Experimental and Modeling Study of Low Temperature Activity Enhancement of Fe-Zeolite SCR Catalyst

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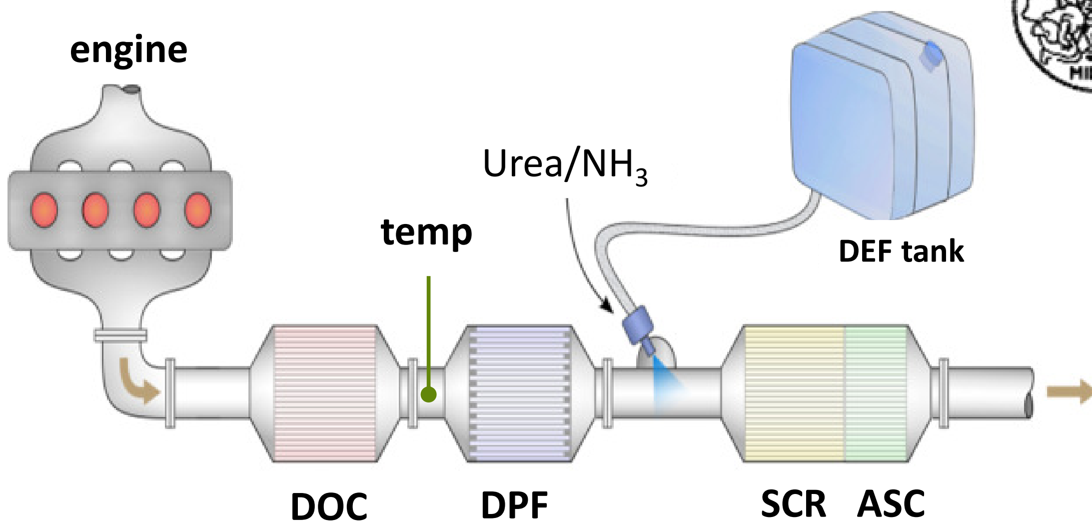
Diesel Vehicle Aftertreatment Processes

Commercial catalysts:
Fe-zeolites, Cu-zeolite,
V_2O_5-WO_3/TiO_2

Operating temperatures:
150 - 550/600°C

Dynamic operation



NO oxidation to NO_2:

$NO + \frac{1}{2} O_2 \rightarrow \mathbf{NO_2}$

Standard SCR reaction: $2NH_3 + 2NO + \frac{1}{2} O_2 \rightarrow 2N_2 + 3H_2O$

NO₂ SCR reaction: $\frac{3}{4}\mathbf{NO_2} + NH_3 \rightarrow \frac{7}{8}N_2 + \frac{3}{2}H_2O$

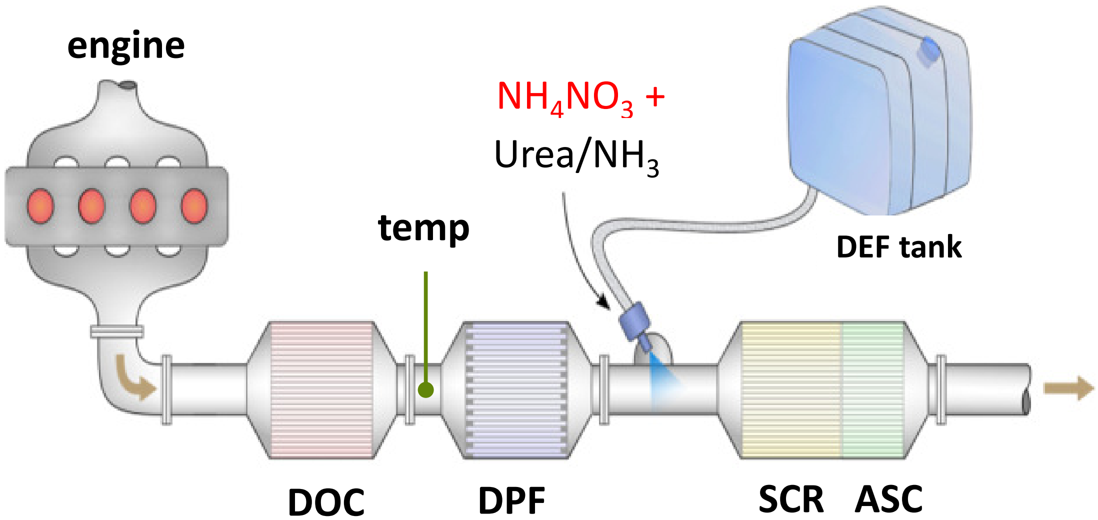
Fast SCR reaction: $NO + \mathbf{NO_2} + 2NH_3 \rightarrow 2N_2 + 3H_2O$

Diesel Vehicle Aftertreatment Processes

Opportunities for improving SCR-based EGA systems:

- enhance low temperature performances of SCR catalyst
- reduce dependence on DOC activity ➔ no need of NO_2 in feed to SCR converter

Commercial catalysts:
Fe-zeolites, Cu-zeolite, V_2O_5-WO_3/TiO_2



New technology: "**Enhanced SCR**" **(E-SCR)** [1]

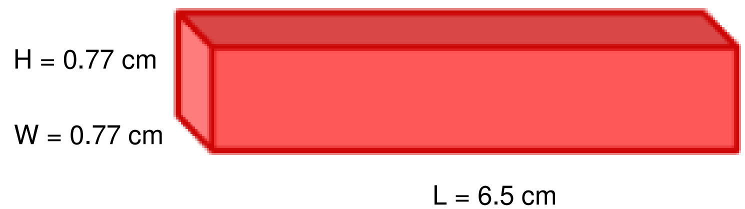
$$2NH_3 + 2NO + \boldsymbol{NH_4NO_3} \rightarrow 3N_2 + 5H_2O$$

