

Supporting Information

Desorption Products during Linear Heating of Copper Zeolites with Pre-adsorbed Methanol

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Calculated density of the adsorption sites and adsorbed carbon containing species in the Cu-ZSM-5, H-ZSM-5, Cu-SSZ-13 and H-SSZ-13 sample

Densities of the adsorption sites , *i.e.* Cu site, Brønsted acid site as well as the sum of Brønsted acid site and Cu site, are calculated with the assumption that all Al are at framework position and all Cu species are at ion-exchange position for the H-ZSM-5, Cu-ZSM-5, H-SSZ-13 and Cu-SSZ-13 samples. The results are presented in Table S1.

Table S1: Calculated density of the Cu site ($[Cu]$), Brønsted acid site ($[BAS]$), the sum of Brønsted acid site and Cu site ($[BAS] + [Cu]$), the amount of carbon containing species adsorbed in total ($[C]$) and adsorbed over the Cu sites ($[C]_{Cu}$) over the H-ZSM-5, Cu-ZSM-5, H-SSZ-13 and Cu-SSZ-13 samples. Unit: mmol/g sample.

	H-ZSM-5	Cu-ZSM-5	H-SSZ-13	Cu-SSZ-13
$[Cu]$	0.00	0.44	0.00	0.20
$[BAS]$	1.15	0.71	1.52	1.32
$[BAS] + [Cu]$	1.15	1.15	1.52	1.52
$[C]$	0.67	1.10	1.10	1.30
$[C]_{Cu}$	0.00	0.43	0.00	0.20

Desorption of pre-adsorbed methanol from the Cu-ZSM-5, H-ZSM-5, Cu-SSZ-13, H-SSZ-13, Cu/SiO₂ and SiO₂ sample

