Low-Temperature Standard-SCR over Cu-SSZ-13: Selective Inhibition of the Oxidation Half-Cycle by Mild Hydrothermal Aging

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Supplementary Information

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1. Characterization

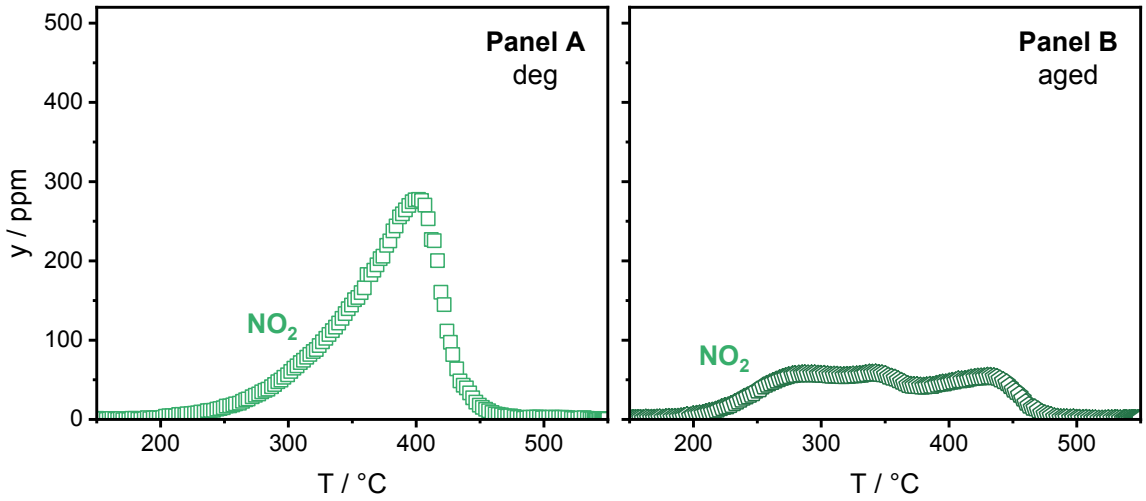

Figure SI.1 – NO_2 TPD outlet profiles from NO_2 adsorption + TPD protocol. Panels: A) Degreened sample, B) Aged sample. Pretreatment feed: GHSV = 266,250 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP), T = 550 °C; O_2 = 8.0 % v/v in He. Adsorption feed: GHSV = 266,250 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP), T = 150 °C; NO_2 = 500 ppm in He. TPD: GHSV = 266,250 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP), T = 150-550 °C at 2 °C min^{-1}; feed: He only.

2. Reduction Half-Cycle

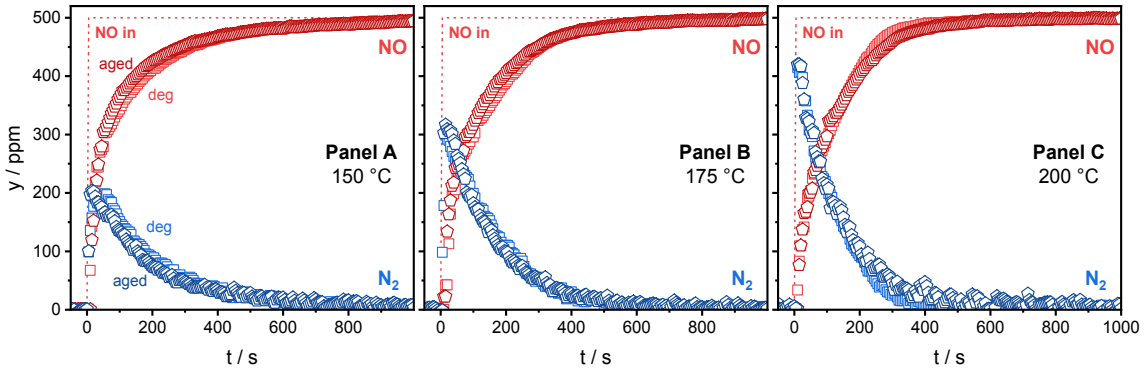

Figure SI.2 – NO and N_2 transient outlet profiles from RHC protocol: direct comparison of experimental data on Degreened and Aged samples. Panels: A) 150 °C, B) 175 °C, C) 200 °C. Legend: squares for deg, pentagons for aged. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm and H_2O= 2.0 % v/v in He.

