Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Revisiting NH_3 — Catalyst Interactions in Cu-SSZ-13 SCR Catalysts: An In-situ Spectro-Kinetics Study

Daniyal Kiani *, Yuanzhou Xi, Nathan Ottinger, Z. Gerald Liu

Cummins Emission Solutions, 1801 US Hwy 51/138, Stoughton, WI, 53589, USA

*corresponding author: daniyal.kiani@cummins.com,; ORCID: 0000-0002-9748-3007

Electronic Supplemental Information

Table S 1. *IR band assignments from the literature for NH_3 adsorbed on relevant catalytic systems.*

Catalyst	IR band (cm^{-1})	Assignment	Ref
Cu-SAPO-34	1460, 3283, 3333	NH_4^+	[1]
Cu-SAPO-34	1617, 3182, 3383	NH_3	
Cu-SSZ-13	1454, 3262	NH_4^+	[2]
Cu-SSZ-13	1620, 3182,3352	NH_3	
Cu-SSZ-13	3728	Si-OH	
Cu-SSZ-13	3610	Si-OH-Al	
Cu-SSZ-13	1449, 1493, 3273, 3355	NH_4^+	[3]
Cu-SSZ-13	1270, 1617, 3181	NH_3	
Cu-SSZ-13	3682	Si-OH	
Cu-SSZ-13	3600	Si-OH-Al	
Cu-SSZ-13	1449, 1493, 3273, 3355	NH_4^+	[4]
Cu-SSZ-13	δs (1150-1270), δas (1617-1624), 3181	NH_3	
Cu-SSZ-13	~3730-3750	Si-OH	
Cu-SSZ-13	~3600	Si-OH-Al	
Cu-SSZ-13	3650	-Cu-OH	
Cu-SSZ-13	3520, 3440, 1550-1510	$-NH_2$	
Cu-SSZ-13	1700, 2770	NH_4^+. $n$$NH_3$	
	3375	Free NH stretching in NH_3	[5]
	3090-3155, 2875-2865	Evans windows; overtones of ~1450 and combination of ~1450, ~1650	
	3383	-stretching of free NH in $N_2H_7^+$	
	1700	Bending of h bonded N-H in $N_2H_7^+$	
SiO2	3526	N-H stretching in Si-O-NH_2	[6]

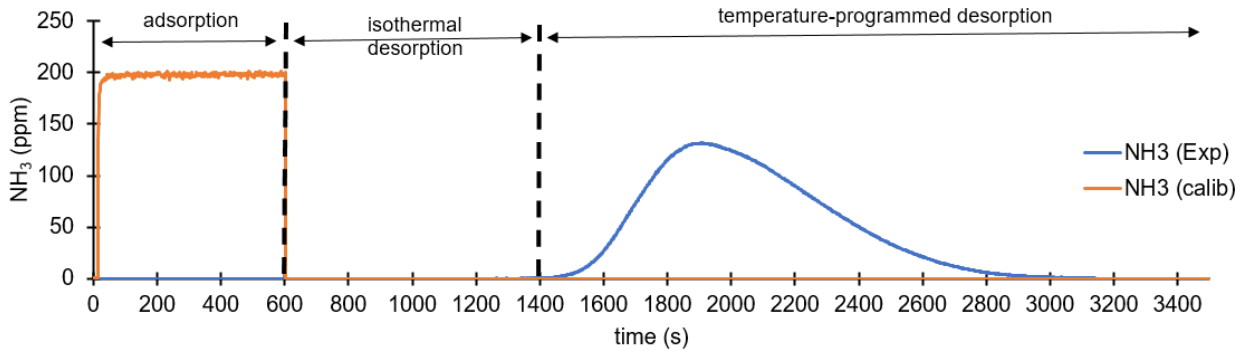


Figure S 1. *Representative NH_3 traces on pilot-reactor rig during 600s long adsorption step at 120°C, followed by 900s isothermal desorption step at 120°C, and finally by a TPD step from 120°C to 650°C at 10°C/min ramp rate. As described in eq (7) in the main text, NH_3 adsorbed/desorbed in each step is quantified by calculating the difference in areas under the blue (exp) and the orange (calibration) traces.*

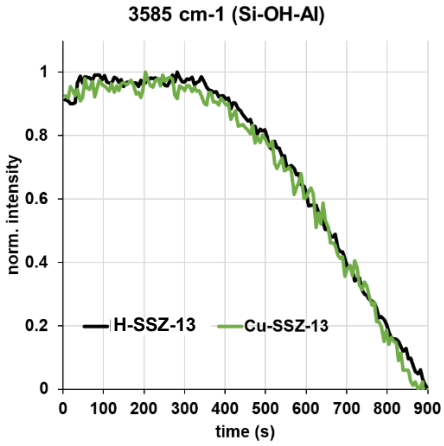


Figure S 2*. normalized band intensities for O-H stretching of the BAS in SSZ-13 catalysts, corroborating the lack of BAS consumption in the first ~300s of NH_3 adsorption.*