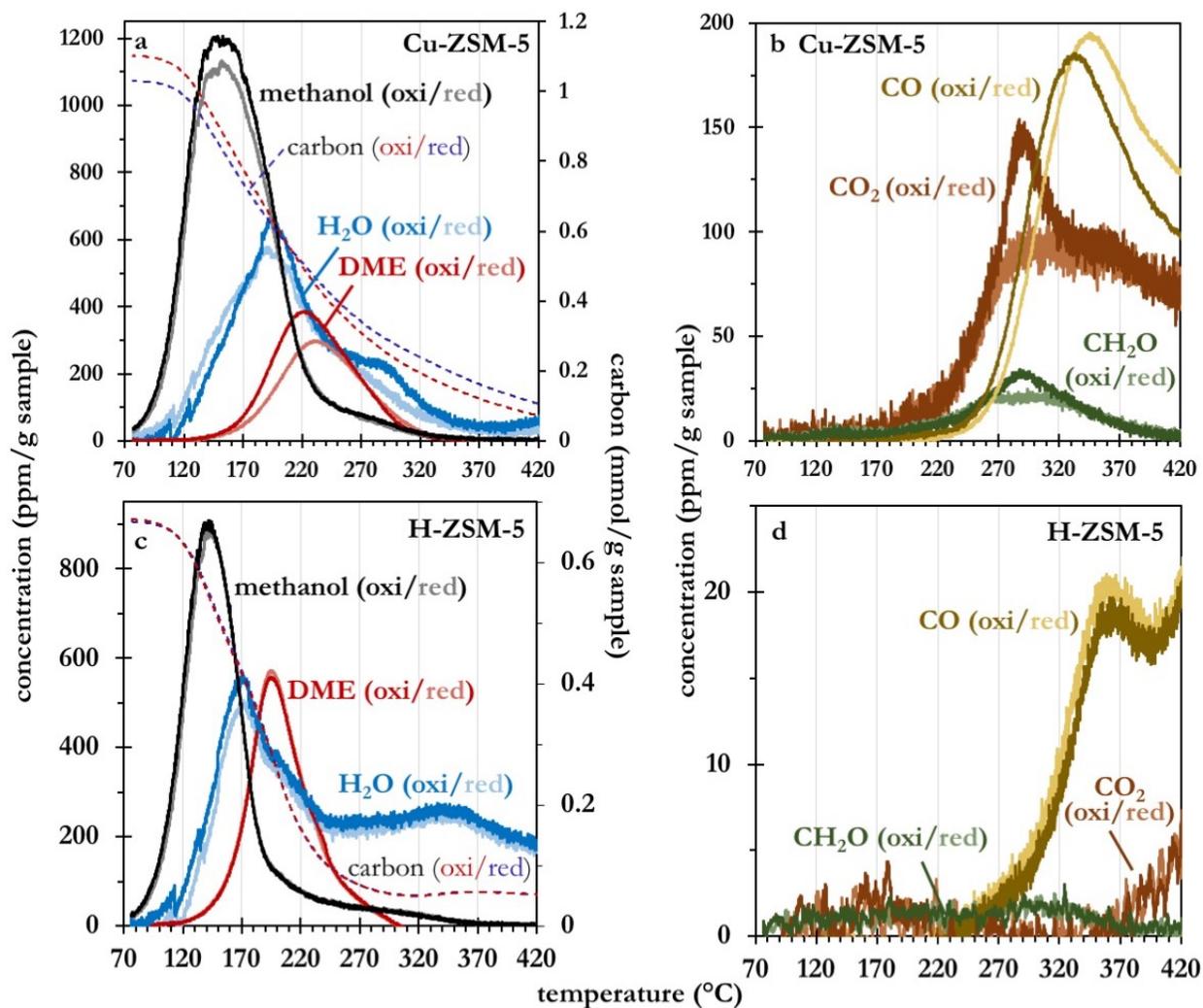


Figure S1: Desorbed gas phase species during methanol desorption experiments from the pre-oxidized (oxi) and pre-reduced (red) samples: (a, b) Cu-ZSM-5 and (c, d) Cu-SSZ-13.

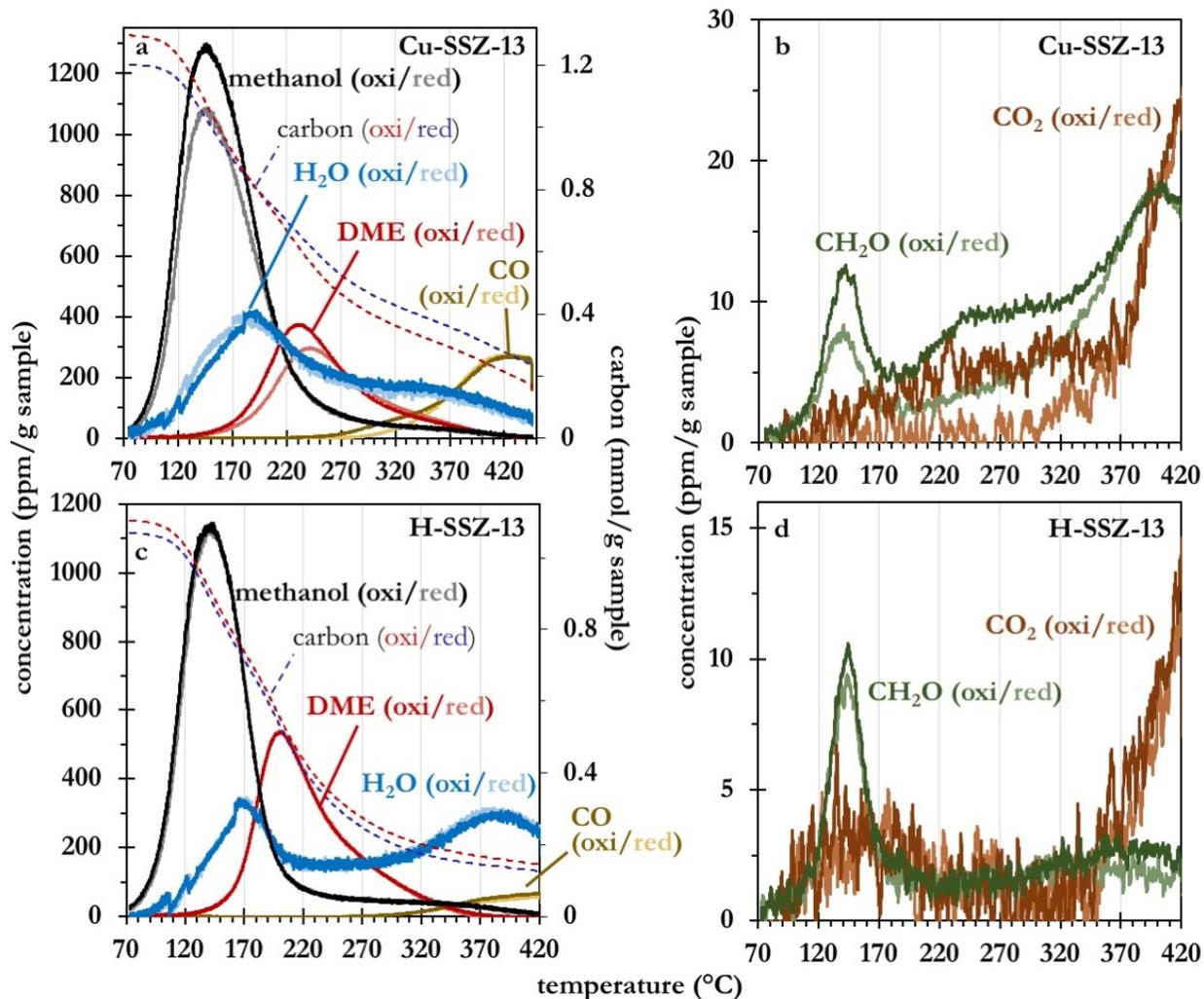


Figure S2: Desorbed gas phase species during methanol desorption experiments from the pre-oxidized (oxi) and pre-reduced (red) samples: (a, b) Cu-SSZ-13 and (c, d) H-SSZ-13.