Reduction Half-Cycle	NO consumed / µmol		N_2 produced / µmol	
	Degreened	Aged	Degreened	Aged
150 °C	11.2	11.3	10.9	11.2
175 °C	11.9	11.5	11.8	11.4
200 °C	10.7	11.3	10.8	10.8

Table SI.1 – Experimental NO consumption and N_2 production during RHC protocol over the Degreened and the Aged samples at the three studied temperatures: 150, 175, and 200 °C. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm and H_2O= 2.0 % v/v in He.

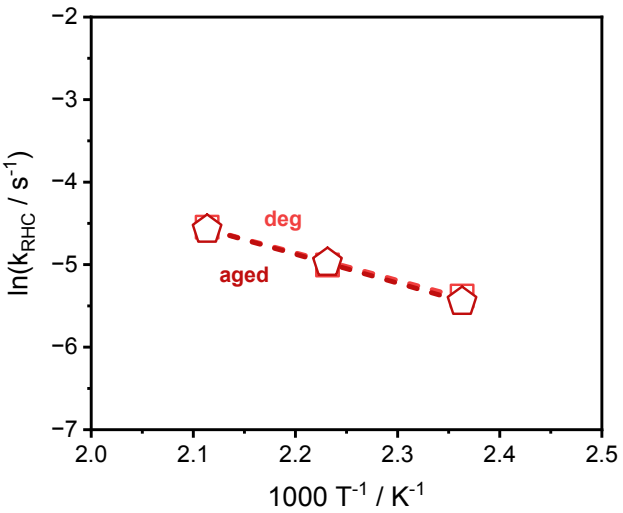

Figure SI.3 – RHC Arrhenius plot of Degreened and Aged samples. Legend: squares for deg, pentagons for aged. Activation energy: 27.7 ± 2.5 kJ mol^{-1} for Degreened, 29.1 ± 0.5 kJ mol^{-1} for Aged sample.

3. Oxidation Half-Cycle

OHC at 150 °C	NO consumed / µmol		N_2 produced / µmol	
t / s	Degreened	Aged	Degreened	Aged
60	1.6	1.0	1.7	0.8
120	3.0	1.6	3.1	1.7
180	3.8	2.1	3.7	2.1
420	5.8	3.2	5.6	3.1
900	8.3	5.4	8.2	5.6
3600	10.8	8.6	10.9	8.3

Table SI.2 – Experimental NO consumption and N_2 production during OHC protocol over the Degreened and the Aged samples at 150 °C. Reduction feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm and H_2O= 2.0 % v/v in He. Oxidation feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); O_2 = 1.0 % v/v and H_2O= 2.0 % v/v in He.

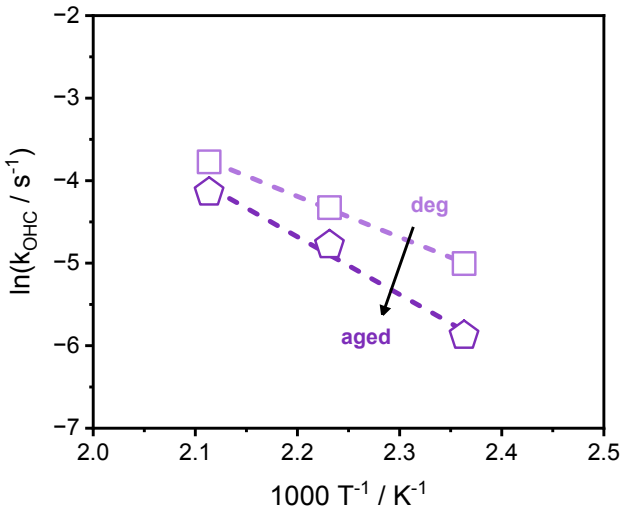

Figure SI.4 – OHC Arrhenius plot of Degreened and Aged samples. Legend: squares for deg, pentagons for aged. Activation energy: 41.1 ± 1.0 kJ mol^{-1} for Degreened, 58.0 ± 6.9 kJ mol^{-1} for Aged sample.

