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Progress on Acidic Zirconia Mixed Oxides for Efficient NH_3-SCR Catalysis

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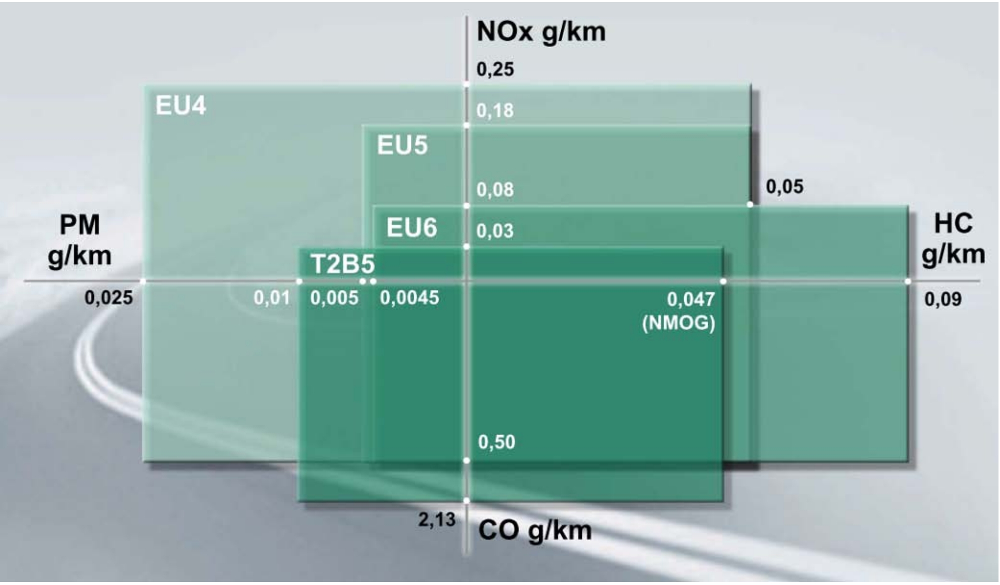
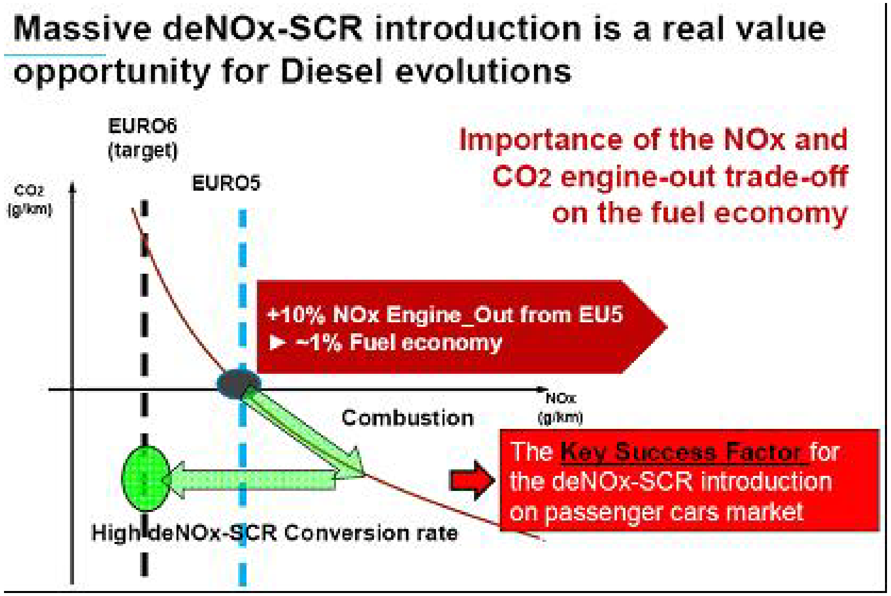
DeNOx SCR for EU6 is the preferred technology to target the NOx regulation limits and low CO_2 emissions



