Supplementary Information

1. NH_3 Amount Added in Urea SCR Mixture (t_R = 4.0 s)

These tests were performed with the aim to compensate the decrease of the NO_x conversion in urea-SCR with t_R = 4.0 s.

Table S1. NO_x conversion in urea-SCR and NH_3-SCR depending on the experimental condition.

Temp. (°C)	NO_x Conv. (%) in NH_3-SCR	NO_x Conv. (%) in Urea-SCR (t_R = 5.2 s)	NO_x Conv. (%) in Urea-SCR (t_R = 4.0 s)	NH_3 Added (ppm) in Urea-SCR (t_R = 4.0 s)	NO_x Conv. (%) in Urea-SCR (t_R = 4.0 s) with Added NH_3
200	48	43	25	80	46
250	74	70	37	135	73
300	89	85	52	130	83
350	93	90	65	103	88
400	93	91	76	60	88
450	91	88	81	30	86
500	87	83	71	50	81

2. Effect of Gaseous NH_3 Added at 200 °C in Urea-SCR for t_R = 4.0 s

Figure S1 shows that during SCR test with urea (t_R = 4.0 s), the NO_x conversion increased with the addition of gaseous ammonia in the feed stream until approximately 50 ppm. This concentration corresponds to the necessary theoretical value to compensate the decrease of the NO_x conversion in urea-SCR with t_R = 4.0 s compared with t_R = 5.2 s at 200 °C. In the presence of excess of ammonia gas (added ammonia concentration higher than 50 ppm), the NO_x conversion becomes constant, indicating a NH_3 reaction order close to zero.

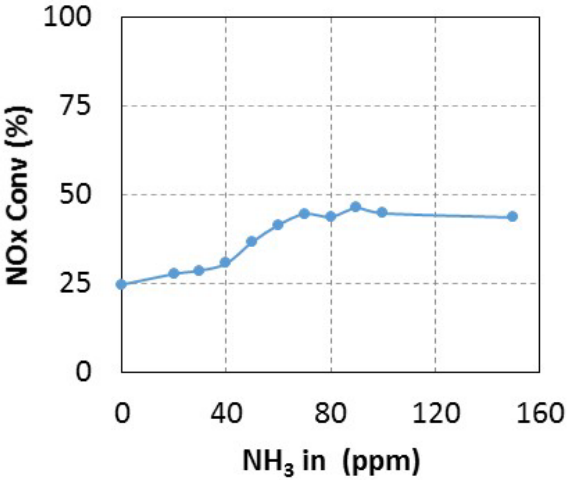

Figure S1. Effect of gaseous NH_3 added at 200 °C in urea-SCR for t_R = 4.0 s.

3. Thermodynamic Calculation

$$2HNCO + NO_2 + 2O_2 \rightarrow 3NO + H_2O + 2CO_2 \quad \text{(S1)}$$

Table S2. Thermodynamic data.

Products	**$\Delta_f H°_{298}$ (kJ·mol^{-1})**	**C_P (J·K^{-1}·mol^{-1})**	**$S°_{298}$ (J·K^{-1}·mol^{-1})**
urea	−333	93	104
HNCO(g)	−116.3	44	238.1
H_2O(g)	−241.8	33.6	188.8
CO_2(g)	−393.5	37.1	213.8
NO(g)	91.3	29.9	210.8
NO_2(g)	33.2	37.2	240.1
O_2(g)	0	29.4	204.8

Data are extracted from “Handbook of chemistry and physics, 78th edition, 1998, crc press” except for urea (Andersson, O.; Matsuo, T.; Suga, H.; Ferloni, P. Low-temperature heat capacity of urea. *Int. J. Thermophys*. 1993, *14*, 149–158) and HNCO (Chase, M.W., Jr. *NIST-JANAF Themochemical Tables*, Fourth Edition, *J. Phys. Chem. Ref. Data, Monograph 9*, 1998, 1–1951).

$$\Delta_r G°_{573} = \Delta_r H°_{573} - 573 \times \Delta_r S°_{573} \quad \text{(S2)}$$

$$\Delta_r H°_{573} = \Delta_r H°_{298} + \int_{298}^{573} (\Delta C_p)_{gaz}\, dT \quad \text{(S3)}$$

$$\Delta_r H°_{298} = 3\,\Delta_f H°(NO) + 2\,\Delta_f H°(CO_2) + \Delta_f H°(H_2O) - 2\,\Delta_f H°(O_2) - \Delta_f H°(NO_2) - 2\,\Delta_f H°(HNCO) = -555.5\ \text{kJ·mol}^{-1} \quad \text{(S4)}$$

$$(\Delta C_p)_{gaz} = 3\,C_p\,(NO) + 2\,C_p\,(CO_2) + C_p\,(H_2O) - 2\,C_p\,(O_2) - C_p\,(NO_2) - 2\,C_p\,(HNCO) = 13.5\ \text{J·K}^{-1}\ \text{constant} \quad \text{(S5)}$$

$$\Delta_r H°_{573} = -555{,}500 + 13.5 \cdot (573 - 298) = -551.8\ \text{kJ} \quad \text{(S6)}$$

$$\Delta_r S°_{298} = 3\,\Delta S°(NO) + 2\,\Delta S°(CO_2) + \Delta S°(H_2O) - 2\,\Delta S°(O_2) - \Delta S°(NO_2) - 2\,\Delta S°(HNCO) = 122.9\ \text{J·K}^{-1}\text{·mol}^{-1} \quad \text{(S7)}$$

$$\Delta_r S°_{573} = \Delta_r S°_{298} + \int_{298}^{573} (\Delta C_p)_{gaz}\, dT/T = 122.9 + 13.5 \ln(573/298) = 131.7\ \text{J·K}^{-1} \quad \text{(S8)}$$

$$\Delta_r G°_{573} = -551{,}800 - 573 \times (131.7) = -627\ \text{kJ} \quad \text{(S9)}$$