4. Combination of RHC and OHC in the Standard-SCR

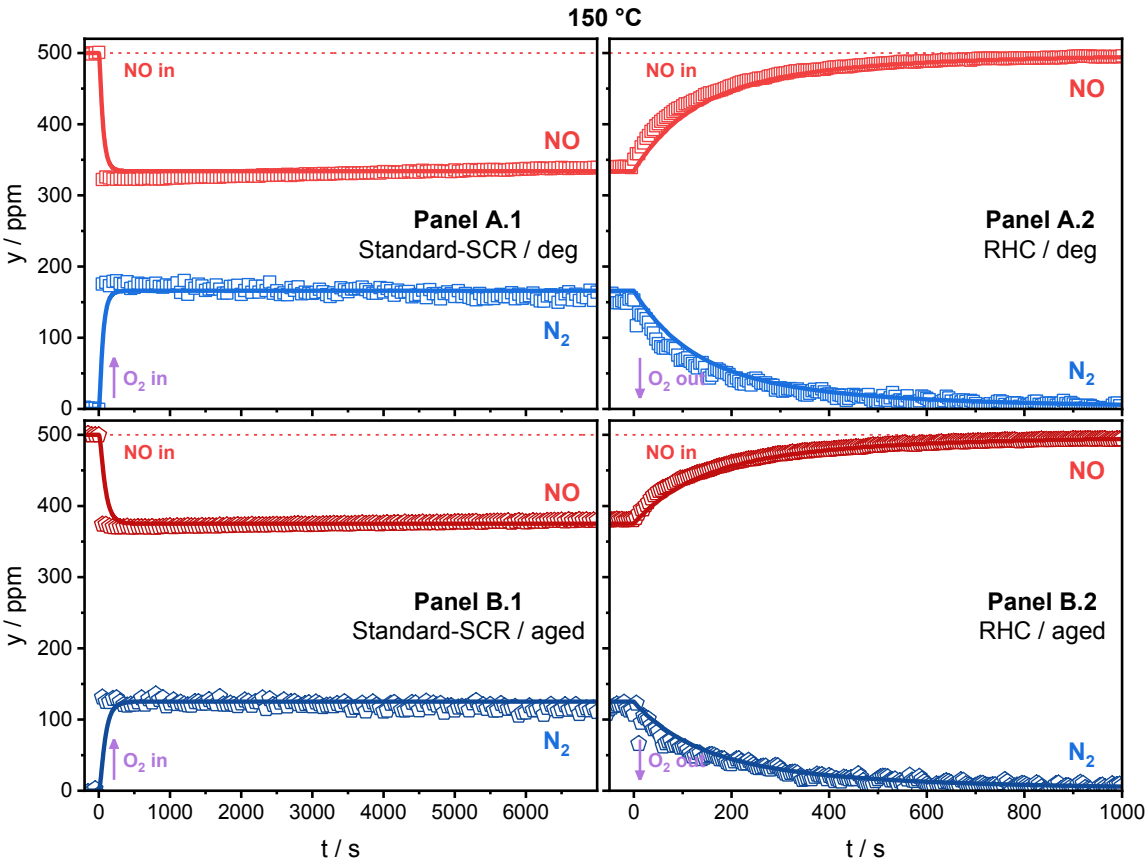

Figure SI.5 – NO and N_2 transient outlet profiles from the Standard-SCR protocol on Degreened and Aged samples at 150 °C. Panels: A) Degreened, B) Aged, 1) Standard-SCR, 2) RHC following Standard-SCR. Symbols: experimental data (red for NO, blue for N_2, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 8.0-0.0 % v/v and H_2O= 2.0 % v/v in He.