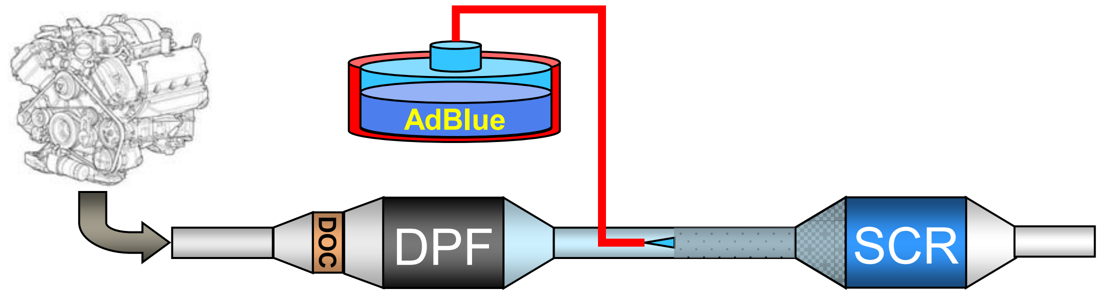
Source: W. Mattes (BMW), Minnox 2008



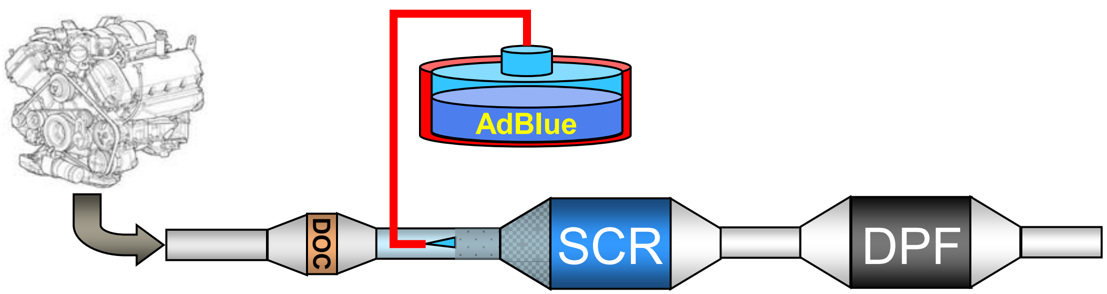
Source: T. Seguelong, IAA 2009

Worldwide emission regulations push the need for DeNOx catalysts
NO_x regulations + pressure on CO_2 emissions = need for NH_3-SCR

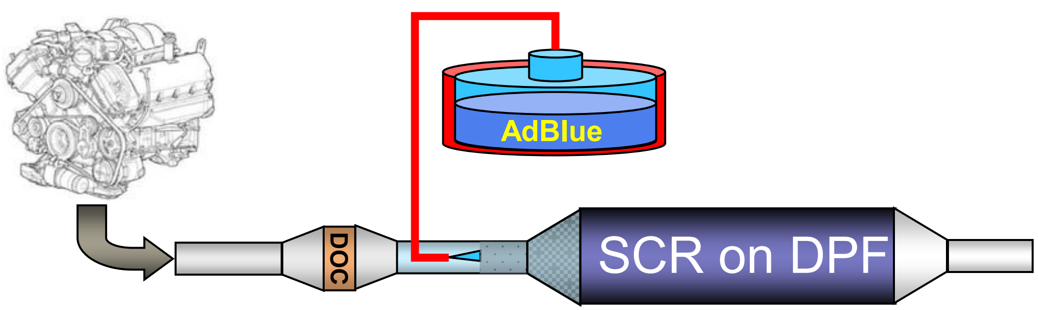
SCR/DPF concepts for EU6



SCR catalyst downstream of filter:
+ SCR catalyst more isothermal due to heat capacity of DPF
+ NO_2 formation in filter improves SCR performance
- Bad NO_x light-off
- Erroneous DPF regeneration may damage SCR catalyst



SCR catalyst upstream of filter:
+ Good NO_x light-off
+ SCR catalyst cannot be damaged by DPF regeneration
- SCR catalyst exposed to larger temperature gradients
- Initiation of DPF regeneration by temperature increase through the SCR catalyst