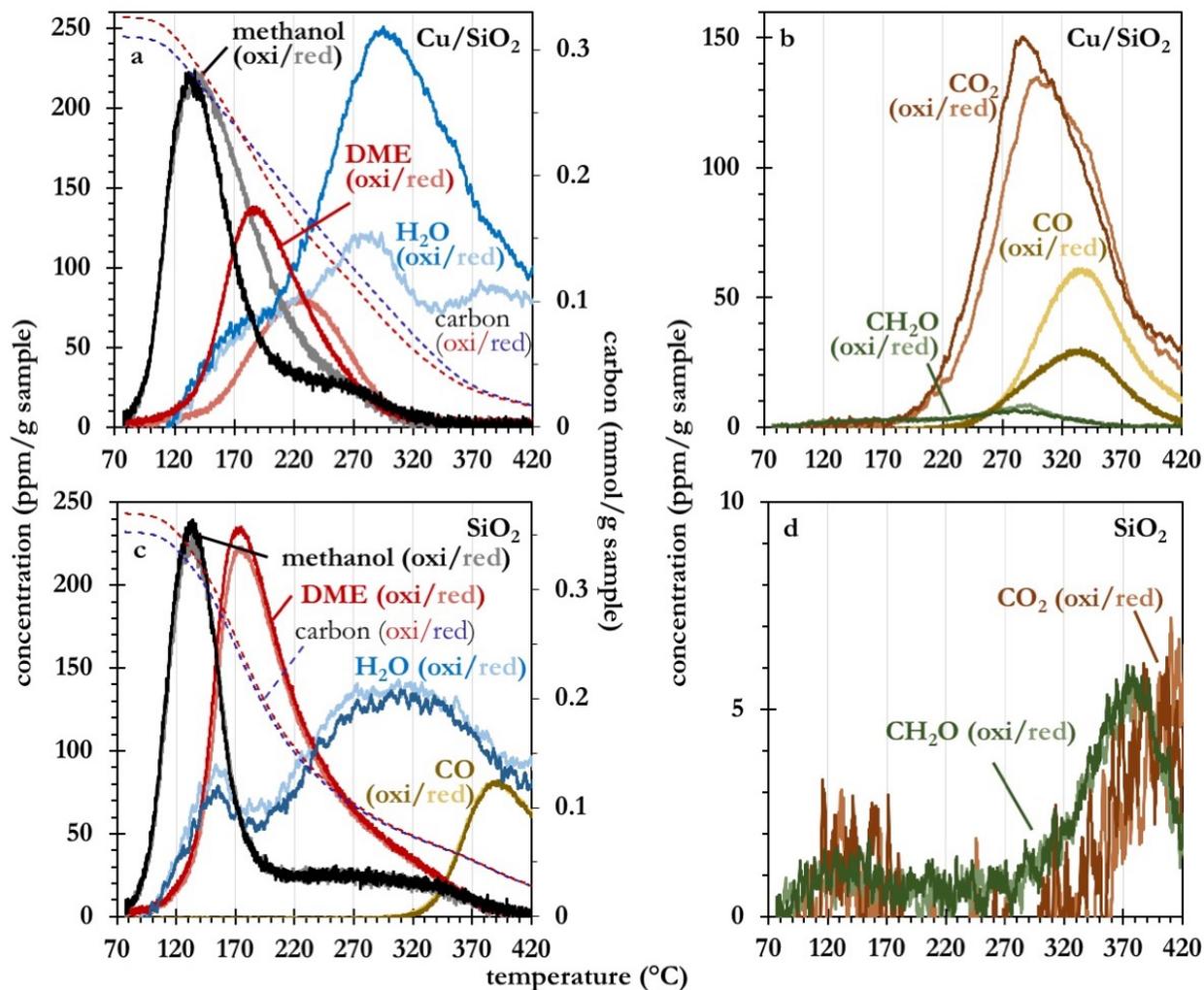


Figure S3: Desorbed gas phase species during methanol desorption experiments from the pre-oxidized (oxi) and pre-reduced (red) samples: (a, b) Cu/SiO₂ and (c, d) SiO₂.

DME desorption

For DME desorption, all samples were pre-treated under either oxidizing (10 vol.% O₂) conditions at 500 °C for 30 min. The samples were then cooled down to 80 °C in pure Ar and fed with 5000 ppm DME for 1 h at 80 °C. After DME adsorption, the samples were kept in Ar at 80 °C for 1 h. The total flow was kept constant at 1500 ml/min (GHSV = 34,000 h⁻¹) with Ar as balancing gas during pre-treatment and DME adsorption. Subsequently, the samples were stabilized under 500 ml/min Ar flow (GHSV = 11,300 h⁻¹) at 80 °C (5 min). The following desorption experiments were carried out under 500 ml/min flow of Ar with a temperature ramp of 5 °C/min. The DME desorption profiles were recorded and presented in Figure S4. The amount of DME desorbed is presented in Table S2.