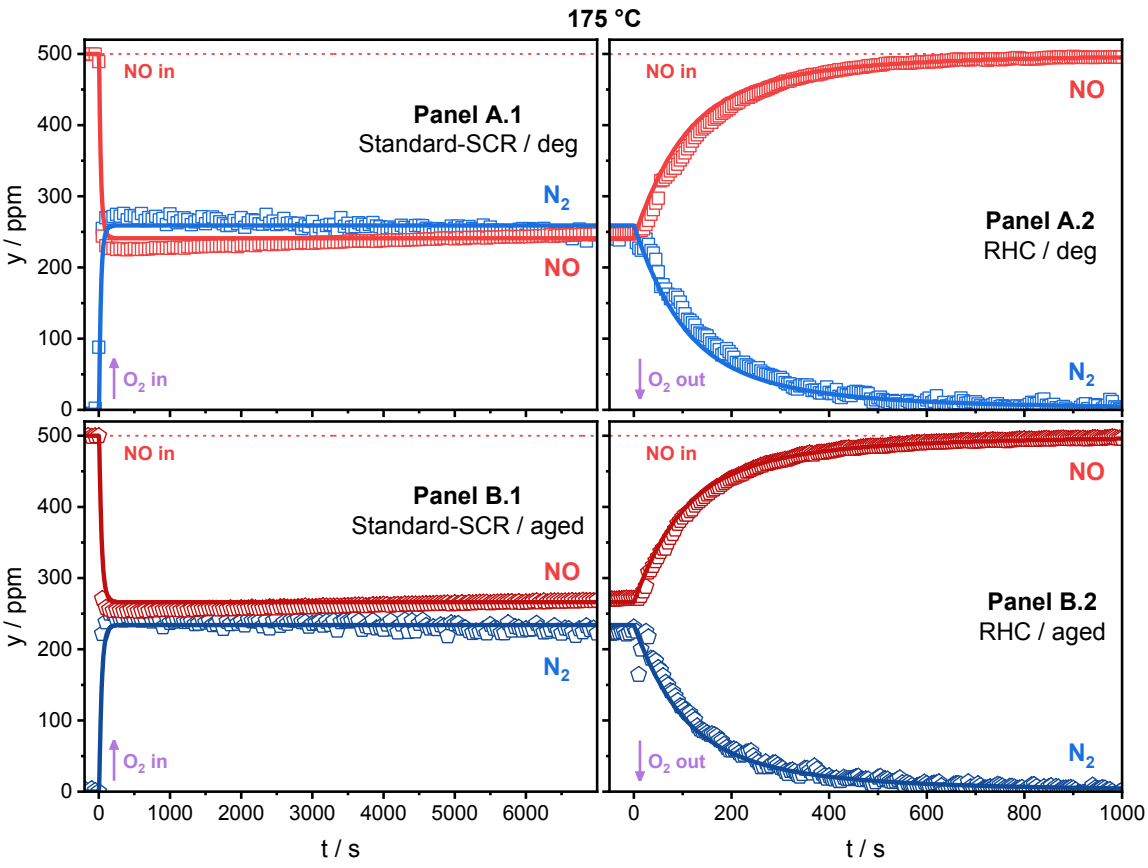

Figure SI.6 – NO and N_2 transient outlet profiles from the Standard-SCR protocol on Degreened and Aged samples at 175 °C. Panels: A) Degreened, B) Aged, 1) Standard-SCR, 2) RHC following Standard-SCR. Symbols: experimental data (red for NO, blue for N_2, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 8.0-0.0 % v/v and H_2O= 2.0 % v/v in He.