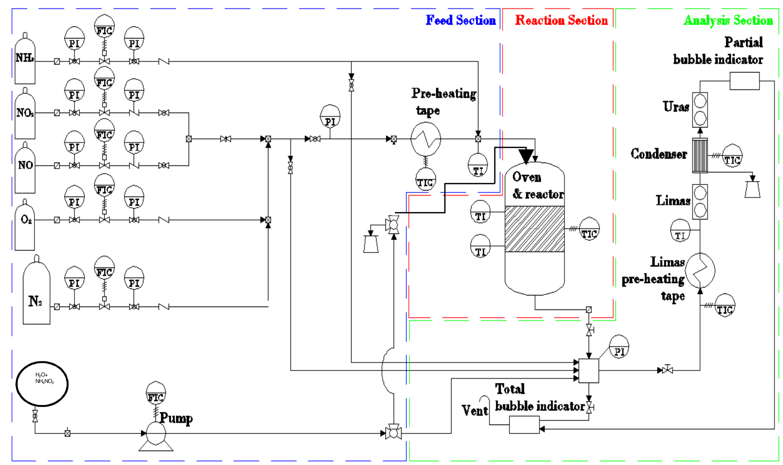
T = 180 - 350°C

[1] P. Forzatti et al. Angewandte Chemie, 121 (2009) 8516-8518

Experimental - SCR Testing Conditions

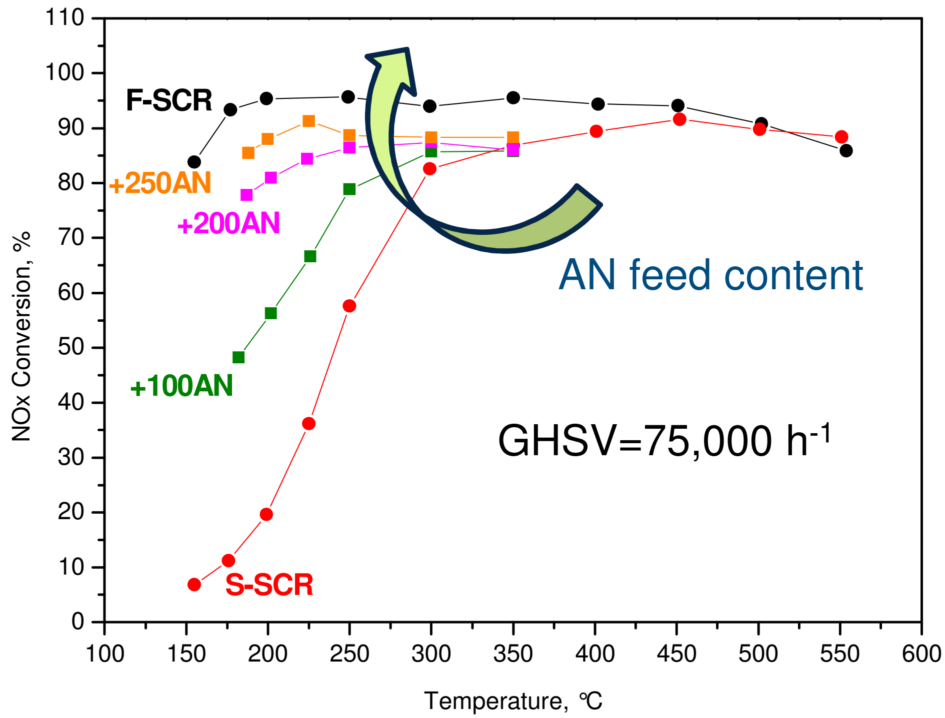
- ✓ **Catalyst sample:**
  - Fe-Zeolite, Umicore
  - Size: 0.77cm x 0.77cm x 6.5cm (6 x 6 cells)
- ✓ **Feed composition:**
  - NH_3 = 500 ppm
  - NO = 500, 400, 250 ppm
  - NO_2 = 0, 100, 250 ppm
  - O_2 = 8% v/v
  - $NH_4NO_3/H_2O(l)$ ➔ 5% H_2O (g)
  - NH_4NO_3 = 0, 100, 200, 250, 350 ppm
- ✓ **Temperature:** 150 - 550°C
- ✓ **GHSV:** 35000, 50000, 75000, 100000 h^{-1}





E-SCR effectiveness

NOx Conversion of S-SCR, F-SCR and E-SCR vs. catalyst temperature



Test Conditions:

GHSV=75000h^{-1};

NH_3=500 ppm (all runs);

NO=500 ppm (S-SCR, E-SCR),

250ppm (F-SCR);

NO_2=0 ppm (S-SCR, E-SCR),

250ppm (F-SCR);

NH_4NO_3/H_2O (l) ➔ 5% H_2O (g);

NH_4NO_3= 0 / 100 / 200 / 250 ppm;

O_2=8%v/v

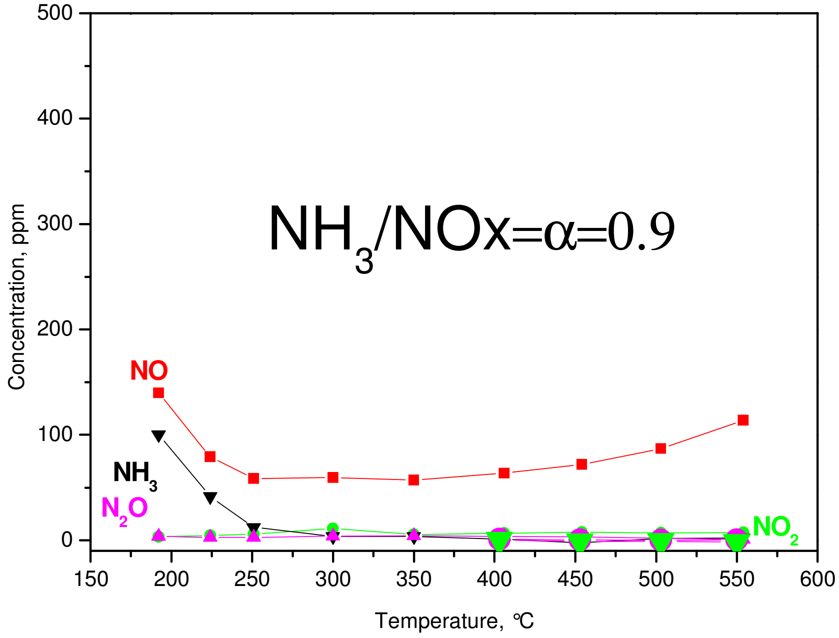
✓ AN boosts the NOx conversion at low temperature, approaching the performance limit of Fast SCR reaction