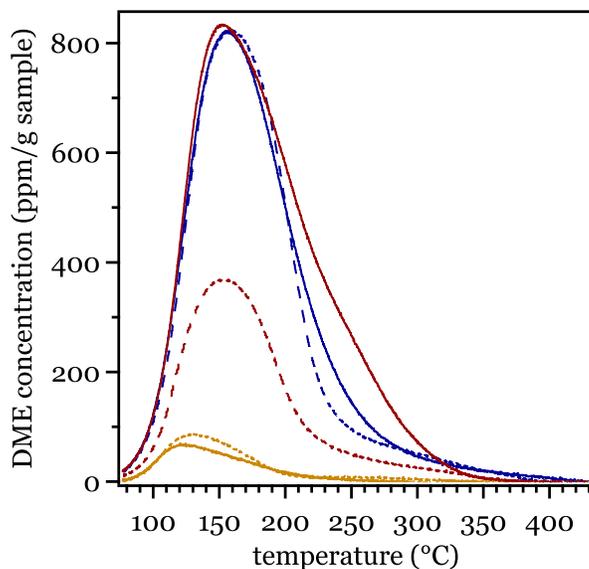


Figure S4: DME desorbed during desorption of pre-adsorbed DME over the oxidized Cu-ZSM-5 (red solid line), H-ZSM-5 (red dashed line), Cu-SSZ-13 (blue solid line), H-SSZ-13 (blue dashed line), Cu/SiO₂ (yellow solid line), SiO₂ (yellow dashed line) sample.

Table S2: The amount of DME desorbed from the H-ZSM-5, Cu-ZSM-5, H-SSZ-13, Cu-SSZ-13, SiO₂ and Cu/SiO₂ samples.

	H-ZSM-5	Cu-ZSM-5	H-SSZ-13	Cu-SSZ-13	SiO ₂	Cu/SiO ₂
DME (mmol g ⁻¹ sample)	0.14	0.38	0.32	0.34	0.027	0.020

NH₃ desorption

For NH₃ desorption, all samples were pre-treated under oxidizing (10 vol.% O₂) conditions at 500 °C for 30 min. The samples were then cooled down to 150 °C in pure Ar and fed with 1000 ppm NH₃ for 1 h at 150 °C. After NH₃ adsorption, the samples were kept in Ar at 150 °C for 1 h. The total flow was kept constant at 1500 ml/min (GHSV = 34,000 h⁻¹) with Ar as balancing gas during pre-treatment and NH₃ adsorption. Subsequently, the samples were stabilized under 500 ml/min Ar flow (GHSV = 11,300 h⁻¹) at 150 °C (5 min). The following desorption experiments were carried out under 500 ml/min flow of Ar with a temperature ramp of 5 °C/min. The gas species desorbed during desorption were recorded using the FTIR spectrometer.