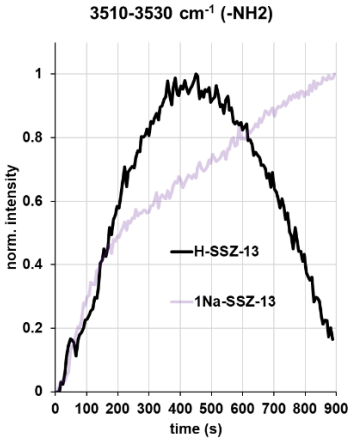


Figure S 3. *normalized band intensities for the NH_2 transient species observed in SSZ-13-based catalysts during NH3 adsorption. Black lines correspond to H-SSZ-13, while purple lines to 1% Na-impregnated sample 1Na-SSZ-13. In both cases, catalyst was cleaned and dehydrated at 500°C for 1 hr in 10% O_2/Ar mixture before cooling down to 120°C, and conducting NH_3 adsorption according to protocol outlines in* ***Figure 4 main section.***

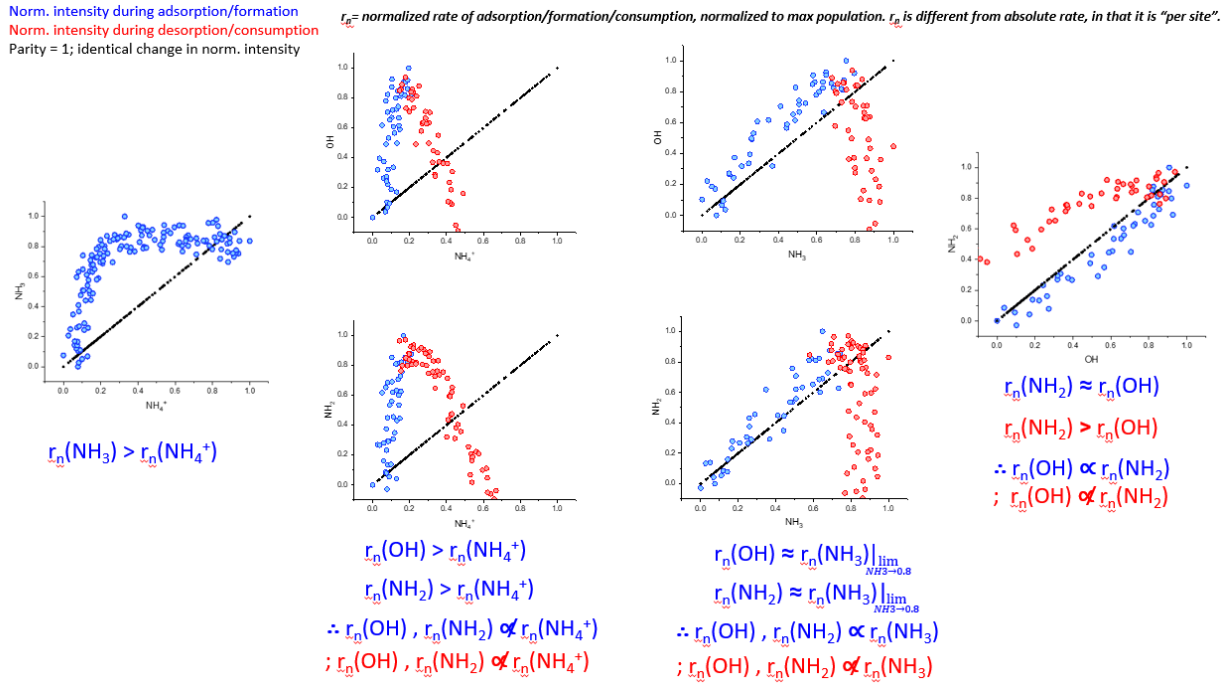


Figure S 4. *Parity plot analysis of normalized intensities of various IR bands in Cu-SSZ-13 during NH_3 adsorption. For the two transient species (NH_2, OH), the blue dots correspond to the time frame during which intensity of the respective bands was increasing, while red dots represent the time range when intensities decreased. The black dotted line signifies parity case i.e 1:1 evolution of the bands on x- and y-axes.*