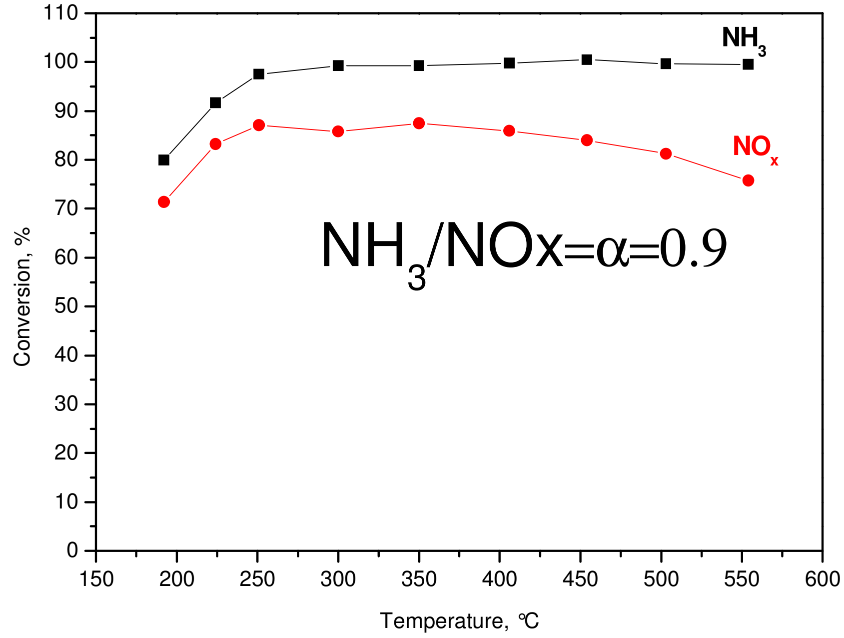
High Temperature Behavior

Test conditions:

GHSV = 75000 h^{-1}; NH_3 = 450 ppm; NOx = 500 ppm; O_2 = 8%v/v

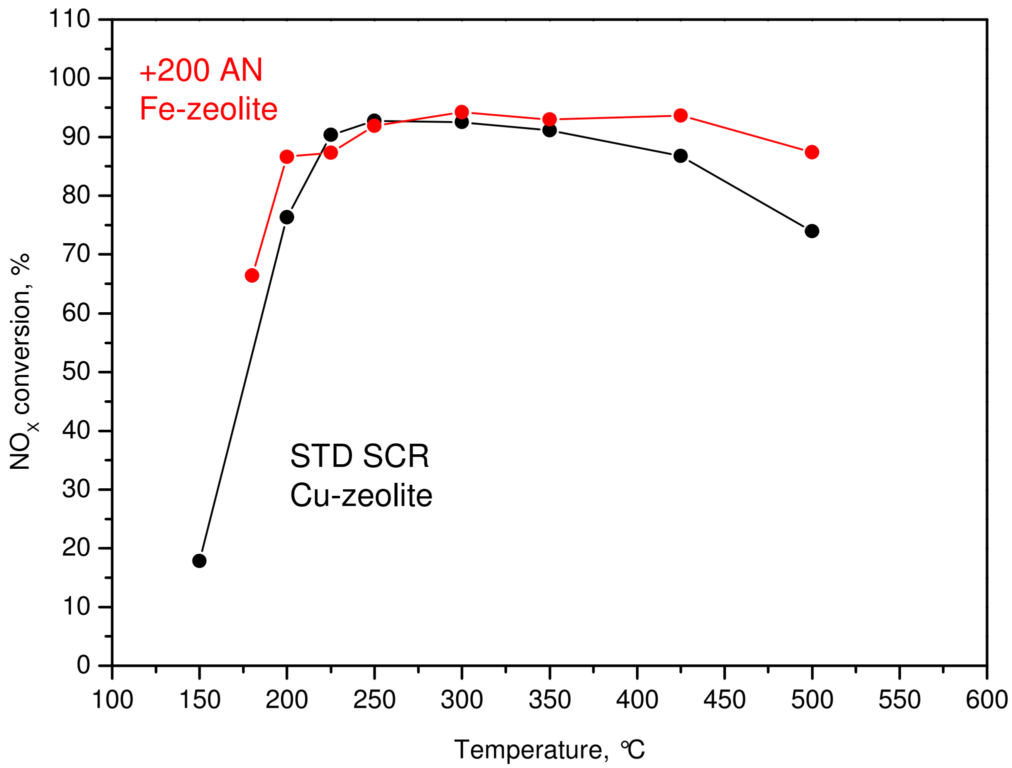
NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g), NH_4NO_3 = 200 ppm;





- ✓ AN has no negative effect on DeNOx activity at high temperature
- ✓ NH_3 slip ➔ 0 if $\alpha < 1$
- ✓ NO_2 and N_2O formation are negligible at all temperatures

