Supplementary Information (SI) for Catalysis Science & Technology.

Supplementary Information

Influence of H_2-ICE exhaust on the activity and stability of Cu-SSZ-13 deNO$_x$ catalysts

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Note S1: Experimental methods

Catalyst synthesis and aging:

An aqueous phase exchange of Cu-ions with NH_4-form SSZ-13 (Si/Al = 12) was performed to prepare Cu-SSZ-13 catalysts. To synthesize the zeolite support, NaOH (0.8 g, Sigma-Aldrich) was first dissolved in deionized water (38 g) to which N,N,N-trimethyl-1- adamantyl ammonium hydroxide (17 g, TMAda-OH, Sachem Inc., 25%) was added. $Al(OH)_3$ (1.6 g, Aldrich) containing around ~54% Al_2O_3 was then slowly added to the solution under constant stirring to ensure a homogenous mixture. Colloidal silica (40 g, AS-30, Sigma-Aldrich) was then added to the mixture which was left under constant stirring for 2 hours. The resulting mixture was sealed in a Teflon-lined stainless-steel autoclave which was kept at 165 °C for 4 days under constant stirring to carry out hydrothermal synthesis of Na-SSZ-13. The solid zeolite was separated from the rest of the suspension via centrifugation and washed 3 times with DI water prior to calcination under stagnant air at 650 °C for 5 hours. The Na-SSZ-13 formed this way was converted into NH_4-SSZ-13 by substituting Na^+-ions with NH_4^+-ions via three-time aqueous phase ion exchange with 0.1 M NH_4NO_3 (Sigma-Aldrich) solution at 80 °C for 2 hours. Finally, Cu-SSZ-13 was prepared by aqueous phase ion exchange of NH_4-SSZ-13 with 0.1 M $Cu(NO_3)_2$ (Sigma-Aldrich) solution at 80 °C under constant stirring for 4 hours. The solid sample was separated by centrifugation, followed by 3-times washing with DI water. The elemental composition of as-synthesized catalysts was determined as 2.18 wt% Cu, Cu/Al ~ 0.33, and Si/Al ~12 by inductively coupled plasma atomic emission spectroscopy (ICP-AES) performed at Galbraith Laboratories, Knoxville, Tennessee.

The fresh sample (FR) synthesized this way was hydrothermally aged at 650 °C for 50 hours under three different gaseous environments: (1) 6% H_2O in air balance, (2) 20% H_2O in air balance and (3) 20% H_2O + 1000 ppm H_2 in air balance. The resulting samples are referred to as HTA-1, HTA-2 and HTA-3, respectively.

SCR activity experiments:

A plug flow reactor consisting of a vertically mounted quartz tube housing ~20 mg of catalyst powder (sieved in 60-80 mesh particle size) mixed with 450 mg SiO_2 was utilized for Standard SCR activity testing. A tubular furnace (Applied Test Systems) controlled with PID controller (Omega model CN3251) was used to heat the catalyst where the temperature was controlled off a K-type thermocouple placed directly above the catalyst bed. Reactant gases were supplied from gas cylinders (Oxarc Inc., Spokane, Washington) via Brooks 5850E series mass flow controllers at appropriate flow rates to create a synthetic exhaust mixture at ~ 0.5 $Lmin^{-1}$ flowrate containing 350 ppm NO, 350 ppm NH_3, 10% O_2, and varying H_2O in N_2 balance (H_2O supplied through a heated Perma Pure MH^{TM}-series humidifier). Five difference H_2O concentrations were used: 0%, 3%, 6%, 10% and 20% to evaluate the impact of H_2O on SCR activity. Moreover, influence of H_2 was investigated by supplying 0, 200, 1000 and 4000 ppm H_2 into the reactor feed gas. Steady state SCR experiments were performed by heating the catalyst to 500 °C and cooling down to desired temperatures with sufficient hold time at each temperature to achieve steady state. NOx conversion was calculated based on the following equation:

$$NOx\ Conversion\ (\%) = \frac{(NO + NO_2)_{inlet} - (NO + NO_2)_{outlet}}{(NO + NO_2)_{inlet}}\ x\ 100$$

The SCR activity data was further analyzed utilizing a first order kinetic equation, $r = \frac{F}{W}(- \ln(1 - X))$, where F is NO_x flow rate (mol/s), W is catalyst amount (g) and X is fractional NO_x conversion. The Arrhenius equation, $k = \frac{r}{[NO]_0} = Ae^{-\frac{E_a}{RT}}$, was used to calculate apparent activation energy (E_a) and pre-exponential factor (A), where $[NO]_0$ is feed NO.