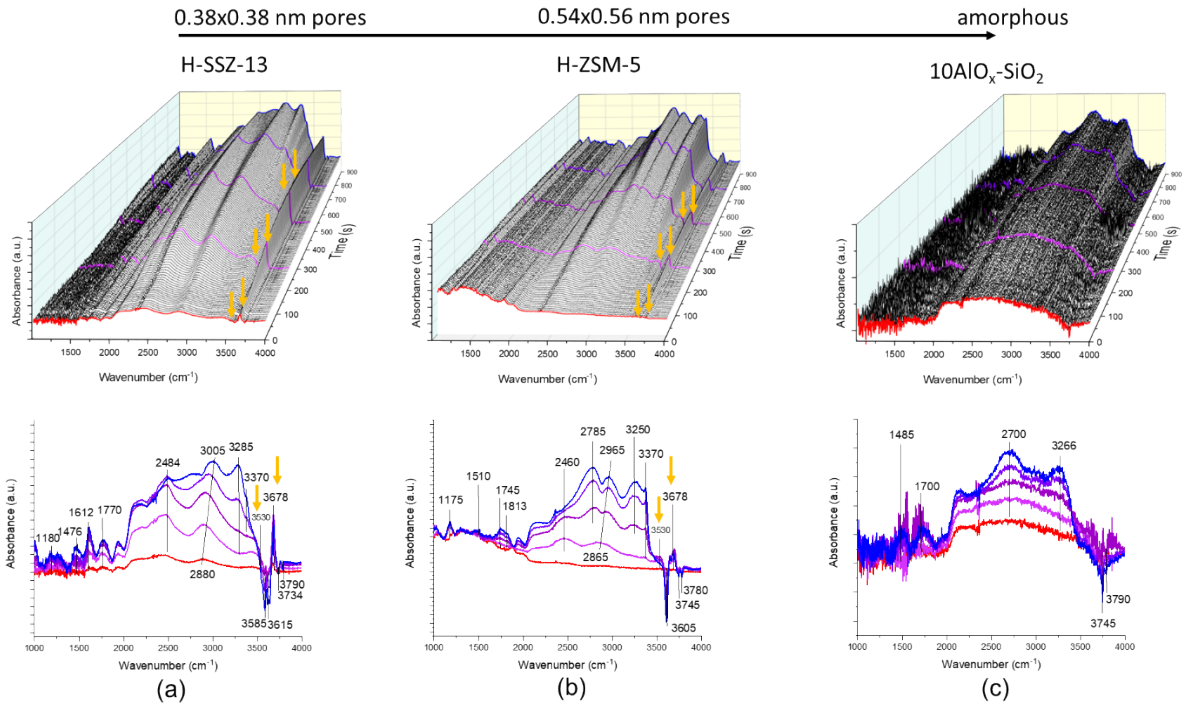


Figure S 5. *temporally resolved in-situ DRIFTS during NH_3 adsorption on (a) H-SSZ-13 (SAR 15), (b) H-ZSM-5 (SAR 15), (c) 10%AlO_x-SiO_2 samples, indicating that NH_2 and O-H bands (marked with yellow arrows) from NH_3 dissociation only evolve in the two zeolitic samples.*

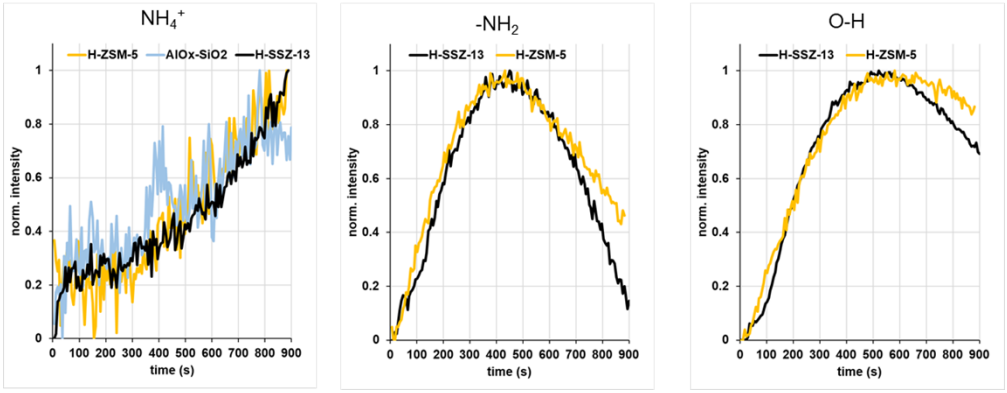
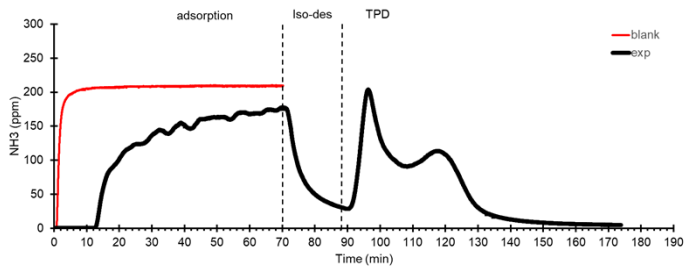