Fe-zeolite + AN vs. Cu-zeolite

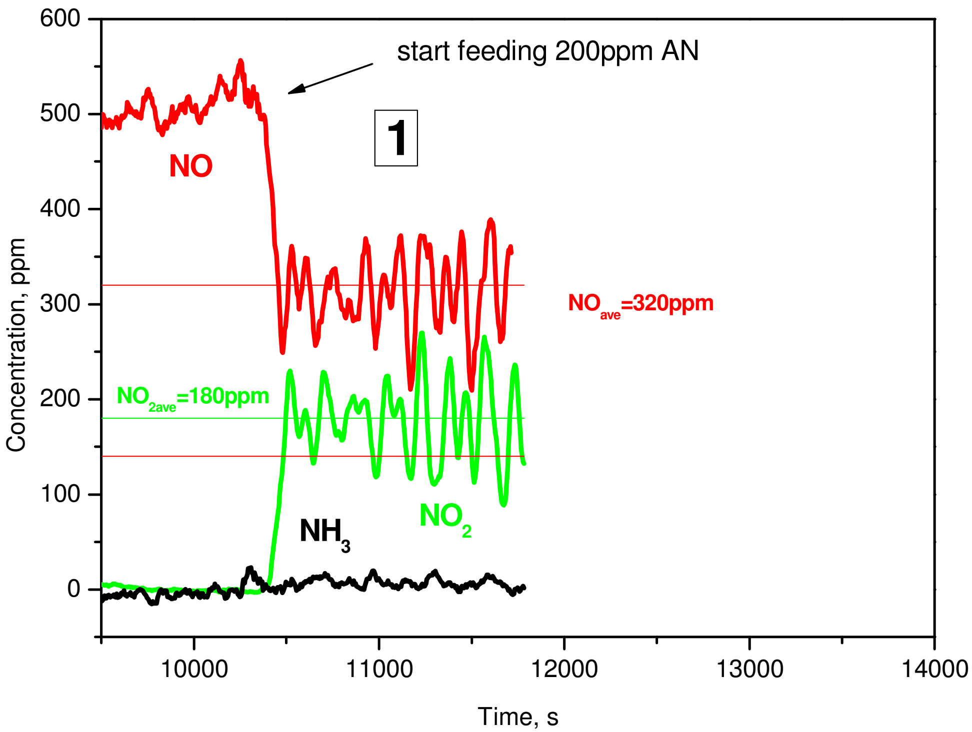


Test conditions:

- GHSV = 100000 h^{-1};
- NH_3 = 500 ppm;
- NO = 500 ppm;
- O_2 = 8% v/v
- $NH_4NO_3/H_2O(l)$ ➔ 5% $H_2O(g)$,
- NH_4NO_3 = 200 ppm

Upon addition of 200 ppm AN, Fe-Zeo cat outperforms Cu-Zeo cat in Standard SCR at both low and high temperatures

Reaction Mechanism



Test conditions:

GHSV = 75000 h^{-1};

NH_3 = 0 ppm;

NO = 500 ppm;

O_2 = 0% v/v

NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g);

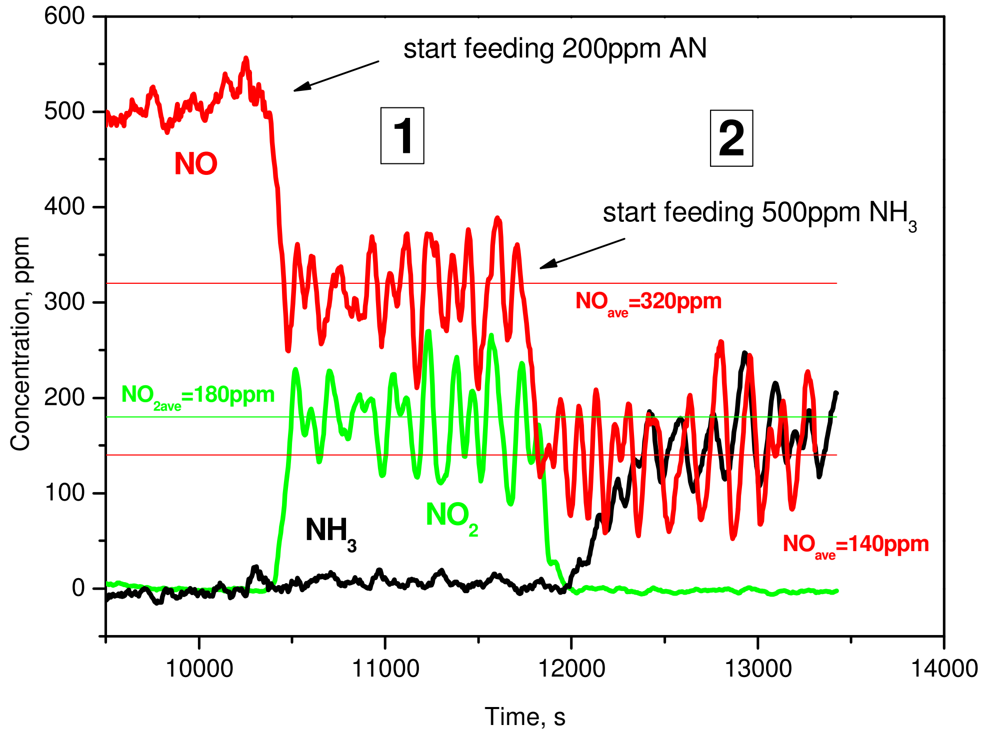
NH_4NO_3 = 200 ppm;

T = 190°C

Stage 1 - NO oxidation by AN: $NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2\,H_2O$

Ciardelli et al., Chem. Commun. 23 (2004) 2718-2719

Reaction Mechanism



Test conditions:

GHSV = 75000 h^{-1};

NH_3 = 0 - 500 ppm;

NO = 500 ppm;

O_2 = 0% v/v

NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g);

NH_4NO_3 = 200 ppm;

T = 190°C

Stage 1 - NO oxidation by AN: $NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2\ H_2O$

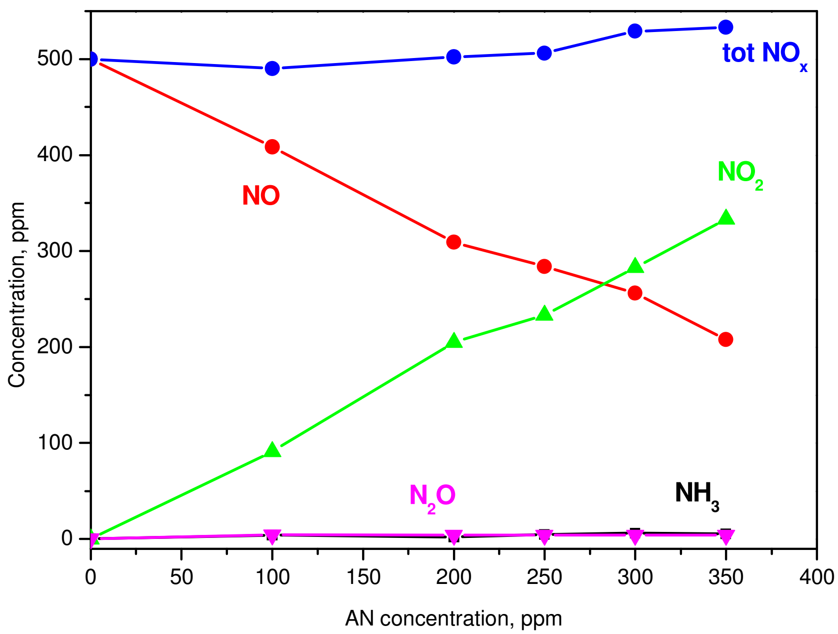
Stage 2 - Fast-SCR: $\underline{NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O}$

