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Supplemental Information
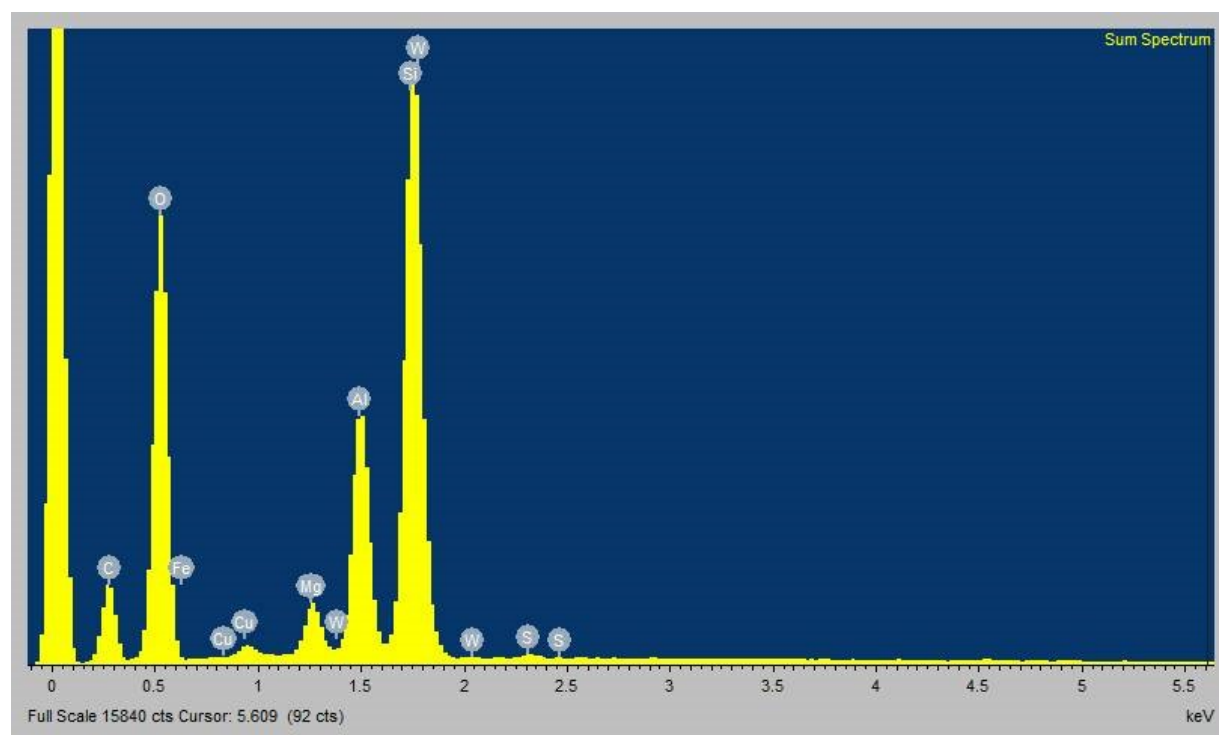

Fig. S1. EDX spectra for the SCR catalyst.

Table S1. Experimental conditions TPSR measurements.

	Condi.	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7
GHSV / h^{-1}	40000	40000	40000	40000	40000	40000	40000	40000
H_2O / vol.%	8	8	8	8	8	8	8	8
CO_2 / vol.%	0	0	6	6	6	6	0	0
O_2 / vol.%	10	0	10	10	10	10	0	0
NH_3 / ppm	0	750	750	750	750	750	0	0
NO_x / ppm	500	0	500	500	500	500	0	0
CH_2O / ppm	0	0	Var. 0, 100	Var. 0, 100	Var. 0, 100	Var. 0, 100	0	0
CO / ppm	0	0	Var. 0, 60	Var. 0, 60	Var. 0, 60	Var. 0, 60	0	0
DME / ppm	0	0	Var. 0, 12	Var. 0, 12	Var. 0, 12	Var. 0, 12	0	0
N_2	Rest	Rest	Rest	Rest	Rest	Rest	Rest	Rest
Temp./ °C	550	200	200	200-550	550	550-200	200	200-550

Temp. Gradient / K/min	0	0	0	5	0	-5	0	5

Table S2. Experimental conditions NH_3-TPD measurements.