Hydrogen temperature programmed reduction (H_2-TPR):

H_2-TPR was performed on a Mcromeritrics Autochem 2920 instrument equipped with TCD and a downstream external MKS Cirrus 2 quadrupole mass. Around ~100 mg of sample was loaded into a U-tube quartz reactor. No oxidative pre-treatment was done on the sample prior to reduction to avoid auto-reduction of Cu sites and dehydration-induced condensation of Z-CuOH sites. The TPR was performed under 50 ccm 5% H_2/N_2 flow while ramping the temperature from RT to 1000 °C at a 10 °C/min rate.

Electron paramagnetic resonance:

Around 20-30 mg of the hydrated samples were loaded into quartz sample tubes for measurement in a Bruker E580 X-band spectrometer. The continuous wave EPR spectra was collected between 2400 G and 3600 G, with a field modulation of 100 kHz, amplitude of 5 G, and microwave frequency of 9.32 GHz with 0.2 mW power. Spectra were collected at −150 °C.

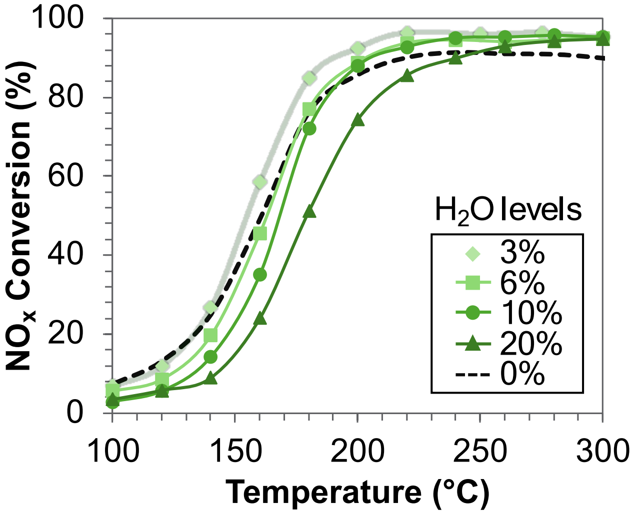

Figure S1: Steady state standard SCR NO_x conversion at different feed H_2O content (0, 3, 6, 10, 20%) on Cu-SSZ-13 catalysts. Feed conditions: 350 ppm NO, 350 ppm NH_3, 10% O_2, varying H_2O, balance N_2.

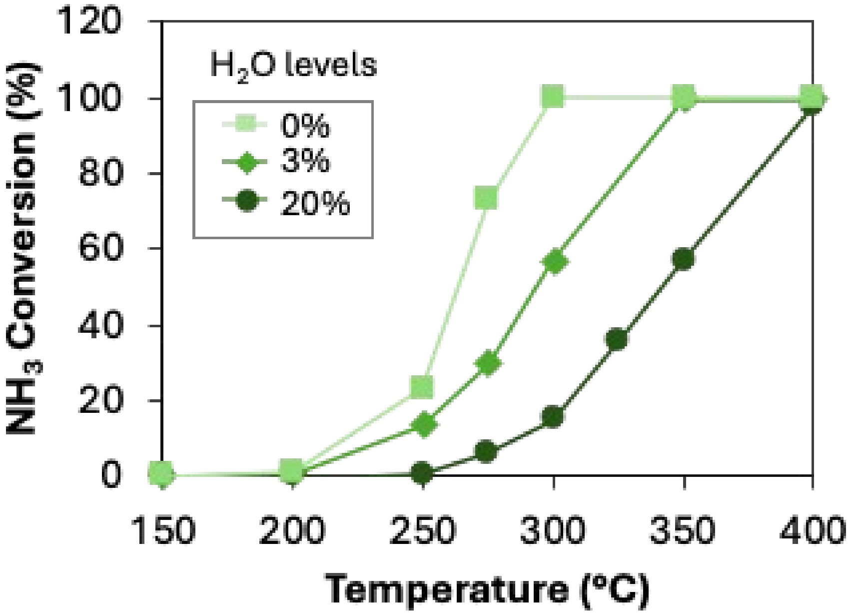

Figure S2: Steady state NH_3 conversion during NH_3 oxidation under 0%, 3% and 20% feed H_2O content on Cu-SSZ-13. Feed conditions: 350 ppm NH_3, 10% O_2, varying H_2O, balance N_2.