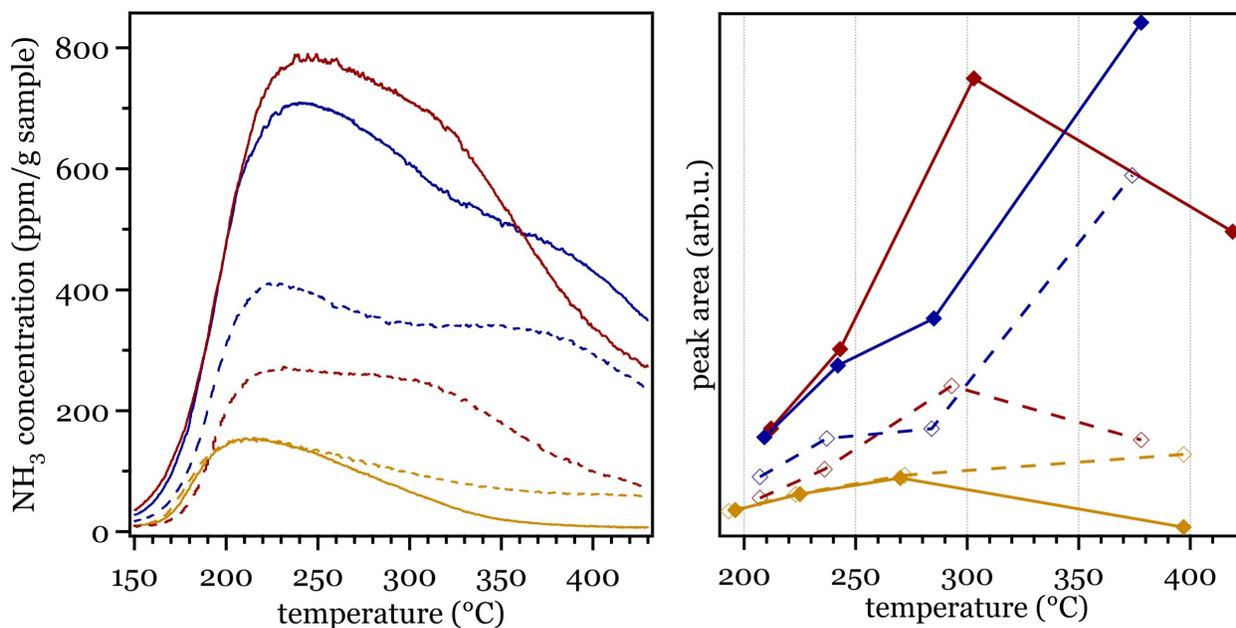


Figure S5: Left panel: NH₃ desorption profile of the Cu-ZSM-5 (red solid line), H-ZSM-5 (red dashed line), Cu-SSZ-13 (blue solid line), H-SSZ-13 (blue dashed line), Cu/SiO₂ (yellow solid line), SiO₂ (yellow dashed line) sample. Right panel: Peak area of the deconvoluted peaks.

For the zeolite samples, the H-SSZ-13 sample exhibit higher NH₃ desorption at the entire temperature range, indicating the existence of larger amount of acid sites in the H-SSZ-13 sample than the H-ZSM-5 sample. Moreover, the difference of the NH₃ desorption is

especially evident at temperature higher than 350 °C (associated with Brønsted acid sites¹), suggesting that the H-SSZ-13 sample possesses higher amount of Brønsted acid sites than the H-ZSM-5 sample.

The Cu-ZSM-5 and Cu-SSZ-13 sample exhibit higher amount of NH₃ desorption through the entire temperature range compared to the H-ZSM-5 and H-SSZ13 sample. This indicates that the introduction of isolated Cu ion/cluster into the zeolites increased the amount of acidic sites with various acidic strength.

The Cu/SiO₂ sample exhibits desorption profile similar to the SiO₂ sample at temperature lower than 250 °C, while lower amount of NH₃ is desorbed at temperature higher than 250 °C for the Cu/SiO₂ sample. This observation indicates that CuO nanoparticles does not bring extra acid sites and covers the strong acidic sites on the SiO₂ surface.

IR spectra during methanol desorption

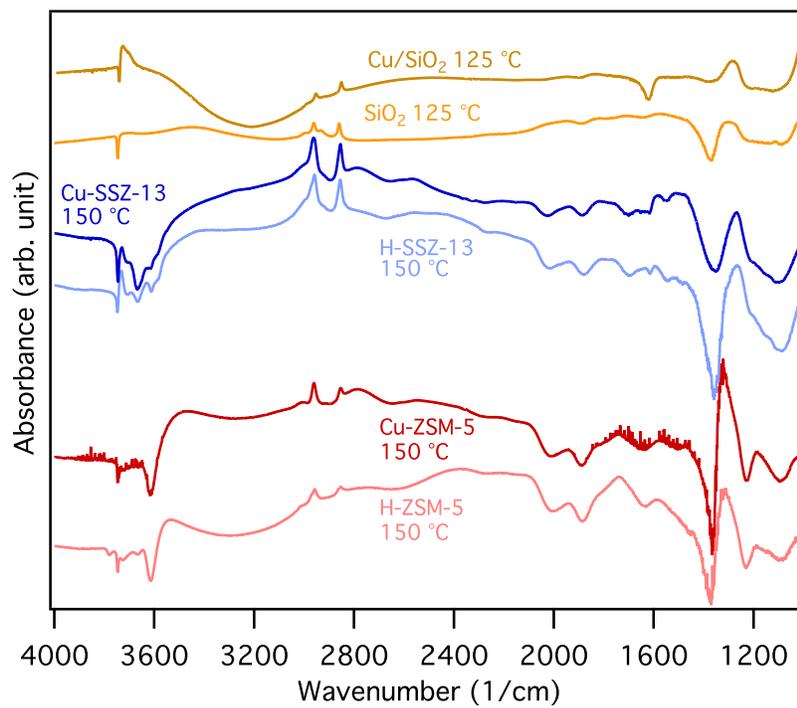


Figure S6: IR spectra collected during methanol desorption at low temperatures for the pre-oxidized samples.