	Conditioning	Step 1	Step 2	Step 3
GHSV / h^{-1}	40000	40000	40000	40000
H_2O / vol.%	8	8	8	8
CO_2 / vol.%	0	0	0	0
O_2 / vol.%	10	10	0	0
NH_3 / ppm	0	300	0	0
NO_x /ppm	500	0	0	0
CH_2O / ppm	0	Var. 0, 100	0	0
CO / ppm		Var. 0, 60	0	0
DME / ppm		Var. 0, 12	0	0
N_2	Rest	Rest	Rest	Rest
Temperature / °C	550	Var. 150, 200, 250, 300, 350	Var. 150, 200, 250, 300, 350	Var. 150-550, 200-550, 250-550, 300-550, 350-550
Temp. Gradient / K/min	0	0	0	5

Table S3. Experimental conditions for the modified desorption investigation measurements.

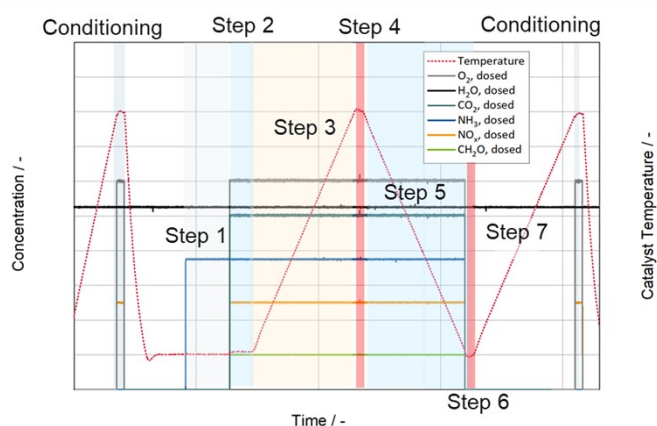|	Conditioning	Step 1	Step 2	Step 3	Step 4	Step 5
GHSV / h^{-1}	40000	40000	40000	40000	40000	40000
H_2O / vol.%	8	8	8	8	8	8
CO_2 / vol.%	0	0	0	0	0	0
O_2 / vol.%	10	0	0	0	0	0
NH_3 / ppm	0	750	0	0	0	0
NO_x /ppm	500	0	0	0	0	0
CH_2O / ppm	0	Var. 0, 100	0	0	0	0
CO / ppm		Var. 0, 60	0	0	0	0
DME / ppm		Var. 0, 12	0	0	0	0
N_2	Rest	Rest	Rest	Rest	Rest	Rest
Temperature / °C	550	Var. 150, 200	Var. 150, 200	Var. 150-100, 200-100	100	100-550
Temp. Gradient / K/min	0	0	0	-5	0	5

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Fig. S2. Schematic representation of a performed TPSR experiment with CH₂O dosing at SGTB. The temperature ramps at the beginning and at the end show the performed conditioning of the catalyst before and after the experiment.
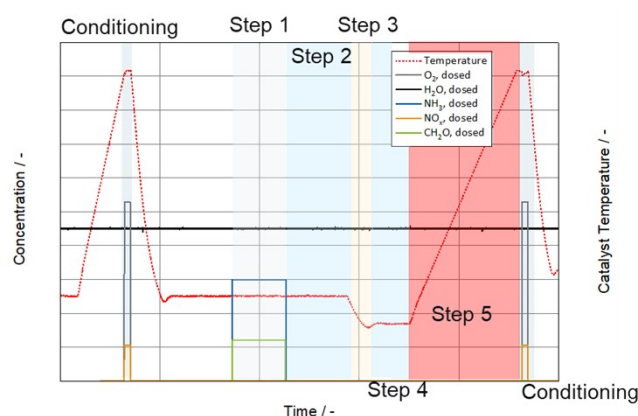

