

# **Supplementary Materials: Effect of Textural Properties and Presence of Co-Cation on NH<sub>3</sub>-SCR Activity of Cu-Exchanged ZSM-5**

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**Table S1.** Calculated parameters for adsorption and desorption kinetics.

	$r_j^{\text{ads}}$		$r_{\text{NO}}^{\text{des}}$		$r_{\text{NH}_3}^{\text{des}}$	
	$k_j^{\text{ads}} \cdot C_j \cdot \theta_{\text{VS}}$		$k_{\text{NO}_x}^{\text{des}} \cdot \theta_{\text{NO}_x}$		$k_{\text{NH}_3}^{\text{des}} \cdot \theta_{\text{NH}_3}$	
	$k_{\text{NO}_x}^{\text{ads}}/\text{s}^{-1}$	$k_{\text{NH}_3}^{\text{ads}}/\text{s}^{-1}$	$k_{\text{NO}_x}^{\text{des}}/\text{s}^{-1}$	$Ea_{\text{NO}_x}^{\text{des}}/\text{kJ mol}^{-1}$	$k_{\text{NH}_3}^{\text{des}}/\text{s}^{-1}$	$Ea_{\text{NH}_3}^{\text{des}}/\text{kJ mol}^{-1}$
<b>H-ZSM-5</b>	$(2.0 \pm 0.3) \times 10^3$	$(5.8 \pm 0.5) \times 10^3$	$(1.9 \pm 0.2) \times 10^{-2}$	$37 \pm 2$	$(1.7 \pm 0.3) \times 10^{-2}$	$29 \pm 3$
<b>Cu-ZSM-5</b>	$(2.0 \pm 0.3) \times 10^3$	$(2.9 \pm 0.5) \times 10^3$	$(7.6 \pm 0.4) \times 10^{-3}$	$84 \pm 4$	$(1.7 \pm 0.3) \times 10^{-3}$	$16 \pm 3$
<b>Na-Cu-ZSM-5</b>	$(2.0 \pm 0.3) \times 10^3$	$(3.7 \pm 0.5) \times 10^3$	$(6.6 \pm 0.3) \times 10^{-3}$	$109 \pm 3$	$(2.5 \pm 0.3) \times 10^{-3}$	$16 \pm 3$
<b>Cu-ZSM-5 (NaOH)</b>	$(2.0 \pm 0.3) \times 10^3$	$(1.5 \pm 0.5) \times 10^3$	$(3.9 \pm 0.1) \times 10^{-3}$	$45 \pm 3$	$(5.7 \pm 0.3) \times 10^{-3}$	$24 \pm 3$
<b>Cu-ZSM-5 (TPAOH)</b>	$(2.0 \pm 0.3) \times 10^3$	$(2.2 \pm 0.5) \times 10^3$	$(5.36 \pm 0.01) \times 10^{-2}$	$47.5 \pm 0.2$	$(2.6 \pm 0.3) \times 10^{-3}$	$23 \pm 3$
<b>Cu-ZSM-5 (NaOH/TPAOH)</b>	$(2.0 \pm 0.3) \times 10^3$	$(1.3 \pm 0.5) \times 10^3$	$(1.6 \pm 0.1) \times 10^{-2}$	$42 \pm 1$	$(1.4 \pm 0.3) \times 10^{-3}$	$20 \pm 1$

\* All rate constants are reported at the temperature of 150 °C. \*\* Temperature influence on the adsorption rate constants was considered negligible.