5. Oxygen-based recovery of activity

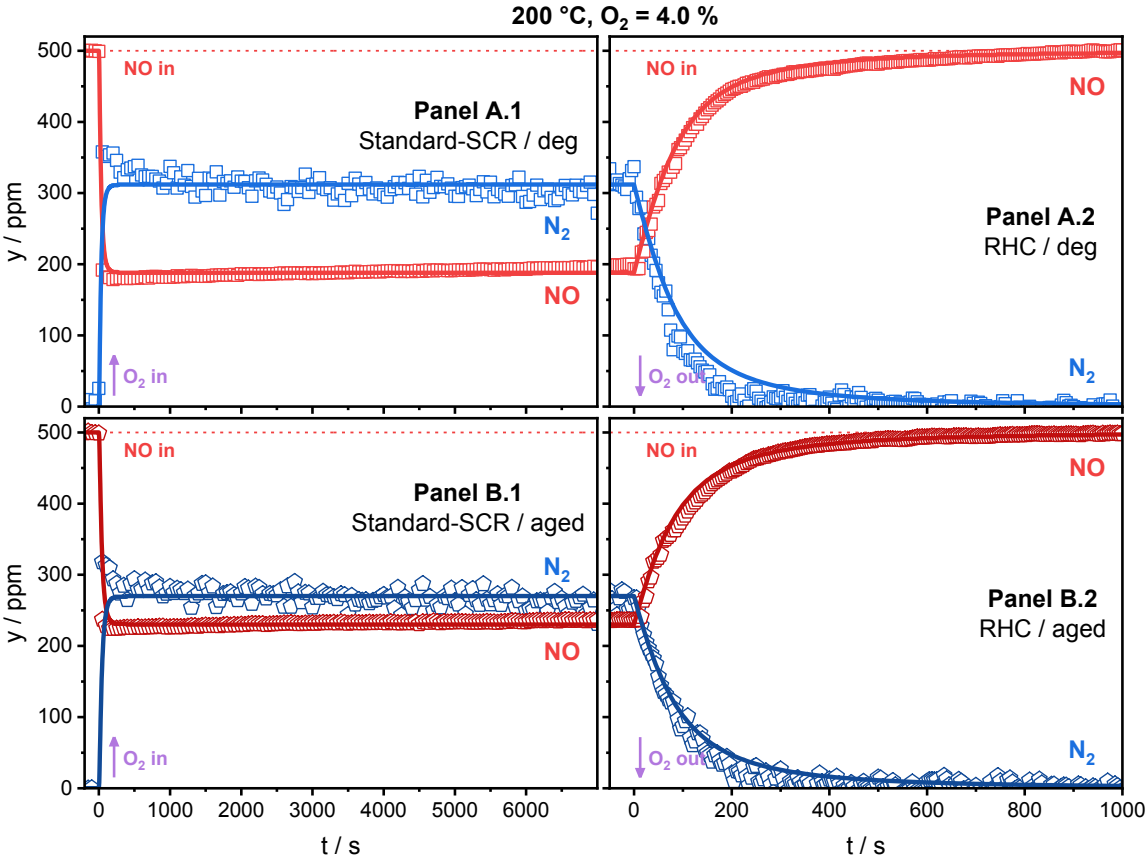

Figure SI.7 – NO and N_2 transient outlet profiles from Standard-SCR protocol on Degreened and Aged samples at 200 °C and 4.0 % of O_2. Panels: A) Degreened, B) Aged, 1) Standard-SCR, 2) RHC following Standard-SCR. Symbols: experimental data (red for NO, blue for N_2, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 4.0-0.0 % v/v and H_2O= 2.0 % v/v in He.

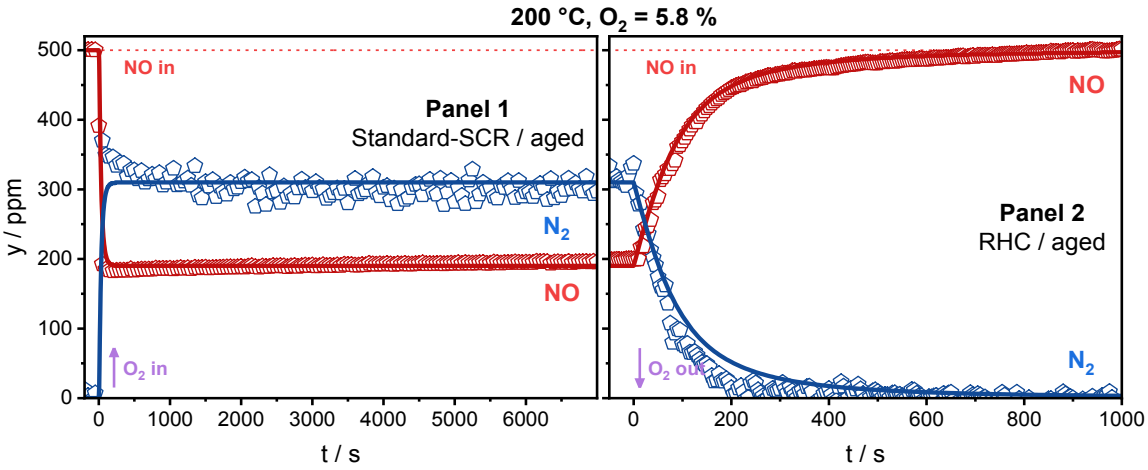

Figure SI.8 – NO and N_2 transient outlet profiles from Standard-SCR protocol on Aged sample at 200 °C and 5.8 % of O_2. Panels: 1) Standard-SCR, 2) RHC following Standard-SCR. Symbols: experimental data (red for NO, blue for N_2). Solid lines: model fit. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 5.8-0.0 % v/v and H_2O= 2.0 % v/v in He.