Fig. S3. Schematic representation of a performed NH₃-TPD experiment with CH₂O dosing at SGTB. The temperature ramps at the beginning and at the end show the performed conditioning of the catalyst before and after the experiment.
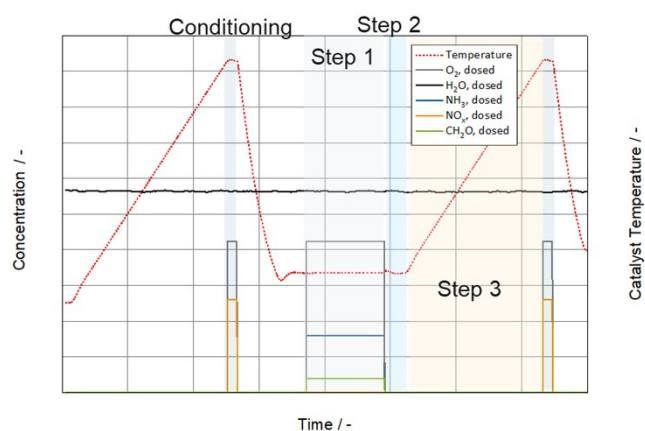

Fig. S4. Schematic representation of a performed modified NH₃-TPD experiment with CH₂O dosing at SGTB. The temperature ramps at the beginning and at the end show the performed conditioning of the catalyst before and after the experiment.

Coverage of surface hydroxyl groups by formaldehyde

In order to perform in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements to study the formaldehyde adsorption on the catalyst surface, the commercial formaldehyde solution was added into water, and dosed into gas mixture. A small amount of methanol was present in commercial formaldehyde solution as the stabilizer, which cannot be avoided in the gas flow. By exposing the catalyst to an atmosphere with/without formaldehyde (CH_2O) under SCR conditions at 300 °C (with only NO_2 present), the results were depicted in Figure S5. The spectrum without CH_2O showed weak bands at 3336 and 3277 cm^{-1}, which are attributed to the stretching modes of NH_3, which is adsorbed to Brønsted acid sites (Al-OH-Si).[1,2] The negative band at 3656 cm^{-1} is related to vibration modes of Cu-OH groups, which are coordinated by NH_3. Besides this, a very weak signal with negative intensity at 3612 cm^{-1} is attributed to OH groups on Brønsted acid sites, as it is partially coordinated by NH_3.[3] When CH_2O was added, it adsorbs on the surface OH groups, leading the bands at 3336 and 3277 cm^{-1} to lose intensity and this finding indicates that the presence of CH_2O promotes the NO_x conversion by NH_3, i.e. that NH_3 adsorption is less likely under these reaction conditions. Unfortunately, the signal at 3612 cm^{-1} is not distinct enough to judge, whether the corresponding site undergoes a similar effect.

In addition, one would expect a change of the signal at 3656 cm^{-1} to positive intensity when CH_2O was added, as NH_3 is consumed under these reaction condition, i.e. presence of NO_2, which would be consistent with our observation on the signal intensity at 3336 cm^{-1} and 3277 cm^{-1}. However, we found that the respective signal just gets less negative, which we attribute to that the presence of CH_2O partially cover the Cu-OH sites.