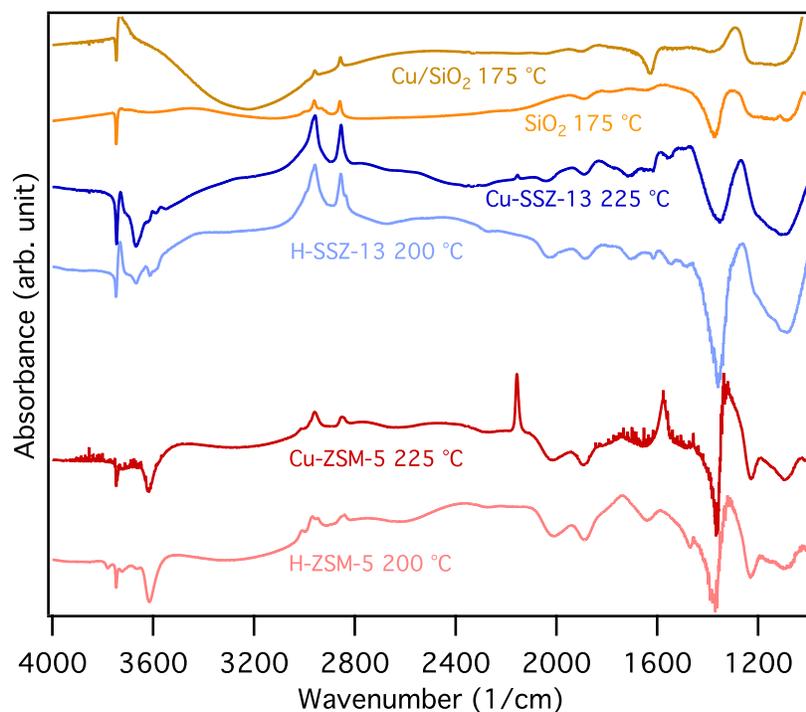


Figure S7: IR spectra collected during methanol desorption at medium temperatures for the pre-oxidized samples.

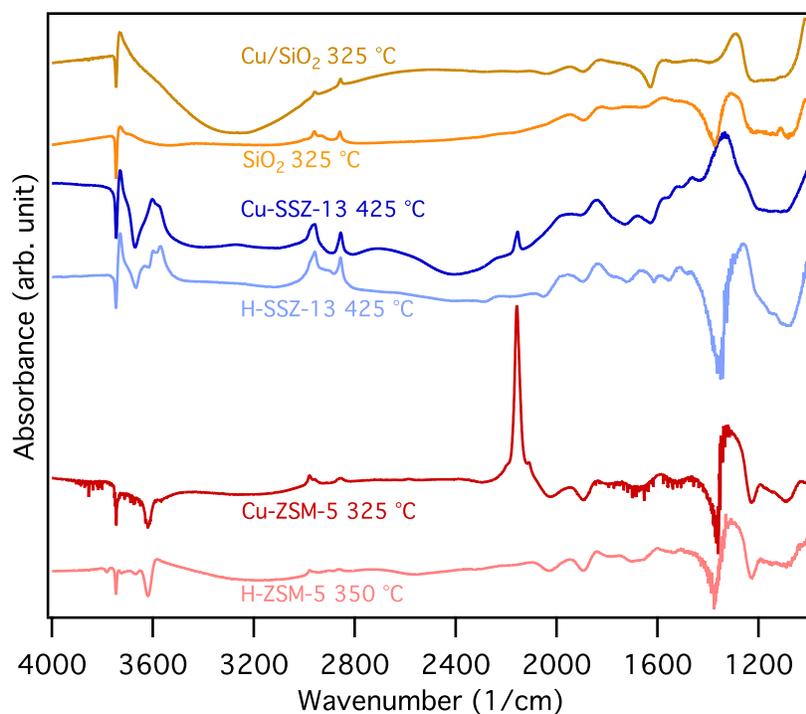


Figure S8: IR spectra collected during methanol desorption at high temperatures for the pre-oxidized samples.

Calculated energies and sensitivity analysis

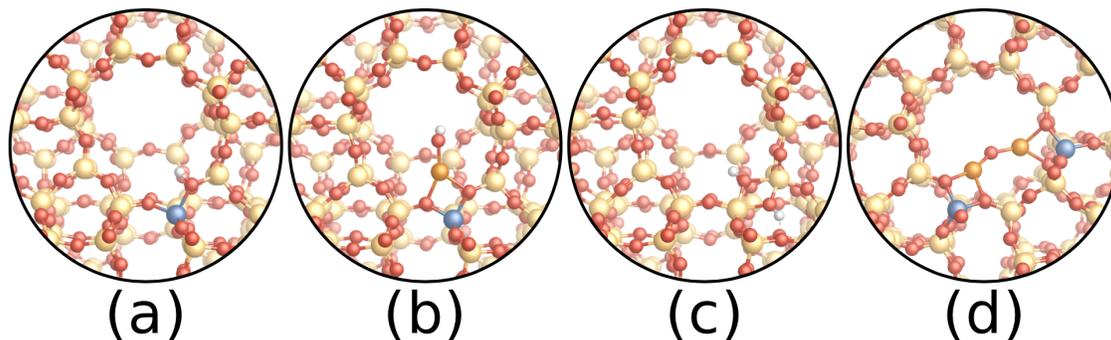


Figure S9: Illustration of the different sites in the MFI framework. a) The Brønsted acid site with aluminium in the T12 site, b) the Cu monomer site, c) the silanol model, d) the Cu-O-Cu site.