= E-SCR: $2NO + 2NH_3 + NH_4NO_3 \rightarrow 3N_2 + 5H_2O$

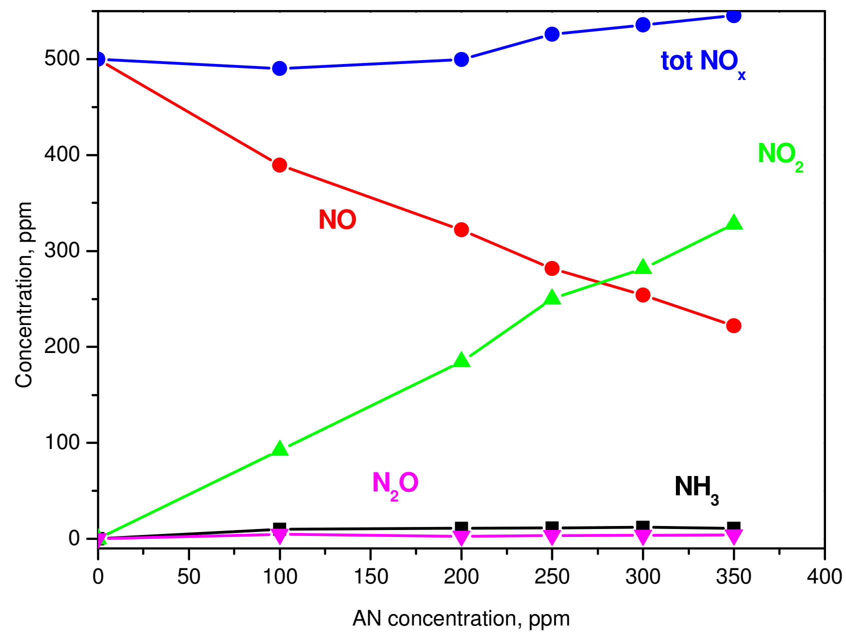
Oxidation of NO by AN

Testing Conditions:

GHSV = 75000 h^{-1}; NH_3 = 0 ppm; NO = 500 ppm;
NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g); O_2 = 0% v/v; T = 200°C



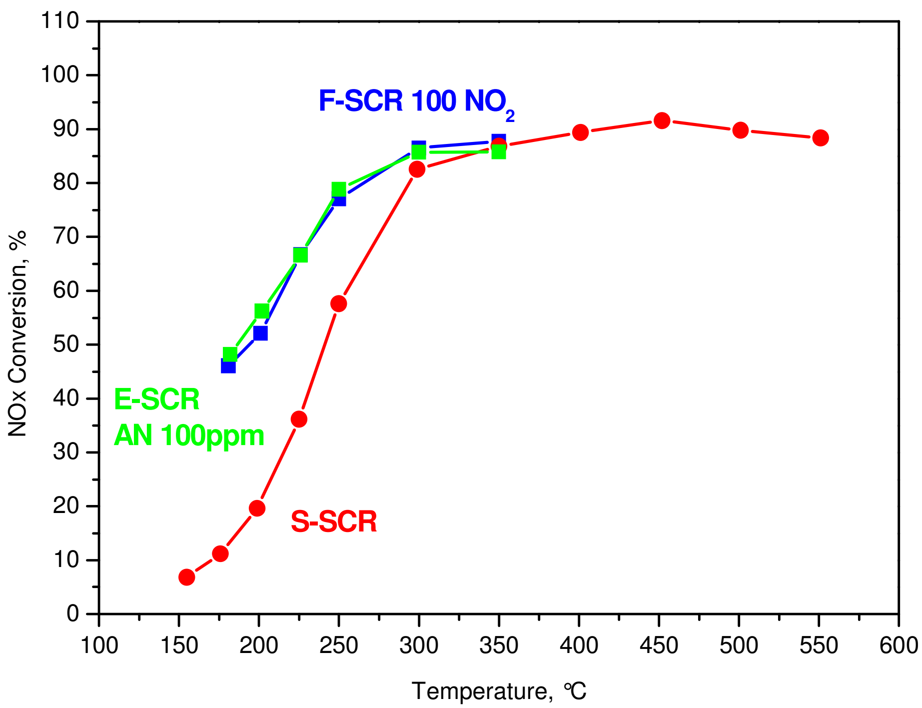
GHSV = 75,000 h^{-1}



GHSV = 35,000 h^{-1}

✓ **AN and NO quantitatively react at all investigated operating conditions**

AN – NO_2 Equivalence



Feed compositions:

E-SCR = 500 ppm NO + 100 ppm AN
F-SCR = 400 ppm NO + 100 ppm NO_2

Test Conditions:

GHSV = 75,000h^{-1};

NH_3 = 500 ppm;

NO = 400/500 ppm;

NO_2 = 100/0 ppm

O_2 = 8% v/v

NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g),

NH_4NO_3 = 0, 100 ppm;

The observed performances are identical:
➔ NH_4NO_3 replaces NO with an equivalent amount of NO_2 in the feed gas

Kinetic Model

Sequential scheme:

$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O$ (1)

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ (2)

$NO + NH_3 + 1/4O_2 \rightarrow N_2 + 3/2H_2O$ (3)

- ✓ Reaction 1 is oxidation of NO by AN, does not require NH_3
- ✓ Reaction 2 is Fast SCR, proceeds only when NH_3 is available
- ✓ Reaction 3 is Std SCR, proceeds only when NH_3 and O_2 are available
- ✓ Second order rate laws assumed for (1) & (2), first order for (3):