Even, with Methanol present as a stabilizer, no indications in the spectra are found for the presence of methanol[4], the signal at 3647 cm^{-1} has to stem from another species. Hence, for the band appearing at 3647 cm^{-1}, which has been observed by Xue *et al*.[3] as well, we tentatively assign it to water species on the zeolite surface.[3]
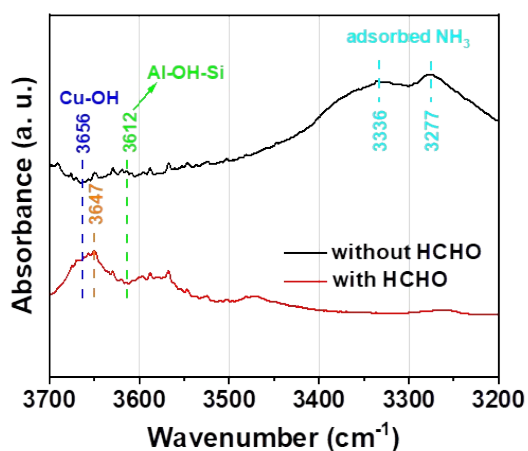

Fig. S6. The DRIFTS result of the catalyst under the NH_3 SCR condition with the presence of CH_2O at 200 °C to 400 °C

Fig. S5. The DRIFTS result of the catalyst under the NO_2 SCR condition with/without the presence of CH_2O at 300 °C

Table S4. DRIFTS Assignment.

IR-Band	Assignment	References
1670 cm^{-1}	Nitrites, NO_2^-	6
1626 cm^{-1}	Bridging nitrates on Al	7–9
1617-1621 cm^{-1}	NH_3 coordinated on Lewis acid site	10
1576 cm^{-1}	Monodentate nitrates on Cu	8
1559 cm^{-1}	Monodentates nitrate	11,12
1546-1539 cm^{-1}	Monodentates nitrate	13,14
1507 cm^{-1}	Nitrites, NO_2^-	8
1489 cm^{-1}	NH_4NO_3	7
1455 cm^{-1}	NH_4^+ on Brønsted acid	7
1457 cm^{-1}	Nitrite	13
1445 cm^{-1}	NH_4^+ from NH_4NO_3	7

Nitrate formation

The catalytic material was subjected to a pretreatment procedure involving exposure to NO and NO_2 at a temperature of 400 °C with a 10% oxygen concentration. Subsequently, the catalyst was subjected to an exposure to 800 ppm of NH_3 in a nitrogen environment at 200 °C for 30 minutes before being switched to an atmosphere containing formaldehyde under Selective Catalytic Reduction (SCR) conditions. The accompanying Figure S6 presents the results of DRIFTS analysis carried out at temperatures ranging from 200 °C to 400 °C. Upon exposure to an atmosphere containing only NH_3, two distinct bands were observed in the spectra, with the primary band at 1444 cm^{-1} attributed to the presence of NH_4^+ species resulting from NH_3 adsorption onto Brønsted acid sites, and a weaker band at 1618 cm^{-1} assigned to molecularly adsorbed NH_3 on Lewis acid sites.[5] Upon introduction of the SCR atmosphere containing formaldehyde, additional spectral bands were identified, including one at 1626 cm^{-1} commonly attributed to surface-bridging nitrates based on aluminum sites.[5]
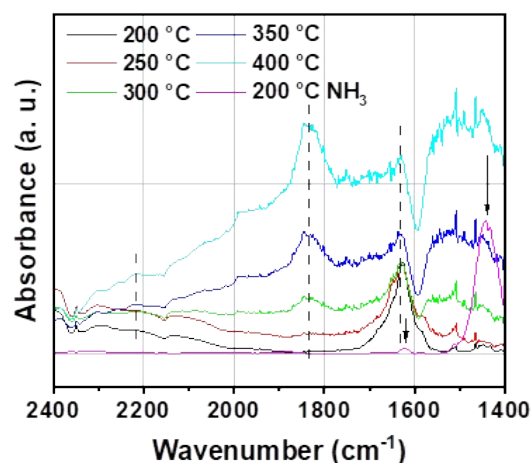
HCN formation