Figure S 6. *Evolution of normalized IR band intensities of BAS-bound NH_4^+, NH_2 and O-H intermediates in H-SSZ-13, H-ZSM-5, and amorphous 10% AlO_x-SiO_2. All samples exhibit NH_4^+ formation, but only the two zeolites exhibit NH_2 and O-H bands during NH_3 adsorption.*



	mmol/L
adsorption	194
isothermal desorption	41
TPD	143
SUM (iso-des+TPD)	184
diff	10

Figure S 7. *Proof-of-concept NH_3 TPD on H-SSZ-13 powder diluted in cordierite (25% zeolite, 75% cordierite) to mimic wash-coated monolith type Cu-SSZ-13 pilot core tested in the study. Our results indicate ~10mmol$_{NH3}$ L$^{-1}_{cat}$ was consumed over H-SSZ-13, where the total adsorbed NH_3 capacity was ~193 mmol$_{NH3}$ L$^{-1}_{cat}$.. It suffices to note that to first approximation, the NH_3 consumed over Cu-SSZ-13 is approximately twice more than over H-SSZ-13, corroborating our DRIFTS results that NH_3 dissociates faster on Cu-SSZ-13 than H-SSZ-13. The NH_3 TPD was carried out in a micro reactor employing quartz 0.25" ID quartz tube. Experimental conditions were kept reasonably close to the pilot reactor study: ~40,000 hr^{-1} SV, ~200ppm NH_3, 10^{o}C/min ramp rate during TPD. Adsorption was conducted at 120^{o}C, followed by isothermal desorption at 120^{o}C, and finally by TPD under N_2 flow from 120^{o}C to 600^{o}C.*

References

(1) Wang, D.; Zhang, L.; Kamasamudram, K.; Epling, W. S. In Situ-DRIFTS Study of Selective Catalytic Reduction of NOx by NH3 over Cu-Exchanged SAPO-34. *ACS Catal.* **2013**, *3* (5), 871–881. https://doi.org/10.1021/cs300843k.

(2) Zhu, H.; Kwak, J. H.; Peden, C. H. F. F.; Szanyi, J. In Situ DRIFTS-MS Studies on the Oxidation of Adsorbed NH3 by NOx over a Cu-SSZ-13 Zeolite. *Catal. Today* **2013**, *205* (x), 16–23. https://doi.org/https://doi.org/10.1016/j.cattod.2012.08.043.

(3) Ma, L.; Cheng, Y.; Cavataio, G.; McCabe, R. W.; Fu, L.; Li, J. In Situ DRIFTS and Temperature-Programmed Technology Study on NH3-SCR of NOx over Cu-SSZ-13 and Cu-SAPO-34 Catalysts. *Appl. Catal. B Environ.* **2014**, *156–157*, 428–437. https://doi.org/10.1016/j.apcatb.2014.03.048.

(4) Giordanino, F.; Borfecchia, E.; Lomachenko, K. A.; Lazzarini, A.; Agostini, G.; Gallo, E.; Soldatov, A. V; Beato, P.; Bordiga, S.; Lamberti, C. Interaction of NH3 with Cu-SSZ-13 Catalyst: A Complementary FTIR, XANES, and XES Study. *J. Phys. Chem. Lett.* **2014**, *5* (9), 1552–1559. https://doi.org/10.1021/jz500241m.

(5) Zecchina, A.; Marchese, L.; Bordiga, S.; Pazè, C.; Gianotti, E. Vibrational Spectroscopy of NH4+ Ions in Zeolitic Materials: An IR Study. *J. Phys. Chem. B* **1997**, *101* (48), 10128–10135. https://doi.org/10.1021/jp9717554.

(6) Peri, J. B. Infrared Study of OH and NH2 Groups on the Surface of a Dry Silica Aerogel. *J. Phys. Chem.* **1966**, *70* (9), 2937–2945. https://doi.org/10.1021/j100881a037.

(7) Greenaway, A. G.; Marberger, A.; Thetford, A.; Lezcano-González, I.; Agote-Arán, M.; Nachtegaal, M.; Ferri, D.; Kröcher, O.; Catlow, C. R. A.; Beale, A. M.

Detection of Key Transient Cu Intermediates in SSZ-13 during NH3-SCR DeNOx by Modulation Excitation IR Spectroscopy. *Chem. Sci.* **2020**, *11* (2), 447–455. https://doi.org/10.1039/c9sc04905c.