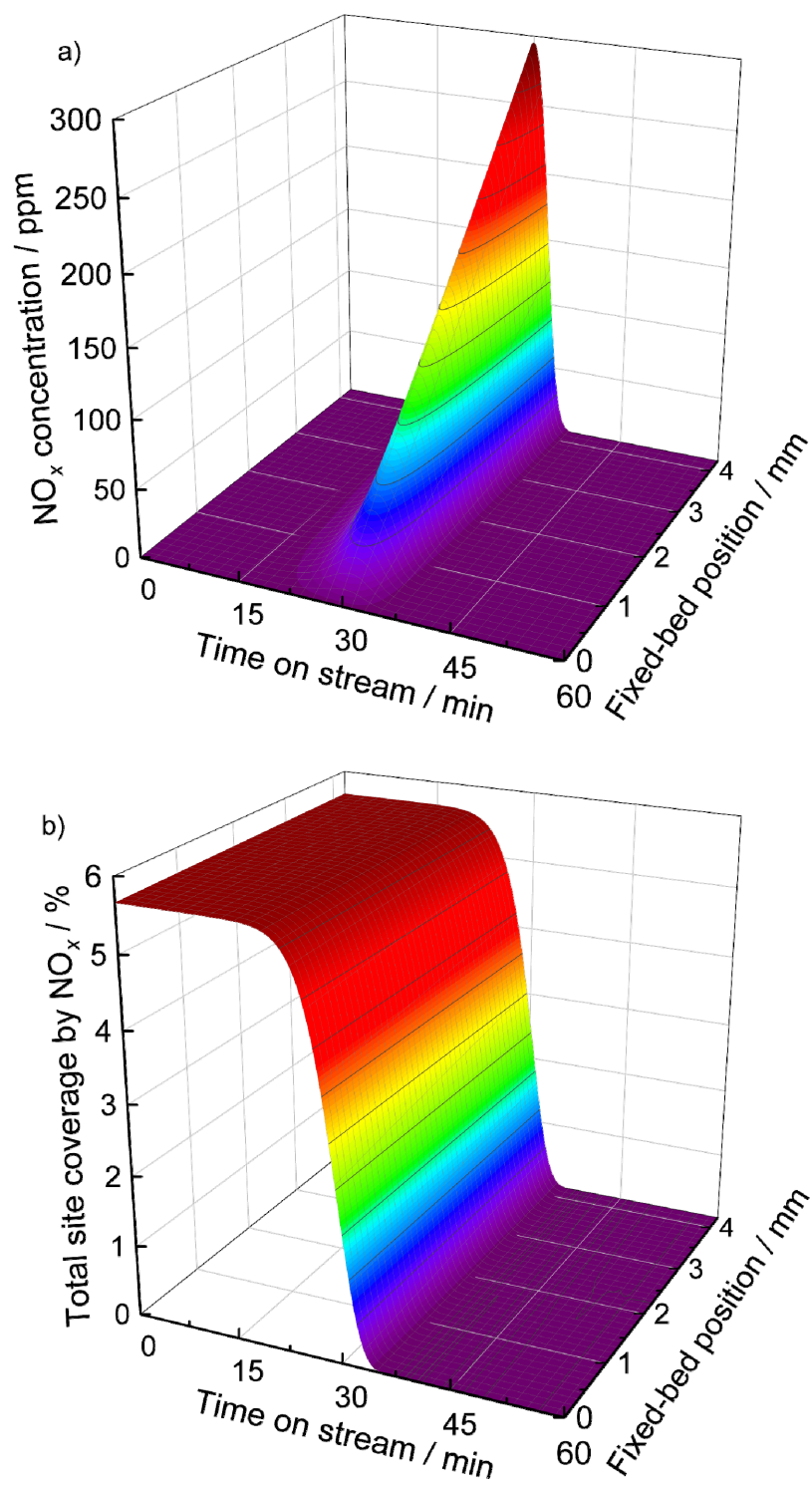
**Table S2.** Preparation procedures applied for modifications of parent ZSM-5.

Samples	Preparation procedure
H-ZSM-5	1) Calcination of $\text{NH}_4^+$ -ZSM-5 (550 °C, 4 h, 1 K min <sup>-1</sup> ).
Cu-ZSM-5	1) Modification of H-ZSM-5 with an aqueous solution of copper precursor (0.05 M, 24 h, RT).
Cu-ZSM-5 (NaOH)	1) Modification of $\text{NH}_4^+$ -ZSM-5 with an aqueous solution of 0.2 M NaOH, TPAOH or mixture of NaOH and TPAOH (65 °C, 2 h under reflux);
Cu-ZSM-5 (TPAOH)	2) A triple ion-exchange with 0.5 M $\text{NH}_4\text{NO}_3$ (60 °C, 1 h) in case of $\text{NH}_4^+$ -ZSM-5 treated with NaOH and NaOH/TPAOH; calcination of obtained materials (550 °C, 4 h, 1 K min <sup>-1</sup> );
Cu-ZSM-5 (NaOH/TPAOH)	3) Modification of H-ZSM-5 with an aqueous solution of copper precursor (0.05 M).
Na-Cu-ZSM-5	1) Modification of H-ZSM-5 with an aqueous solution of co-cation precursor (0.05 M, 80 °C, 2 h); 2) Modification of Na-ZSM-5 with an aqueous solution of copper precursor (0.05 M, 24 h, RT).