The accompanying figure displays the DRIFTS results for the investigation of the effect of CH_2O and the NO_2 / NO_x ratio on SCR conditions at 200 °C. The presence of CH_2O and a NO_2 / NO_x ratio of 0% is indicated by the C-H vibration bands at 2886 cm^{-1} and 2955 cm^{-1}, which are assigned to HMT according to previous studies.[15,16] This observation suggests the formation of HMT on the surface. Additionally, the IR band at 1313 cm^{-1} suggests the presence of formamide, which can undergo dehydration to form HCN.
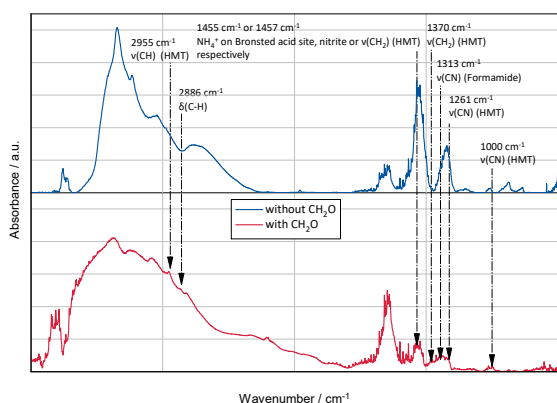

Fig. S7. DRIFTS spectra at 200 °C between 3800 and 600 cm^{-1} after dosing NO, O_2, H_2O and, in the lower measurement, additional CH_2O being dosed over the investigated SCR catalysts with preadsorbed NH_3 at 200 °C. Before preadsorbing NH_3, the catalyst was pretreated with NO and NO_2 at 400 °C with 10% O_2.

Fig. S8. DRIFTS spectra at 200 °C between 1700 and 950 cm^{-1} after dosing NO, O_2, H_2O and, in the lower measurement, additional CH_2O being dosed over the investigated SCR catalysts with preadsorbed NH_3 at 200 °C. Before preadsorbing NH_3, the catalyst was pretreated with NO and NO_2 at 400 °C with 10% O_2
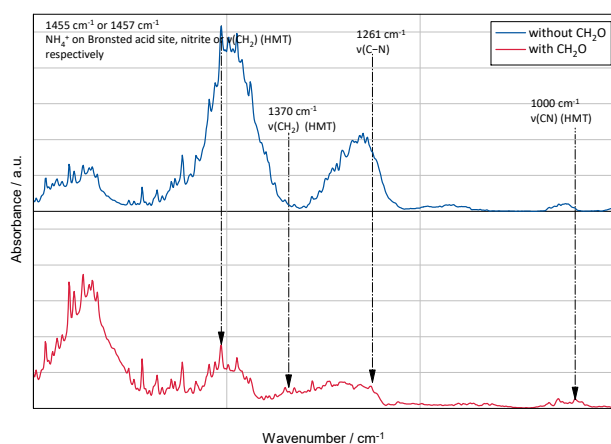
Table S5. DRIFTS Assignment.

IR-Band	Assignment	References
2955 cm^{-1}	$\nu(CH_2)$ stretch	[15,16]
2886 cm^{-1}	$\delta(C–H)$	[16,17]
1688 cm^{-1}	C=O	[18]
1588 cm^{-1}	OCO	[19]
1457 cm^{-1}	$\nu(CH_2)$ scissor (HMT)	[15,16]
1458 cm^{-1}		
1370 cm^{-1}	$\nu(CH_2)$ wag (HMT)	[15,16]
1372 cm^{-1}		
1313 cm^{-1}	CN	[18]
1261 cm^{-1}	$\nu(C–N)$	[17]
1000 cm^{-1}	$\nu(CN)$ stretch (HMT)	[15]