Mass balances:

$$\frac{dC_{NO}}{d\tau} = -k_1 C_{NO} C_{AN} - k_2 C_{NO} C_{NO2} - k_3 C_{NO}$$

$$\frac{dC_{NO_2}}{d\tau} = +k_1 C_{NO} C_{AN} - k_2 C_{NO} C_{NO2}$$

$$\frac{dC_{AN}}{d\tau} = -k_1 C_{NO} C_{AN}$$

Initial conditions:

$\tau = 0$

$C_{NO} = C_{NO}^0$

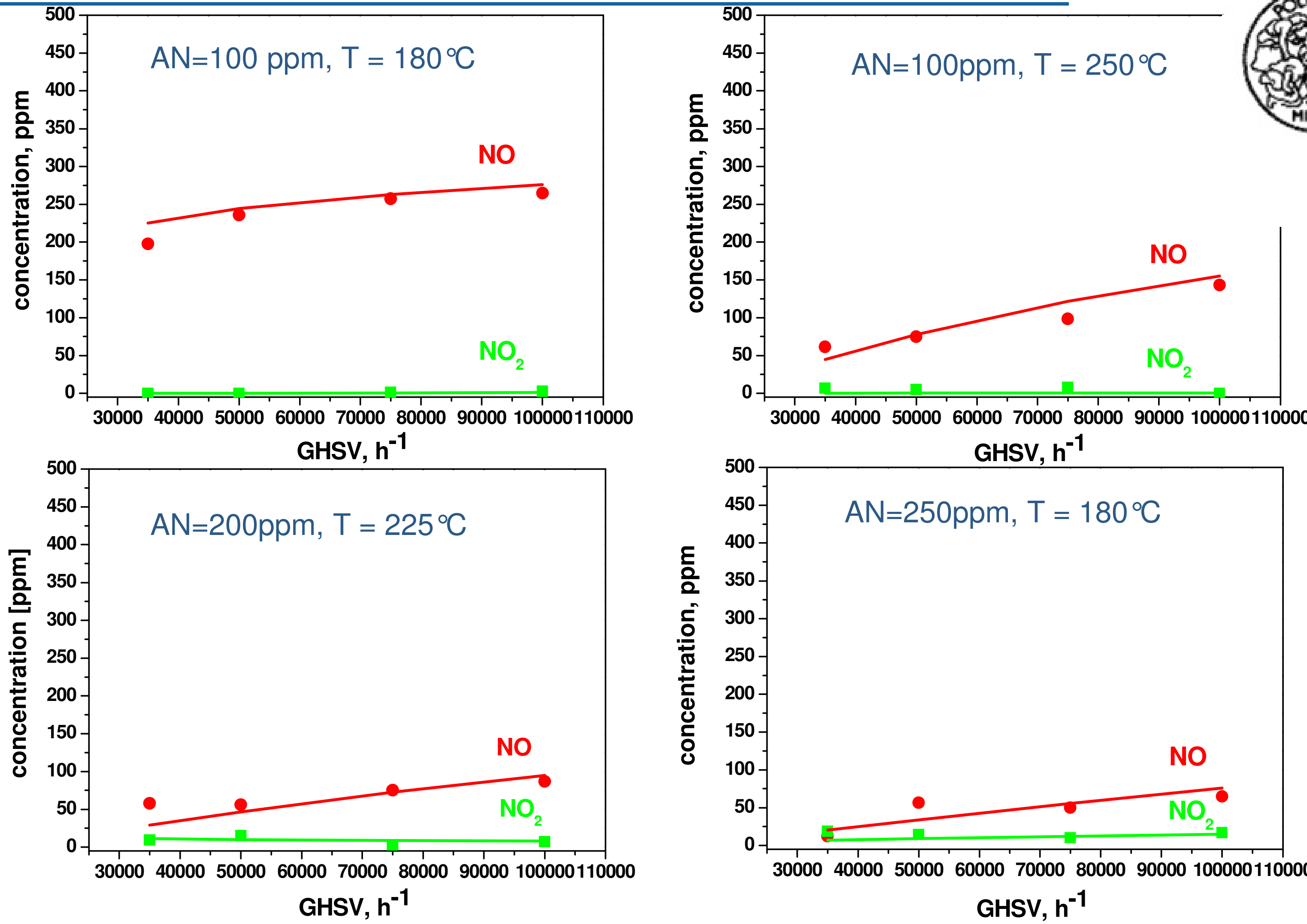
$C_{NO2} = C_{NO2}^0$

$C_{AN} = C_{AN}^0$

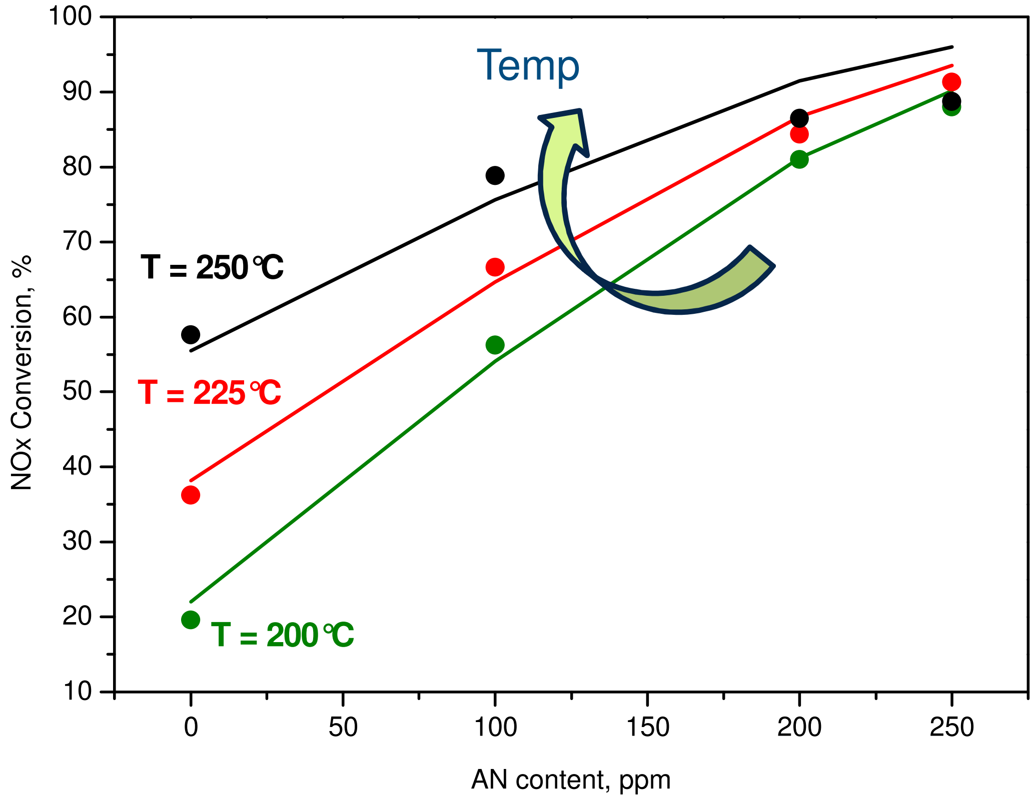
$$\tau = \frac{1000}{GHSV}$$

$\alpha > 1$

Kinetic Fit Results



Experimental Vs. Fitted Effect of AN Feed



Test conditions:

GHSV = 75,000h^{-1};

NH_3 = 500 ppm;

NO = 500 ppm;

O_2 = 8% v/v;

NH_4NO_3 / H_2O (l) ➔ 5% H_2O (g);

✓ Good agreement between experimental (dots) and fitting curves (solid lines)

System Configuration Options

Option 1:

– Two separate liquid supply subsystems for urea and AN solutions

– Independent AN injection algorithm

Pros

– Maximal benefit of the AN injection can be achieved

– Minimal side effects of occasional over-injection of AN

Cons

– Cost and complexity - new hardware

Option 2

– Single liquid supply subsystem: urea+AN solution

– Single reductant injection algorithm

Pros

– Minimal change in hardware

– Lower cost and complexity

Cons

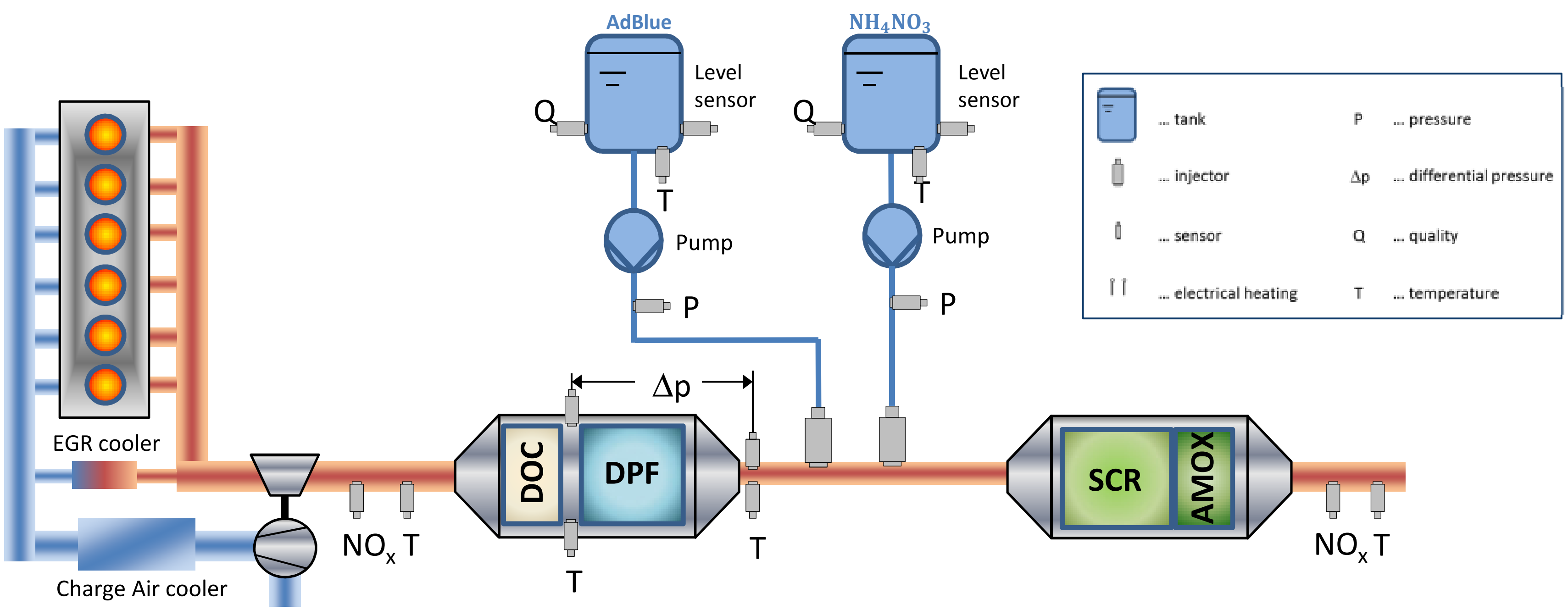
– Lower performance improvement

– Potential impact of over-stoichiometrical AN injection

→ System 1 was chosen for the performance improvement evaluation

System Layout

Engine			
Displacement	8 liter	Active Regeneration	yes
Power	255 kW	EGR	cooled
Calibration	Euro V	Injection system	CR