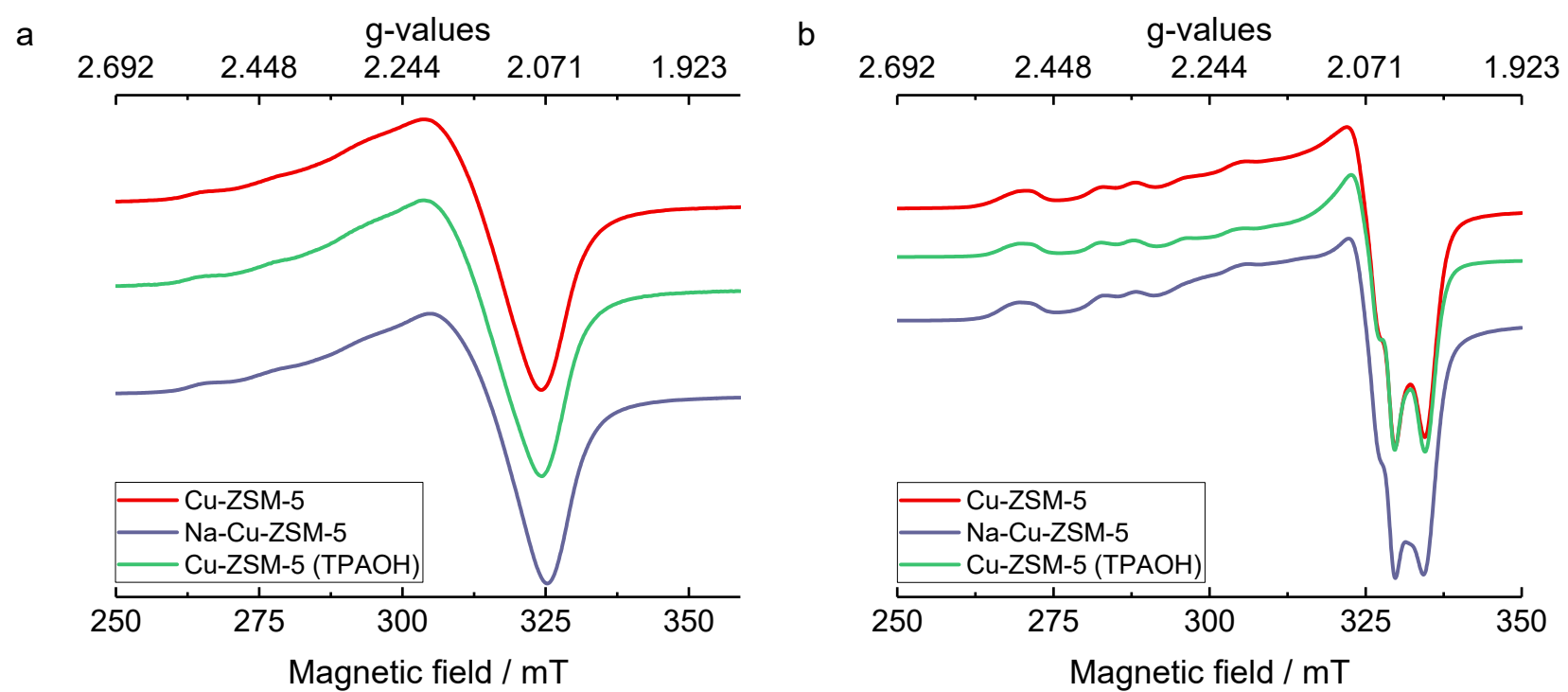
**Table S3.** Relevant parameters for kinetic modelling.