H_2O and formaldehyde influence under NO_2 SCR conditions

The TPSR experiments with and without CH_2O, described in the original draft, were repeated accordingly, but now with the absence of H_2O vapor, fed into the gas stream. Figure S9 displays the NO_x conversion efficiency of the NH_3 SCR with a NO_2 / NO_x ratio of 100% under the presence and absence of H_2O and CH_2O. The characteristic increase of NO_x conversion efficiency at low temperatures with CH_2O can be observed with and without H_2O added during the experiment. This shows that even without H_2O, no NH_4NO_3 was formed from the reaction of NH_3 and NO_2 and no deactivation of the catalyst occurs. At high temperatures of T > 370 °C a significant promoting effect of H_2O can be observed, while at temperatures of T < 320 °C a lesser deactivation effect of NH_4NO_3 occurred. Additionally, the overall selectivity to N_2O increased in the absence of H_2O, for both experiments with and without CH_2O. Displayed in Figure S10, with the absence of H_2O an increased N_2O peak from 108 ppm to 160 ppm can be seen for the experiment without CH_2O. In the presence of CH_2O no peak is detected, but the N_2O concentration is elevated with H_2O. These results go in line with the results, described by Han et al.[20], where H_2O hinders the NH_4NO_3 formation and increases the selectivity for decomposition to NO_2 instead of N_2O.
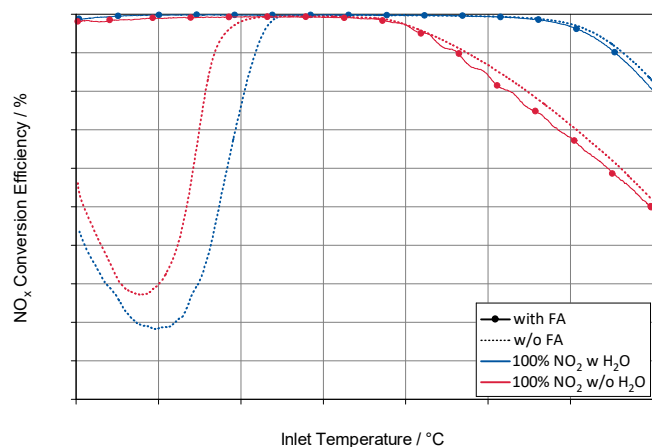
Fig. S9. NO$_x$ conversion efficiency in % versus inlet temperature in °C for the investigated Cu-CHA SCR catalyst in the presence (100 ppm CH$_2$O) and the absence of formaldehyde and in the presence (8% H$_2$O) and the absence of H$_2$O vapor. The dotted line refers to the curves without formaldehyde; red: without H$_2$O vapor; blue: with H$_2$O vapor

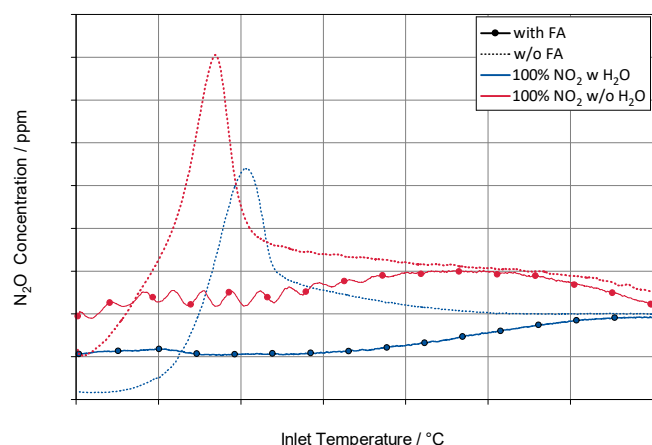**Fig. S10.** N$_2$O concentration versus inlet temperature in °C for the investigated Cu-CHA SCR catalyst in the presence (100 ppm CH$_2$O) and the absence of formaldehyde and in the presence (8% H$_2$O) and the absence of H$_2$O vapor. The dotted line refers to the curves without formaldehyde; red: without H$_2$O vapor; blue: with H$_2$O vapor

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