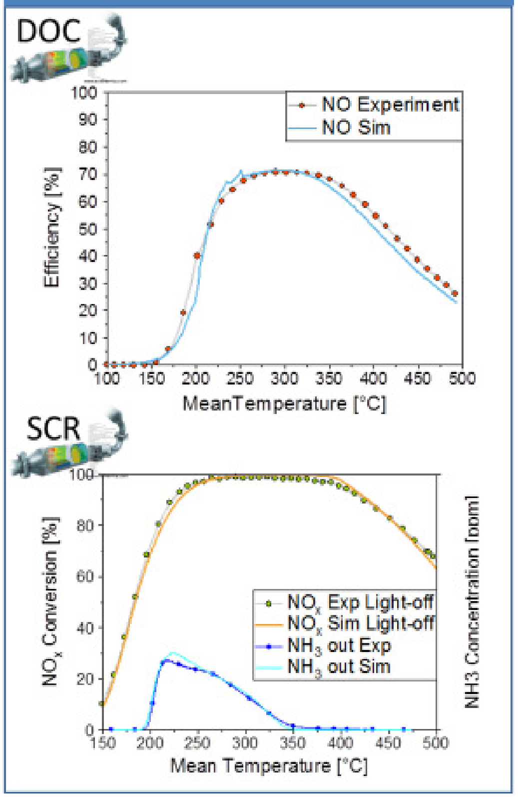
Injection Control Strategy

- AdBlue injection
  - as needed to maintain desired NH_3 storage level
- AN injection
  - as needed to maintain $NO:NO_2 = 1:1$ at the SCR inlet
- Injection activation
  - $T_{exh} < 180°C$ - no injection enabled
  - $180°C < T_{exh} < 350°C$ - both urea and AN injection
  - $T_{exh} > 350°C$ - urea only; no AN injection enabled

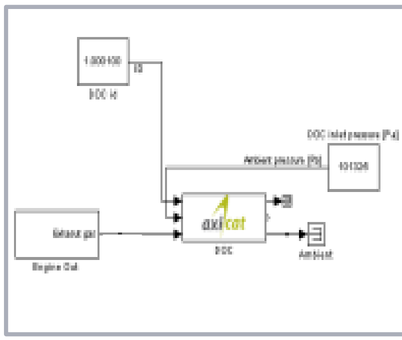
System Simulation

Components Models (AxiSuite)

quasi stationary calibration



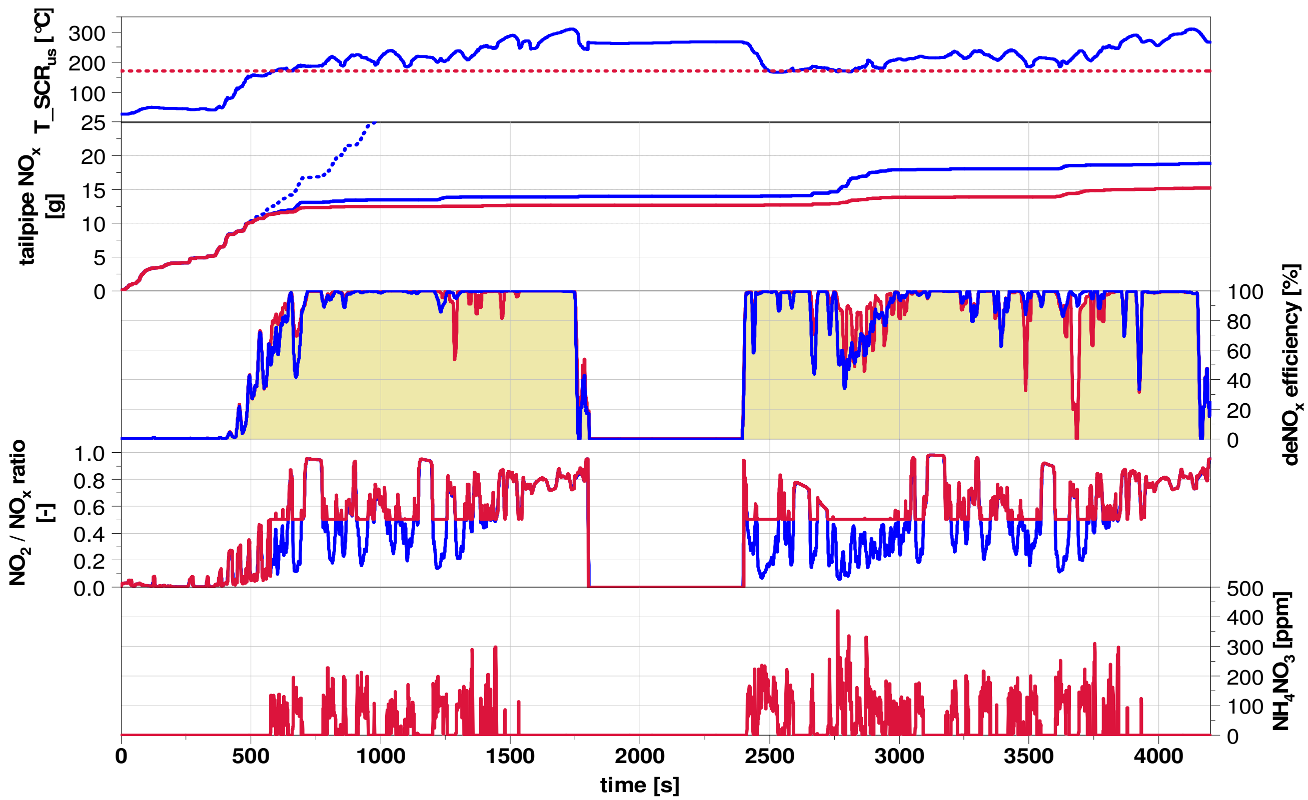
Simulink S-function



System Simulation

VeLoDyn environment

WHTC Simulation Results



Cycle emission, g/kWh	Cold	Hot	Weighted
Baseline	0.581	0.204	**0.264**
AN-assisted	0.532	0.101	**0.176**

→ **Significant improvement with ideal injection strategy**

Conclusions

- ✓ NH_4NO_3 has a strong promoting effect on the SCR – DeNOx activity at low T over the tested Fe-SCR catalyst.
- ✓ Complete conversion of the fed NH_4NO_3 is achieved under lab testing conditions without N_2O formation.
- ✓ AN acts as an equivalent to NO_2 without the DOC. In other words, NO_2 is generated "in situ".
- ✓ A simple "Quasi-DOC" kinetic model fits well the experimental data under all testing conditions.
- ✓ Various system design and control strategy options are considered for AN injection.
- ✓ Simulation of an SCR system with independent AN injection demonstrates significant SCR performance improvement potential.

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http://co2re.eu/

Laboratory of Catalysis and Catalytic Processes LCCP

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Thank You

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