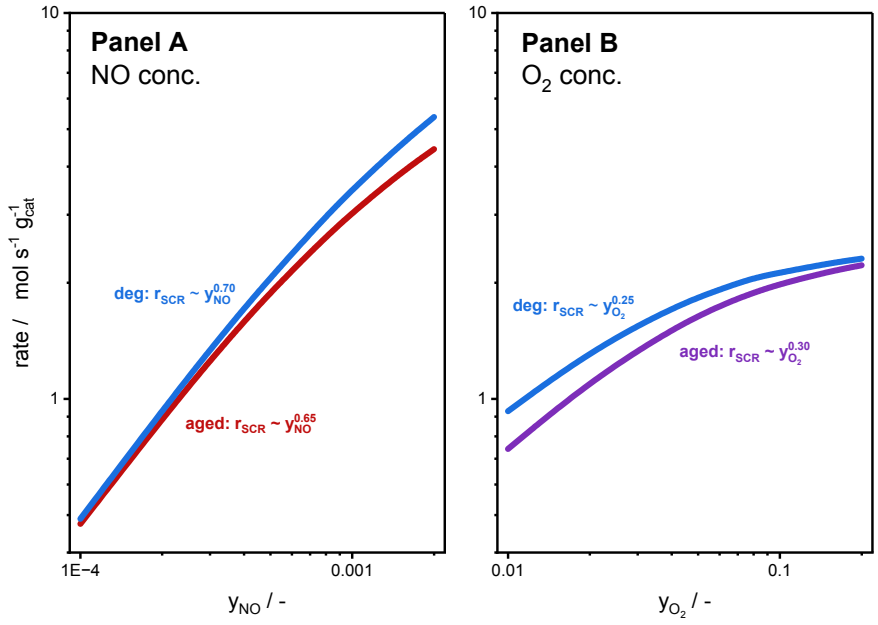

Figure SI.9 – Simulated NO conversion rates at 200 °C as a function of (1) NO concentration and (2) O_2 concentration. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 8.0 % v/v and H_2O= 2.0 % v/v in He, except as noted. The colored full lines correspond to the simulated rates, while the black dotted curves correspond to the fit of the rates with a $r = ky^{\alpha}$ type equation.

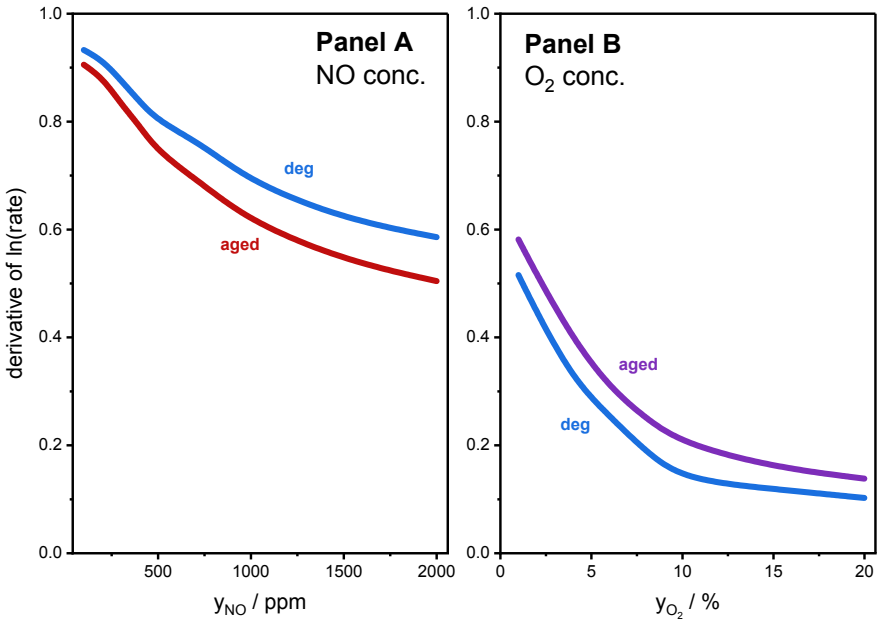

Figure SI.10 – Derivative of the simulated $\log_{10} r_{SCR}$ versus the (A) NO concentration and (B) O_2 concentration. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 8.0 % v/v and H_2O= 2.0 % v/v in He, except as noted.