SCR catalyst on filter:
- DPF regeneration may damage SCR catalyst

Three investigation levels

1) ***Rhodia lab tests on powder model catalysts as preliminary screening of Ac Zr materials***

2) Paul Scherrer Institute (Switzerland) lab tests on coated catalysts as first indicator for real-world performance

3) Engine Bench Test on Full size model catalysts as proof of concept

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Focus on the progress and testing of Acidic Zirconia (Ac Zr)

Powder Model Catalysts

Label		Surface area fresh (m^2/g)	Surface area hydrothermally aged at 750 °C for 16 h (m^2/g)
Acidic Mixed Oxide REV1	Acidic Zr sample with low CeO_2 loading	85	63
Acidic Mixed Oxide REV3	New Process Acidic Zirconia sample	60	44

Introduced at SAE 2008

Last generation of Ac Zr successfully up-scaled to the pilot level

Ammonia storage capacity of Ac Zr materials

Fresh

REV 1	0.236 mol / kg
REV 3	0.252 mol / kg

Hydrothermal aged
750°C/16 h

REV 1	0.170 mol / kg
REV 3	0.180 mol / kg

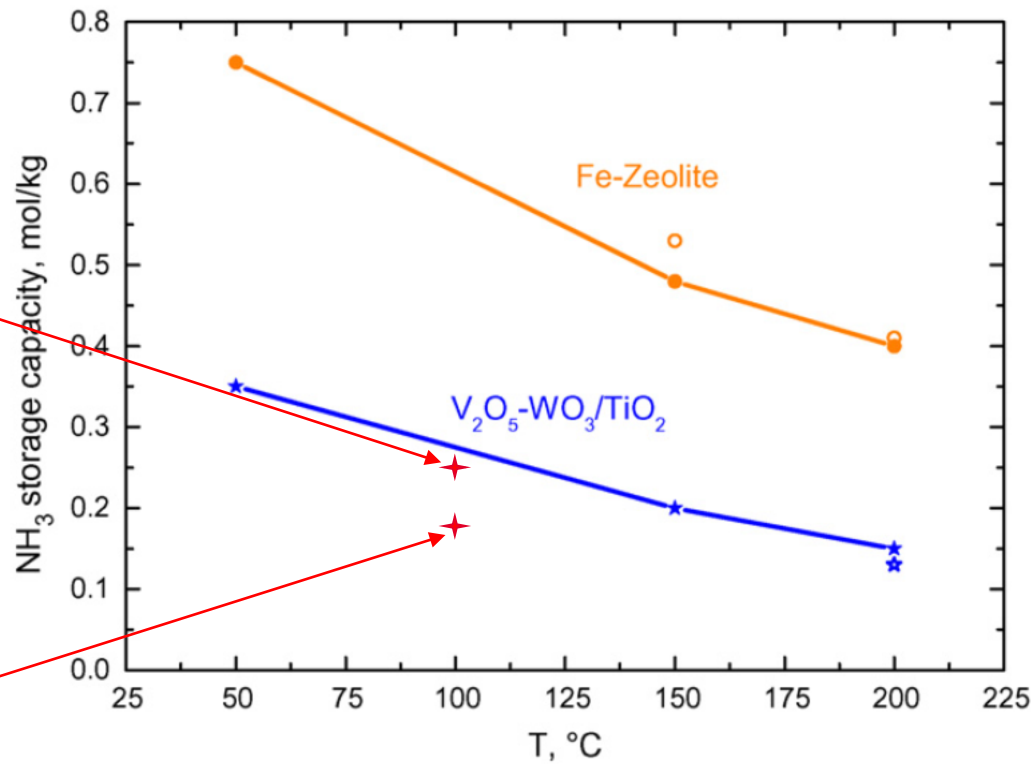
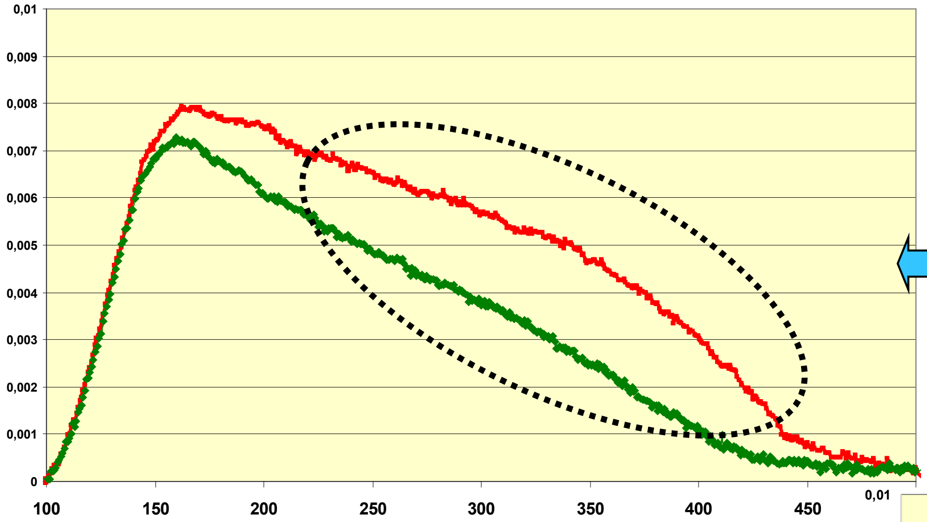