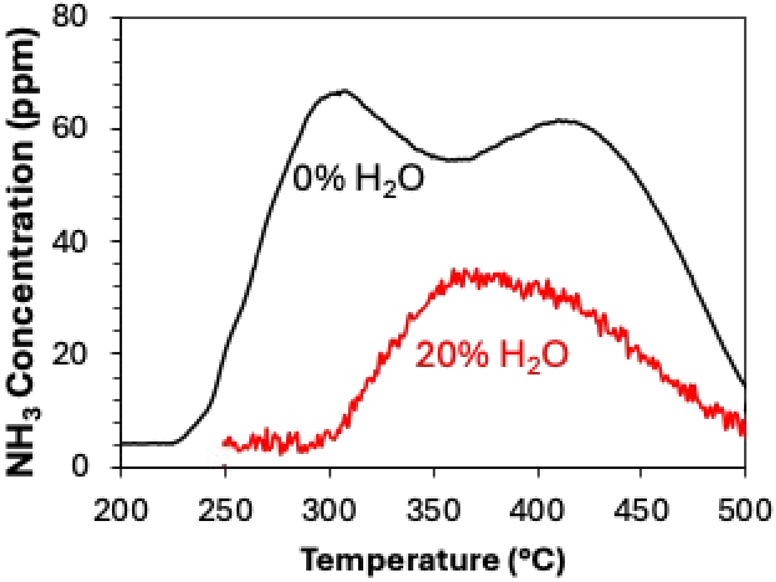

Figure S3: NH_3 evolution during NH_3 temperature-programmed desorption from Cu-SSZ-13 sample under 0% and 20% feed water levels. It is evident from the amount of NH_3 desorbed that the presence of H_2O impedes NH_3 adsorption.

For these experiments, NH_3 was first adsorbed on 100 mg of catalyst by flowing 350 ppm NH_3 + 10% O_2 in N_2 balance (in presence or absence of H_2O) at 200 °C, followed by a 90 mins isothermal flush with N_2. Temperature-programmed desorption was carried out under N_2 flow by increasing the reactor temperature from 200 °C to 500 °C at a 3 °C/min ramp rate.

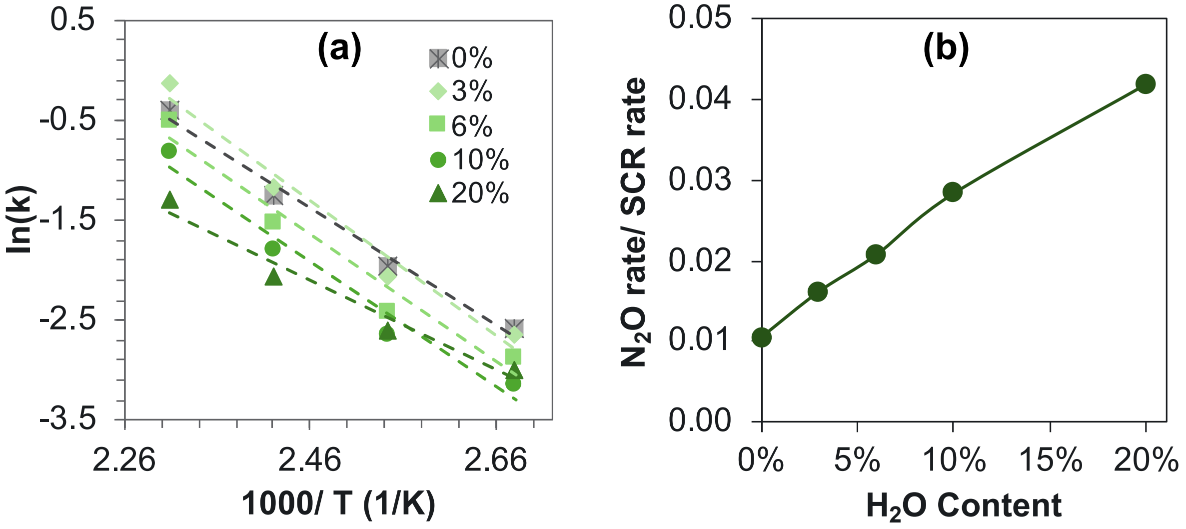

Figure S4: (a) Arrhenius plot [ln(k) vs 1/T] obtained from SCR NO_x conversion data shown in Fig. 1a and Fig. S1. Only those data points below 20% NO_x conversion were used to obtain Arrhenius plot to stay within differential region. Slope of ln(k) vs 1/T plot provides activation energy while the y-intercept provides pre-exponential factors plotted in Fig. 1b and 1c. (b) N_2O selectivity (rate of N_2O formation divided by rate of NOx consumption by SCR, where rate: mol/min/g_{cat}) plotted against feed H_2O levels. Feed conditions: 350 ppm NO, 350 ppm NH_3, 10% O_2, varying H_2O, balance N_2.