6. Combined effect of H_2O and HTA on RHC, OHC, and Standard-SCR

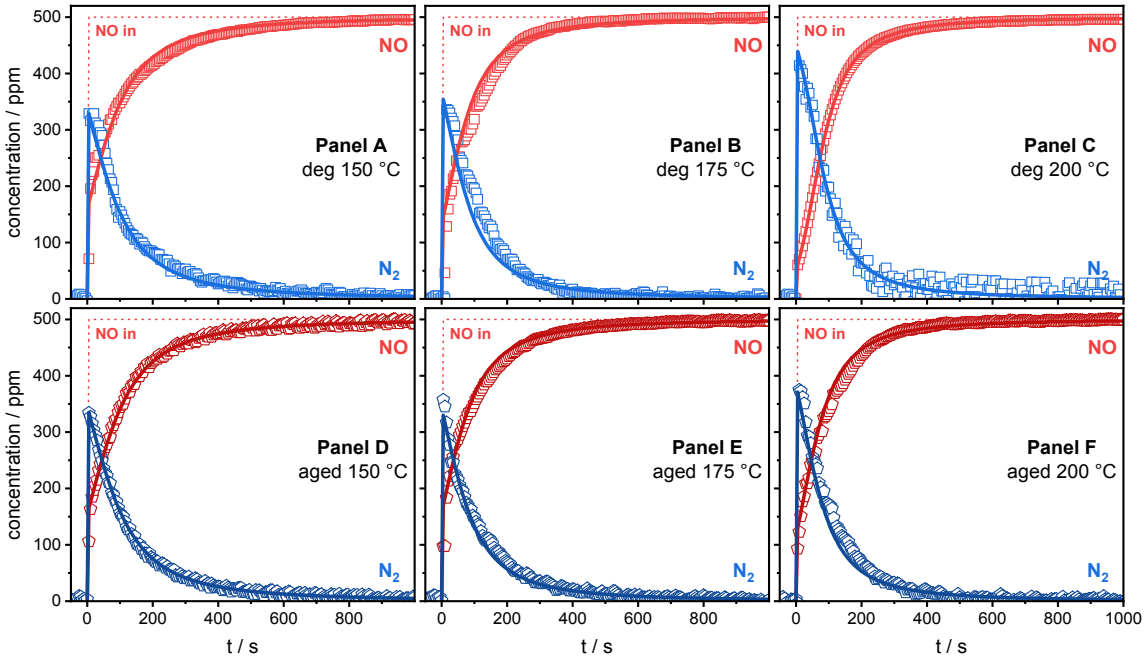

Figure SI.11 – NO and N_2 dynamics during RHC protocols in dry-gas conditions on Degreened and Aged samples. Panels: A) deg 150 °C, B) deg 175 °C, C) deg 200 °C, D) aged 150 °C, E) aged 175 °C, F) aged 200 °C. Symbols: experimental data (red for NO, blue for N_2, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm and H_2O = 0.0 % v/v in He.

k_{RHC} / s^{-1}	Degreened		Aged	
	Dry	Wet	Dry	Wet
150 °C	7.4 E-03	4.6 E-03	7.0 E-03	4.3 E-03
175 °C	11.0 E-03	6.7 E-03	10.4 E-03	6.9 E-03
200 °C	13.9 E-03	10.6 E-03	13.1 E-03	10.3 E-03

Table SI.3 – RHC rate constants in dry-gas conditions over the Degreened and the Aged samples at the three studied temperatures: 150, 175, and 200 °C. The wet RHC rate constants reported in Table 1 are reproduced here for direct comparison.