Property	Symbol	Value
Bed length	$Z$	8.6 mm *
Bed porosity	$\alpha$	0.29
Catalyst mass	$m_{\text{cat}}$	200 mg **
Volumetric velocity	$\dot{V}$	120 ml min <sup>-1</sup> ***
Temperature of the mass flow controllers	$T_{\text{MFC}}$	293 K

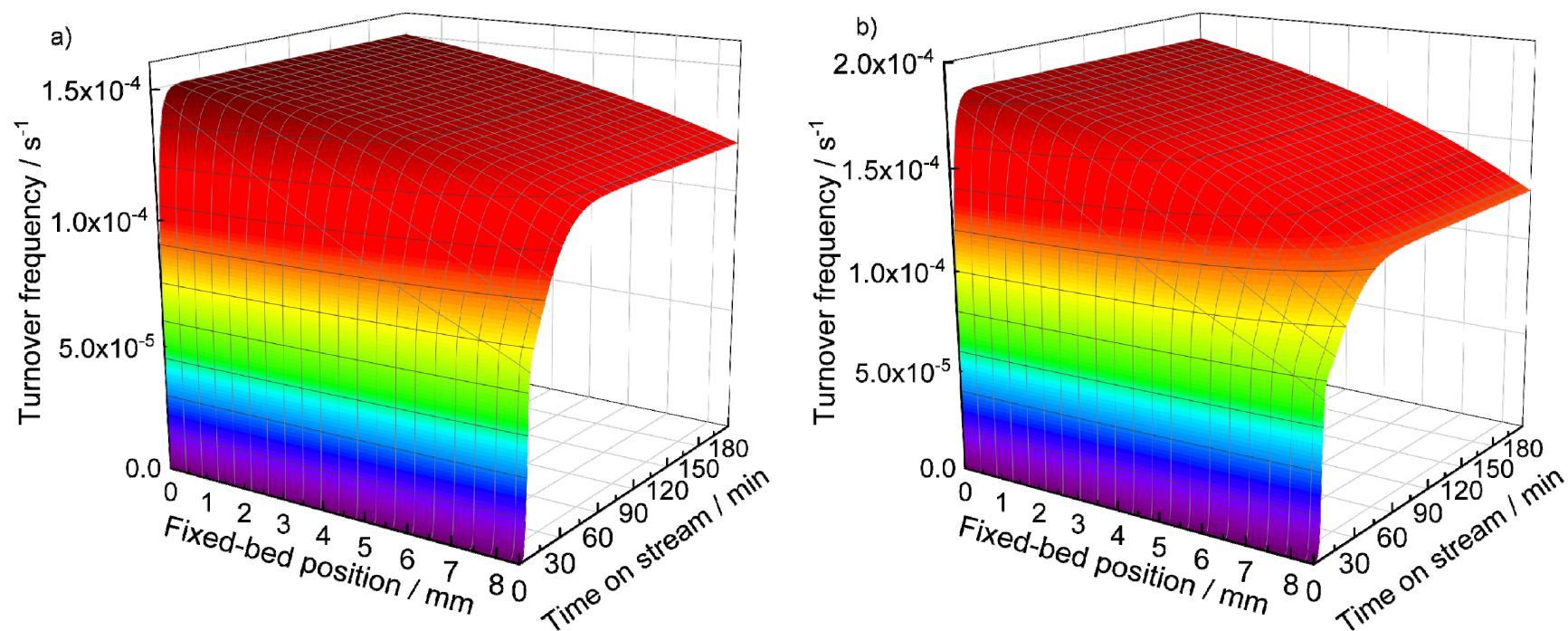
\*4.3 mm for TPD-NO<sub>x</sub> tests; \*\*100 mg for TPD-NO<sub>x</sub> tests; \*\*\*50 ml min<sup>-1</sup> for TPD-NO<sub>x</sub> tests



**Figure S1.** (a) NO concentration in the gas phase and (b) NO surface coverage as a function of time on stream and position in the reactor during the TPD-NO<sub>x</sub> at 150 °C over Na-Cu-ZSM-5 conversion (conditions: 0.1 g of catalyst, 50 mL min<sup>-1</sup>, 0 ppm NO, heat-up rate 10 K min<sup>-1</sup>, initial temperature 50 °C).



**Figure S2.** Experimental cw-EPR spectra of (a) hydrated and (b) dehydrated Cu-ZSM-5 acquired at room temperature.



**Figure S3.** TOF<sub>1</sub> as a function of time on stream and position in the reactor for NH<sub>3</sub>-SCR at 150 °C over Cu-ZSM-5 conversion in (a) absence and (b) presence of 5 vol.-% H<sub>2</sub>O (conditions: 0.2 g of catalyst, 120 mL min<sup>-1</sup>, 500 ppm NO, 575 ppm NH<sub>3</sub>).