Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI)

NOx SCR by urea: exceptional reactivity of HNCO toward NO_2

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Experimental set-up for catalytic tests (Urea-SCR and NH_3-SCR).

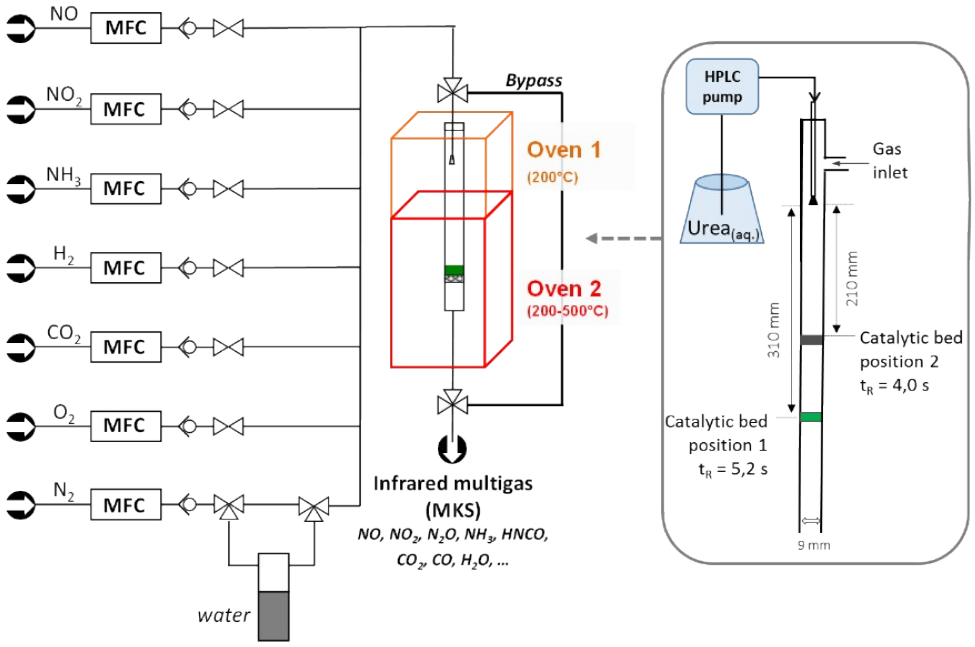

Figure S1. Scheme of the experimental set-up for catalytic tests (Urea-SCR and NH_3-SCR).

The synthetic gas bench was adjusted to powdered catalysts (100 mg) and allowed the direct comparison of NH_3-SCR and Urea-SCR reactions was recently developed.
The total flow rate was fixed at 20 L h^{-1}, which corresponds to a GHSV of about 160,000 h^{-1}. For water and urea addition, an aqueous solution containing urea (1.33 10^{-1} M, i.e. 0.794 $_{wt}$%) was vaporized via a micro-nozzle (Ø=50 µm), provided by The Lee Company, into a heated zone at 200°C upstream the catalytic bed. The liquid flow rate (19 µL min^{-1}) was controlled by a HPLC micro pump (Jasco PU-2085, ΔP_{pump}=10 bar).
The catalyst was placed in a quartz tubular micro-reactor (internal diameter of 8 mm) and its location can be changed in order to examine different residence time between the urea injection (placed upstream the catalytic bed into a heated zone at 200°C), and the catalytic bed, which is placed in a subsequent oven at temperature controlled between 200 and 500°C. The residence time (elapsed time for the gaseous mixture between urea injection zone and the catalytic bed) was fixed at 5.2 s or 4.0 s. Note that the velocity of the urea ejection at the nozzle outlet is not considered for this calculation.

The compositions of the feed gas and effluent stream were monitored continuously using online MKS 2030 multigas infrared analyzer for NO, NO_2, N_2O, HNCO, NH_3, CO, CO_2 and H_2O. It is important to note that without catalyst, in Urea-SCR condition, complete urea decomposition into ammonia is fully achieved at the analyser level, due to a long residence time between the catalyst and the analyser of about 34 s (all pipes are heated at 200°C, no HNCO is recorded). Consequently, only NH_3 is detected, and the urea analysis is expressed as equivalent detected ammonia, denoted "NH_3(eq)".

The specifications of the MKS 2030 Multigas infrared analyser are reported below:
- Accuracy (difference between measured value and reference value): ≤ 2% of reference value.
- Repeatability (variation in measured values of the same reference cylinder measured several times, each time after performing the zero and span steps): ≤ 1% of reference value.
- Noise (short term repeatability of measured value in zero gas): ≤ 1% of instrument range.

- Linearity (defines the correlation between measured values and reference values spanning the full concentration range): Slope between 0.99 and 1.01; Intercept ≤ 1.0%; SEE ≤ 1.0%, R2 ≥ 0.998
- Drift (drift of measured value from span cylinder and zero cylinder during interval of 24 hours, with no zeroing or spanning in between): ≤ 2% of instrument range
- Interference (cross-sensitivity or bias due to typical levels of 10% H2O and 10% CO2): ≤ 0.5% of instrument range
- Detection Limits (minimum concentration which can be differentiated from "zero" in a gas stream containing the main interferent gases 10% H_2O and 10% CO_2): See Table S1 below

Table S1: Detection Limits in a gas stream containing the main interferent gases 10% H_2O and 10% CO_2.

Gas	NO	NO_2	NH_3	N_2O	CO
Detection limit (ppm)	1	0.6	0.4	0.4	0.75

Experimental data obtained in "NO_2 only" SCR

Table S2. Experimental data obtained in "NO_2 only" SCR. Gas mixture: urea =200 ppm (t_R = 4.0 s), 400 ppm NO_2, 10 % O_2, 8 % H_2O) and detailed N-species balance at 200°C.

"NO_2 only" SCR with urea					Detailed data recorded at 200°C			
T (°C)	NO out (ppm)	NO_2 out (ppm)	NOx conv. (%)	Reduct. conv. (%)		Inlet Conc. (ppm)	Outlet conc. (ppm)	Δ (ppm)
200	42	272	21	97	NOx	400	314	**-86**
250	38	253	27	98	*NO_2*	*400*	*272*	*- 128*
300	42	235	31	97				
350	35	233	33	97	*NO*	*0*	*42*	*+42*
400	36	236	32	99				
450	39	238	30	98	$NH_{3\,(eq)}$	400 $_{(eq)}$	**12**	-388
500	32	254	28	99				