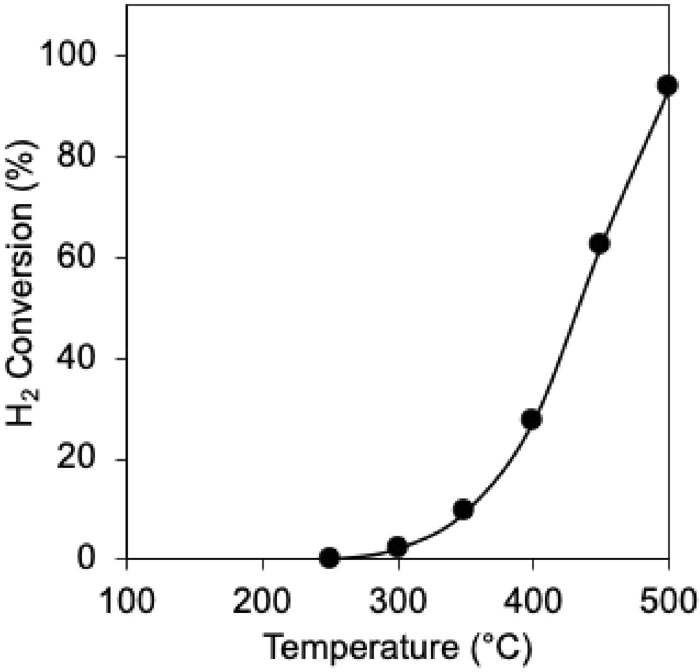

Figure S5: H_2 Conversion as a function of temperature on Cu-CHA catalysts. Feed: 0.4% H_2, 10% O_2, 10% H_2O (120k/h space velocity).

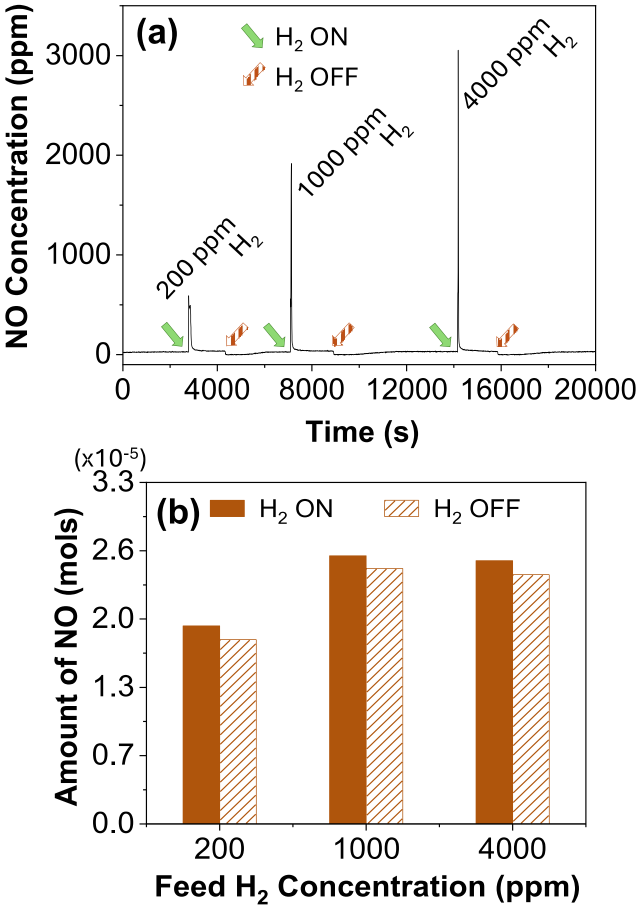

Figure S6: (a) NO concentration dynamics during SCR at 250°C when H_2 is turned ON or OFF. Green arrow indicates the point where H_2 is turned on while brown stripped arrow indicates where H_2 is turned off. Three different H_2 concentrations were turned on which produces three NO spikes (200, 1000 and 4000 ppm H_2 at ~ 2800 s, ~7200 s and ~14200 s, respectively). Consumption of NO below steady state values were observed when H_2 was turned off after each concentration event. Areas under NO spikes (formed when H_2 is turned on) and NO consumption (formed when H_2 is turned off) were calculated and plotted on Fig. S5b. These two areas for each H_2 concentration are within 10% of each other. Feed conditions: 350 ppm NO, 350 ppm NH_3, 10% O_2, 20% H_2O, varying H_2, balance N_2.

