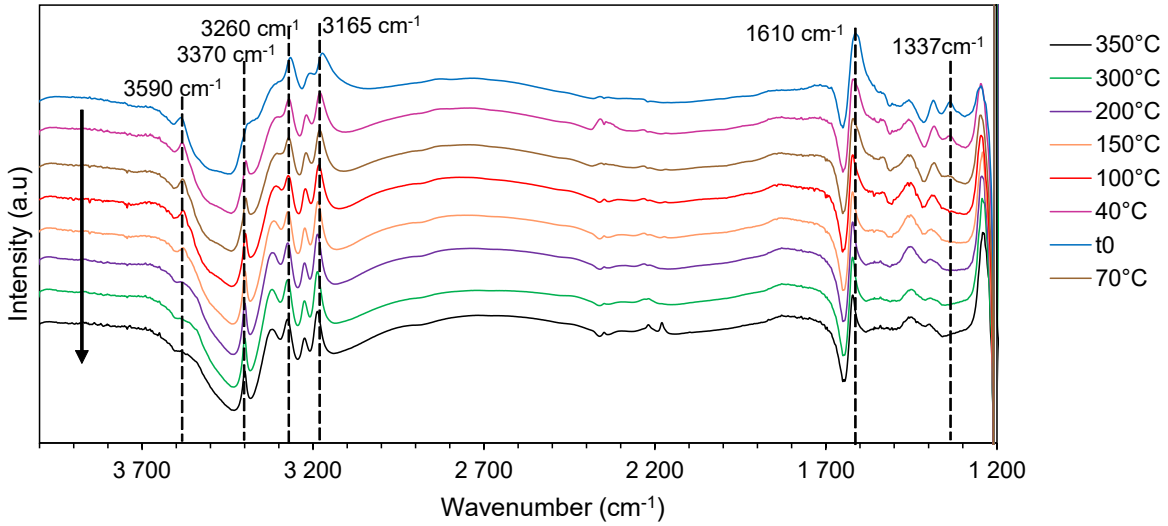

Figure S17. DRIFT spectra of Ag-LTA as a function of NH_3 desorption temperature.

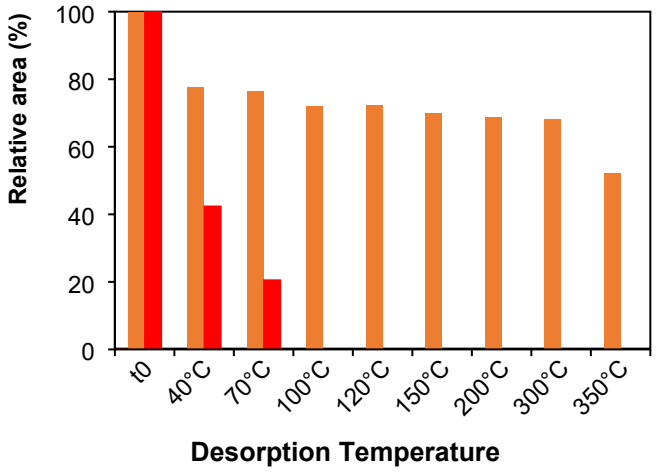

Figure S18. Relative area of signal at 3300 cm^{-1} (blue) and signal at 1337 cm^{-1} (red) as a function of desorption temperature on Ag-LTA.

XANES spectra

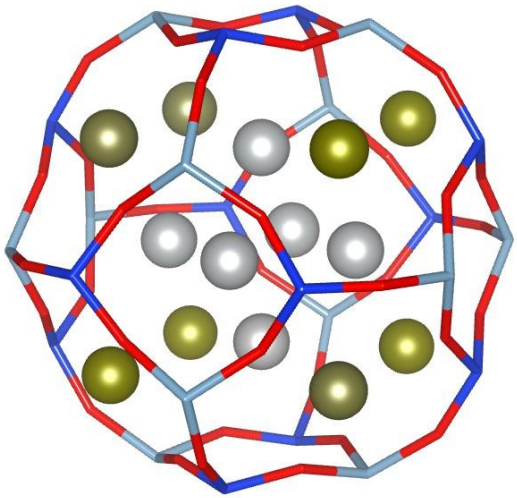

Figure S19. Ag_{14} cluster in sodalite cage for the simulated XANES spectra. The small molecules were added on the external (golden) atoms of silver.