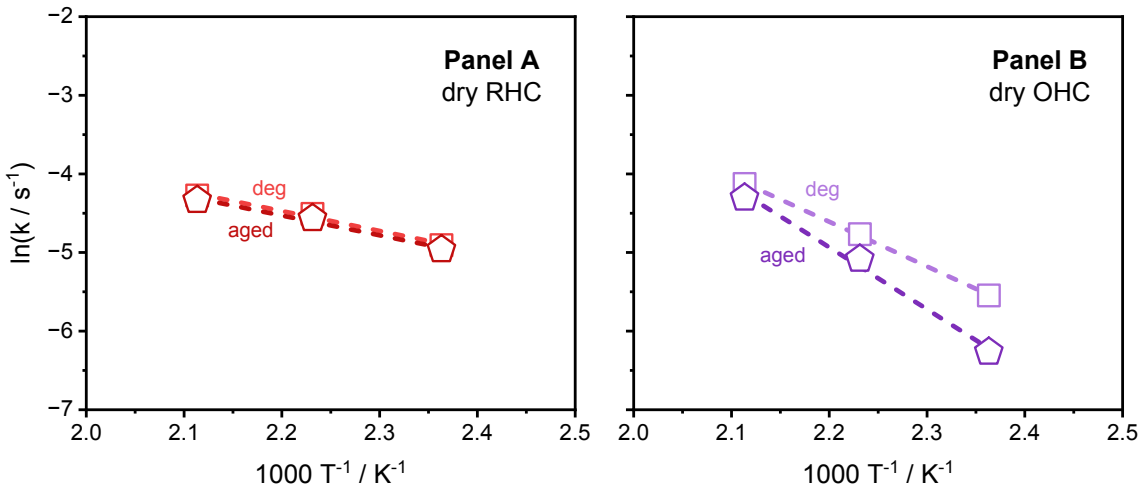

Figure SI.12 – Arrhenius plot in dry-gas conditions for RHC and OHC, panels (A) and (B) respectively, over the Degreened and the Aged samples. Legend: squares for deg, pentagons for aged.

Dry Standard-SCR	Exp. (Model) X_{NO} / %		Exp. (Model) σ_{ss} / %	
	Degreened	Aged	Degreened	Aged
150 °C	35.1 (34.8)	25.3 (25.4)	44.6 (44.7)	41.5 (41.3)
175 °C	54.8 (54.0)	49.8 (49.2)	51.5 (51.7)	47.7 (47.9)
200 °C	77.8 (76.8)	72.8 (71.0)	60.0 (60.1)	57.7 (57.7)

Table SI.4 – Experimental NO conversion (X_{NO}) and bed-average oxidized Cu fraction (σ_{ss}) during steady-state Standard-SCR in dry-gas conditions over the Degreened and the Aged samples at the three studied temperatures: 150, 175, and 200 °C. In parenthesis the values obtained from the model using the rate constants of Tables SI.5 and SI.7. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = 500 ppm, NH_3 = 500 ppm, O_2 = 8.0 % v/v, and H_2O = 0.0 % v/v in He.

k_{OHC} / s^{-1}	Degreened		Aged	
	Dry	Wet	Dry	Wet
150 °C	3.9 E-03	6.7 E-03	1.9 E-03	2.8 E-03
175 °C	8.5 E-03	13.2 E-03	6.2 E-03	8.4 E-03
200 °C	16.1 E-03	23.0 E-03	13.5 E-03	15.9 E-03

Table SI.5 – OHC rate constants in dry-gas conditions over the Degreened and the Aged samples at the three studied temperatures: 150, 175, and 200 °C. The wet OHC rate constants reported in Table 2 are reproduced here for direct comparison.

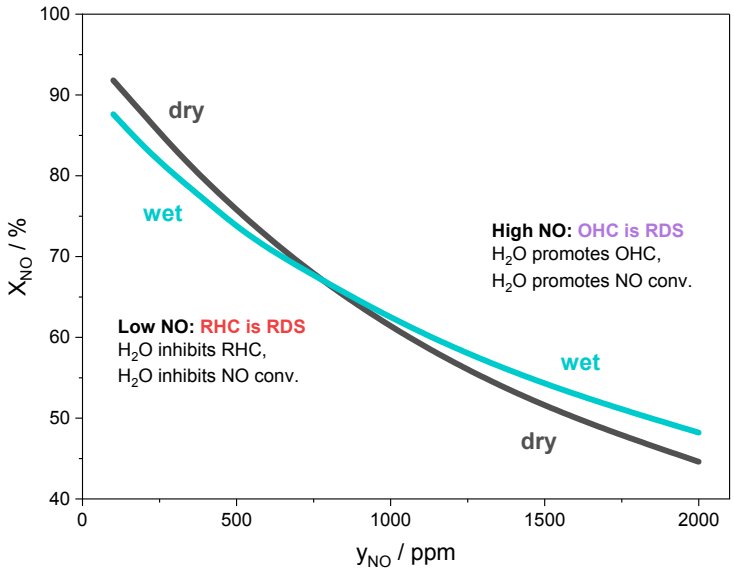

Figure SI.13 – Simulated NO conversions at 200 °C as a function of feed NO concentration in dry and wet conditions over the Degreened sample. Feed: GHSV = 450,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (STP); NO = NH_3 = 100-2000 ppm, O_2 = 8.0 % v/v and H_2O= 0.0-2.0 % v/v in He.