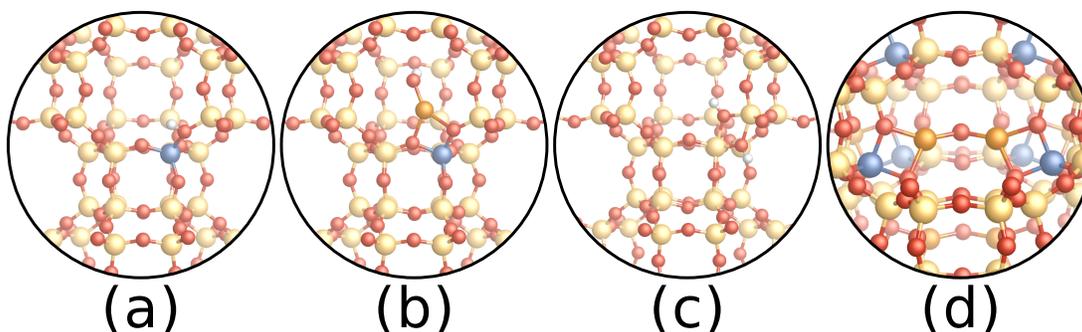


Figure S10: Illustration of the different sites in the CHA framework. a) The Brønsted acid site, b) the Cu monomer site, c) the silanol model, d) the Cu-O-Cu site.

A table of calculated methanol binding energies

$$\Delta E = E_{\text{MeOH}^*} - (E_* + E_{\text{MeOH(g)}})$$

and the calculated peak temperature of the desorption curves can be found in table S3.

A sensitivity analysis of the calculated desorption curves can be found in figure S11. By changing the methanol binding energy $\Delta E \pm 0.1$ eV, the desorption curves shift around ± 35 °C.

Table S3: Calculated methanol adsorption energies and desorption peak temperatures for the different adsorption sites in the MFI and CHA frameworks.

Site	MFI		CHA	
	ΔE	T_{\max}	ΔE	T_{\max}
Silanol	-0.96 eV	38.60 °C	-0.99 eV	68.80 °C
Brønsted	-1.22 eV	139.20 °C	-1.12 eV	118.90 °C
Cu	-1.68 eV	340.30 °C	-1.71 eV	258.10 °C
CuO	-0.63 eV	-61.65 °C	-0.57 eV	-53.25 °C
CuOH	-0.68 eV	-15.70 °C	-0.63 eV	-51.10 °C
Cu-Cu	-2.32 eV	448.90 °C	-2.01 eV	312.50 °C
CuOCu	-0.61 eV	-78.75 °C	-0.60 eV	-51.05 °C
CuOHCu	-0.89 eV	42.10 °C	-1.06 eV	61.90 °C