Fig. 1. Ammonia storage capacity of Fe–zeolite and V_2O_5–WO_3/TiO_2 crushed powders (solid symbols) and core monoliths (open symbols).

A. Grossale, I. Nova, E. Tronconi, Catal. Today 136 (2008) 18-27.

REV3 shows a rather flat temperature NH_3-TPD profile

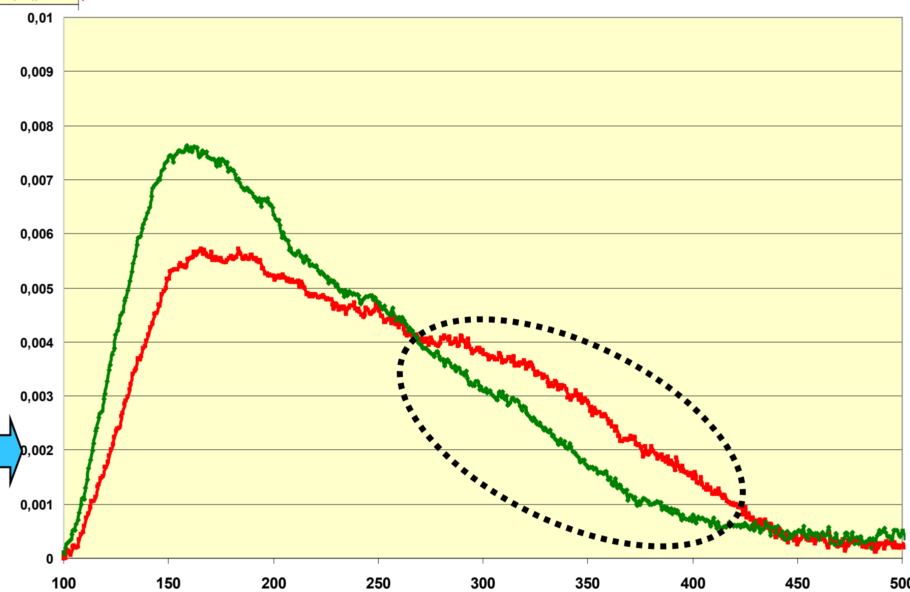
NH_3-TPD profiles of fresh powder samples



Rev1 & Rev2 samples show very similar NH_3-TPD profile.
Rev3 sample shows a flat profile even after ageing.