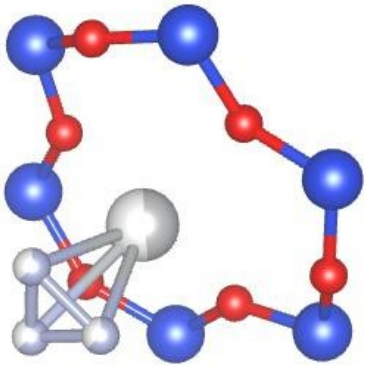

Figure S20. Cyclotriazane in the LTA alpha cage complexed with 6-ring centered Ag proposed by Kim and Seff.

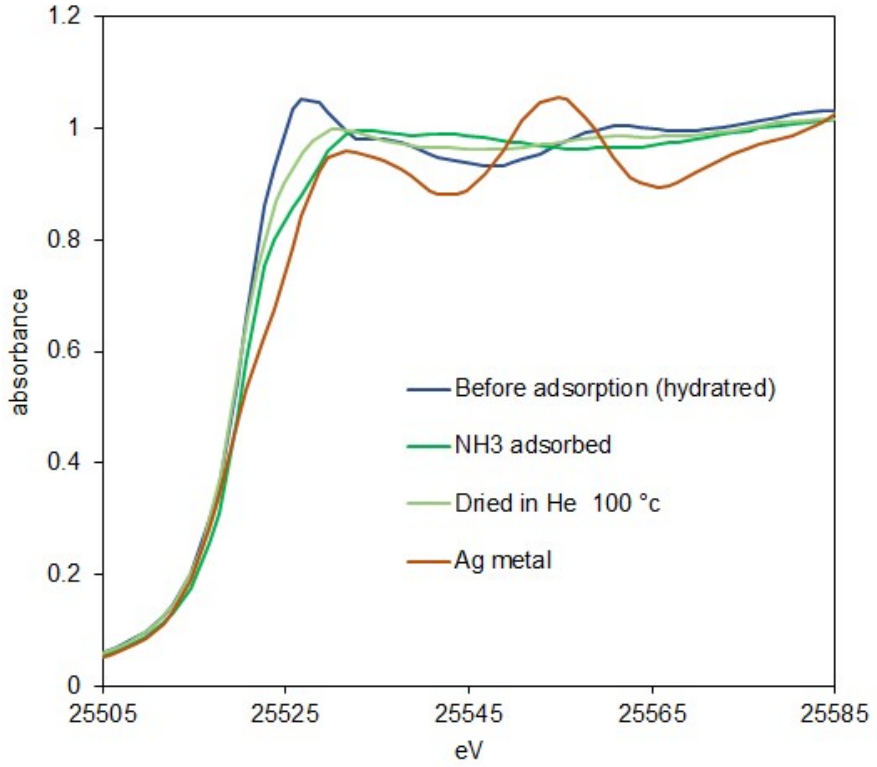

Figure S21. Operando XAS spectra of Ag-LTA under He hydrated, dried and afterNH_3 adsorption.

Gibbs standard free enthalpy of ammonia auto-oxidation

$$21\ NH_{3\,(g)} \rightarrow 3\ N_3H_{5\,(g)} + 4\ N_3H_{3\,(g)} + 18\ H_{2\,(g)}$$

Figure S 21. Equations for the formation of triazane and cyclotriazane by auto-oxidation of ammonia by sodalite unit with Ag as catalyst

Table S2. Thermodynamic data and standard Gibbs free enthalpy of the ammonia auto-oxidation reaction

	$\Delta_f H°$(kJ/mol)	$\Delta_f S°$(J/(mol.K))	$\Delta_r G°$(kJ/mol)
NH_3	-45,90 [a]	192,66 [a]	-
H_2	0,00	130,57 [a]	-
N_3H_5	294,09 [b]	249,39 [b]	-
N_3H_3	486,14 [b]	245,12 [b]	-
$T_{studied}$ 298 K	-	-	3780
$T_{studied}$ 373 K			3778

[a] collected from the *Perry's chemical engineer's Handbook* Edition 1999 at 298 K

[b] data from *Mager et al.* (1988)