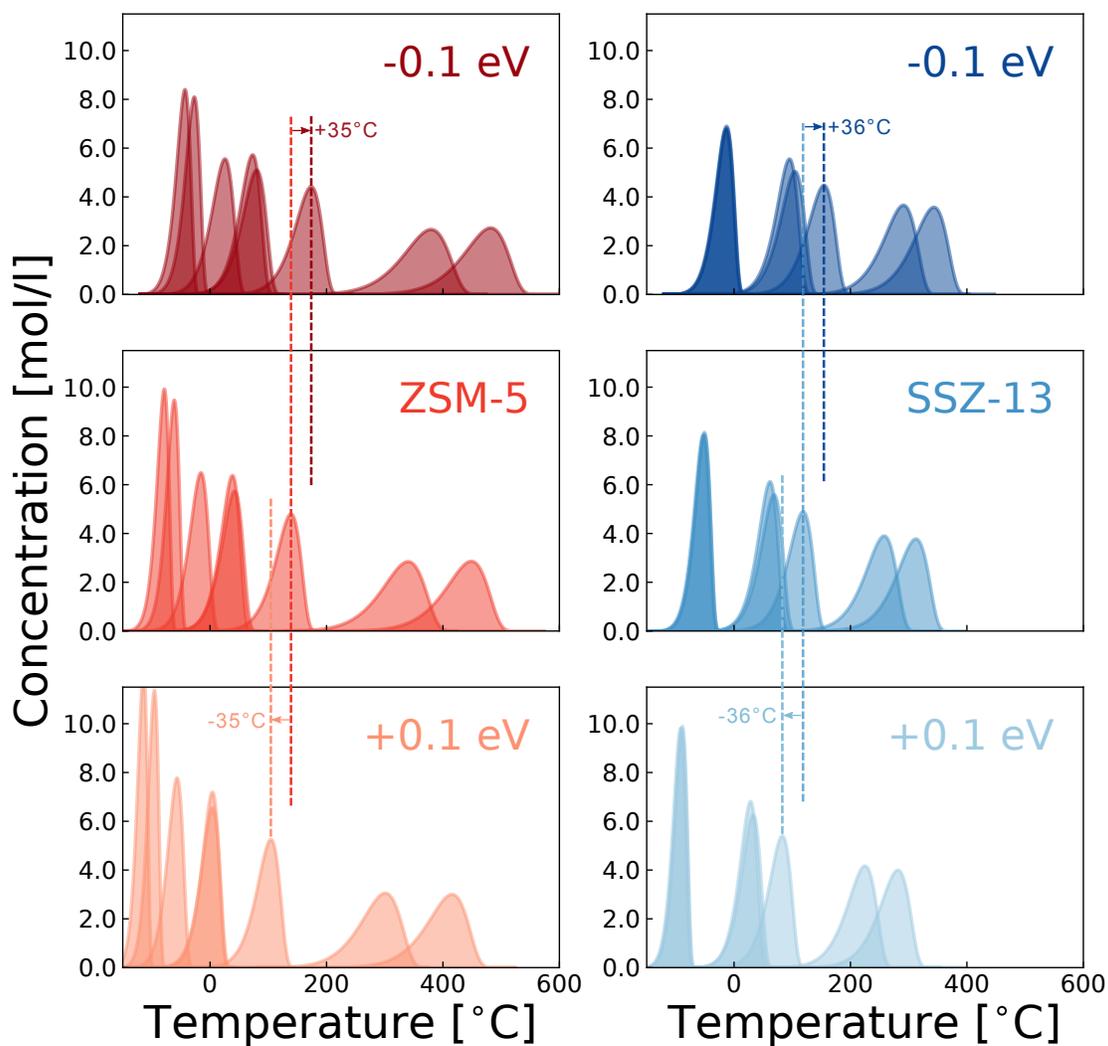


Figure S11: Sensitivity analysis of calculated desorption curves when changing the methanol binding energy ± 0.1 eV. The middle plots are the unperturbed desorption curves. The shift for the Brønsted acid site is highlighted in the figure.

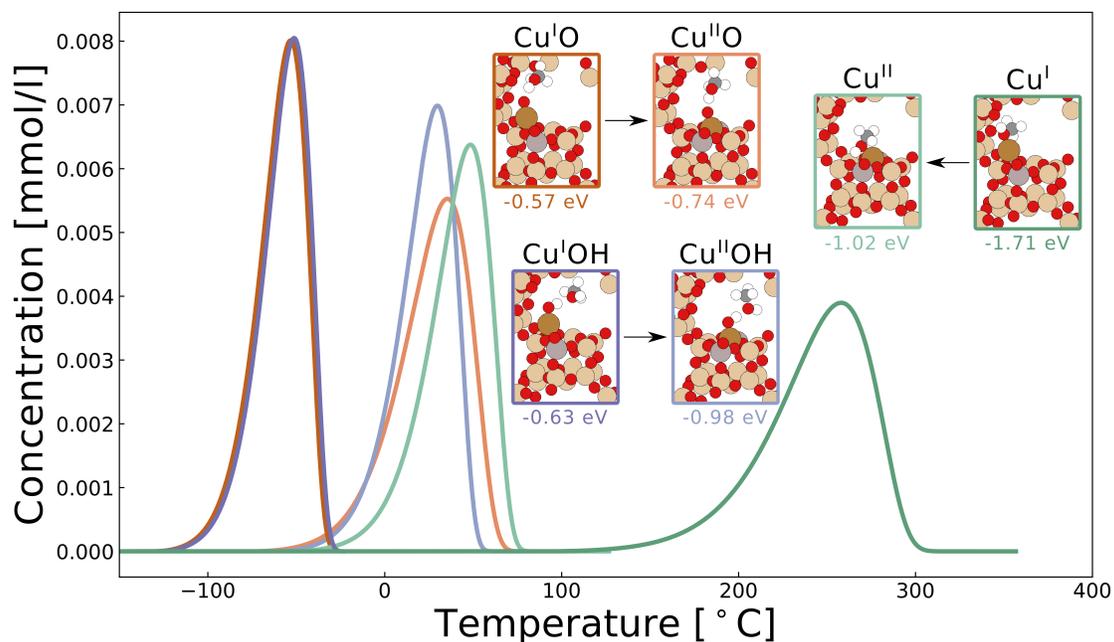


Figure S12: Comparison of simulated TPD curves for Cu^{I} and Cu^{II} monomers in Cu-SSZ-13. Since Cu is bound more strongly with two Al in the six-membered ring, the binding energy of methanol on Cu decreases. For the same reason, the methanol binding to CuO and CuOH is stabilized, making all Cu^{II} monomers potentially relevant methanol adsorption sites.

References

- (1) Leistner, K.; Xie, K.; Kumar, A.; Kamasamudram, K.; Olsson, L. Ammonia Desorption Peaks Can Be Assigned to Different Copper Sites in Cu/SSZ-13. *Catal. Lett.* **2017**, *147*, 1882–1890.