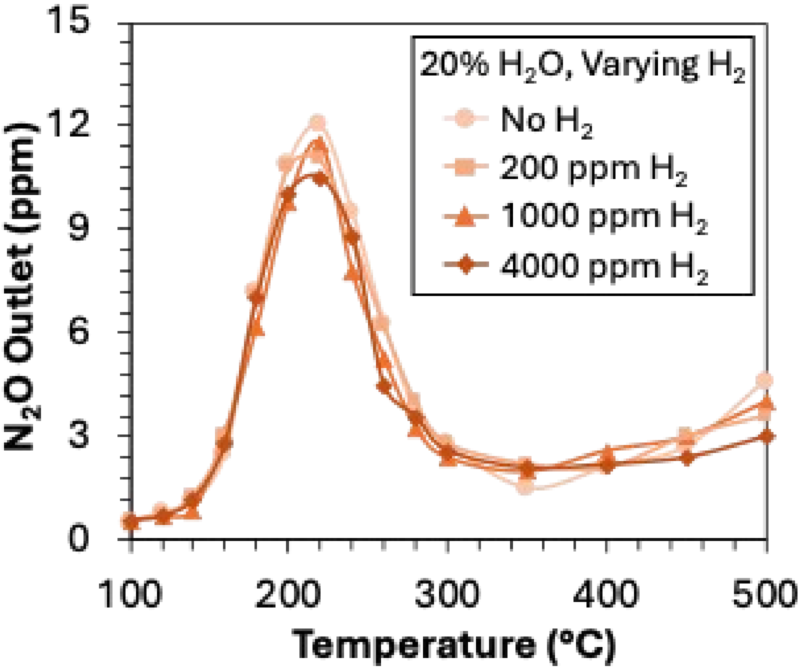

Figure S7: N_2O byproduct formation during steady state standard SCR on fresh Cu-SSZ-13 catalyst under various feed H_2 content: 0, 200, 1000, 2000 ppm H_2. Feed conditions: 350 ppm NO, 350 ppm NH_3, 10% O_2, 3% or 20% H_2O, balance N_2.

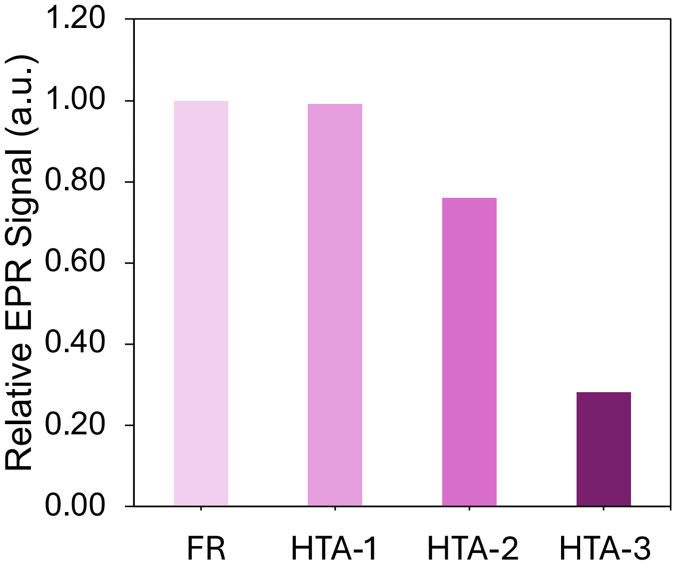

Figure S8: Total EPR signal of various Cu-SSZ-13 samples (FR, HTA-1, HTA-2, HTA-3) relative to the total EPR signal of the fresh (FR) sample.

All samples were in their hydrated and oxidized forms. Double integration of EPR signal can provide a straightforward measure of EPR active Cu sites, and the relative content of thus-calculated Cu sites in HTA-1, HTA-2 and HTA-3 compared to that of FR sample could provide a quantified measure of the lost isolated Cu sites in these catalysts. Consequently, HTA-1 has similar number of isolated Cu as FR, while it decreases by ~24% and ~72% in HTA-1 and HTA-2, respectively.