REV 1	0.236 mol / kg
REV 3	0.252 mol / kg

NH_3-TPD profiles of aged (*)powder samples



(*) Ageing : 750 °C / 16 h
10% H_2O, 10% O_2, balance N_2

REV 1	0.170 mol / kg
REV 3	0.180 mol / kg

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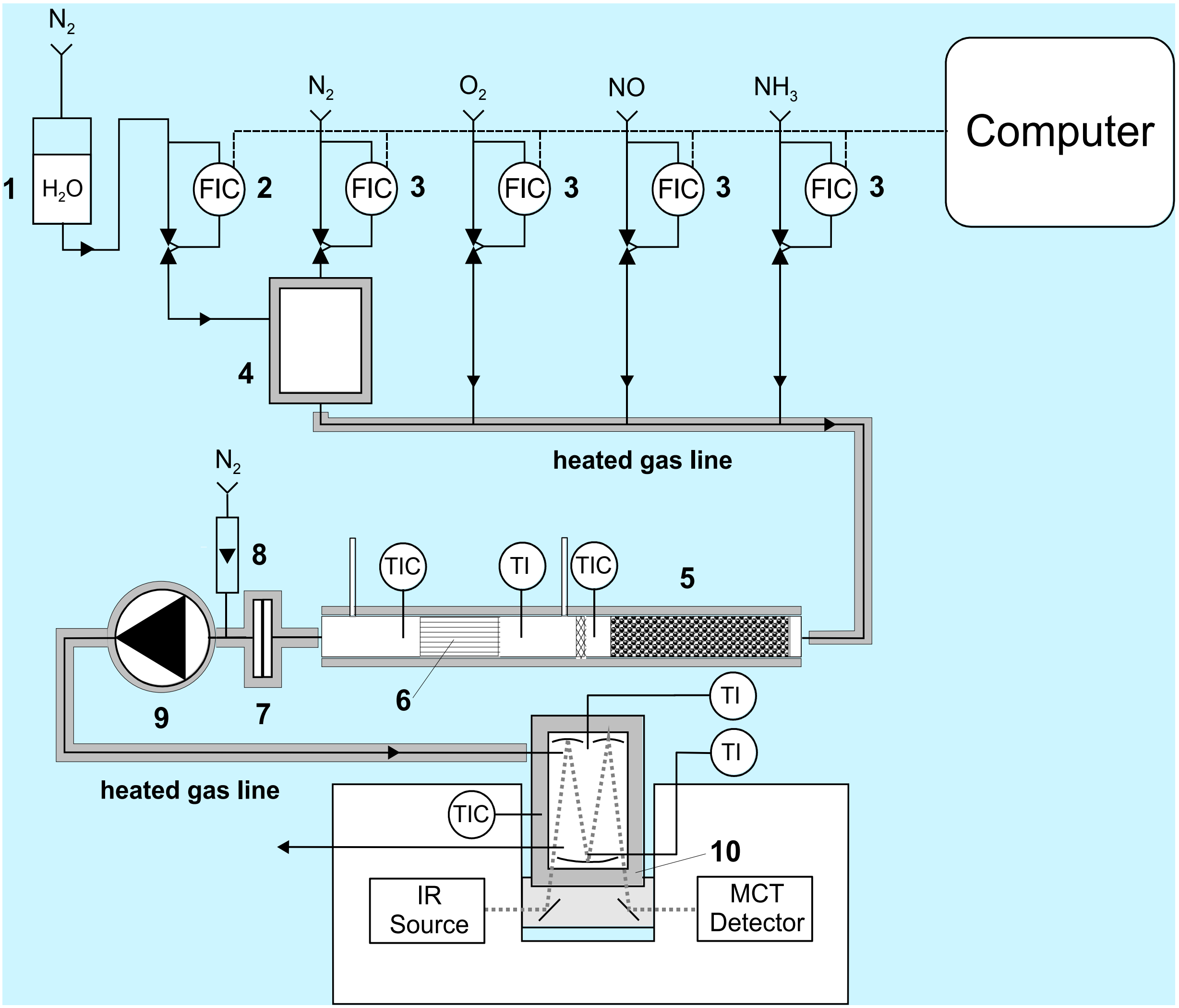
PSI laboratory test apparatus



Testing conditions:

- Ac Zr powders coated on cordierite substrates of 400 cpsi, 7.5 cm^3
- T = 200 - 650 °C
- GHSV = 30000 - 52000 h^{-1}
- Gas composition NO-SCR:

10% O_2, 5% H_2O, 1000 ppm NO, 0 - 1500 ppm NH_3, balance N_2

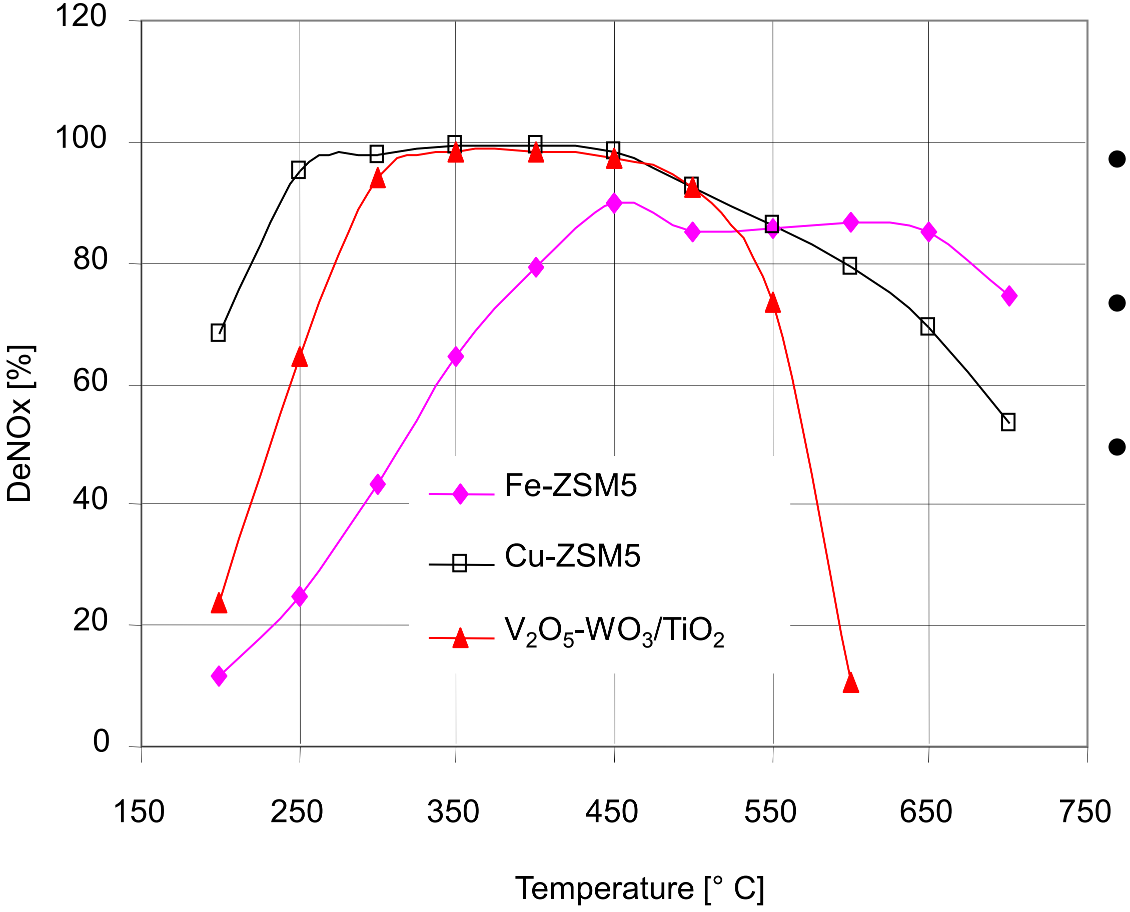
- Gas composition NO/NO_2-SCR:

10% O_2, 5% H_2O, 500 ppm NO, 500 ppm NO_2, 0 - 1500 ppm NH_3, balance N_2

1. Water reservoir
2. Liquid MFC`s
3. MFC`s
4. Water evaporator
5. Reactor
6. Catalyst sample
7. Filter
8. Flow meter
9. Diaphragm pump
10. Gas cell

NO-only SCR: M-zeolite and V-TiO_2

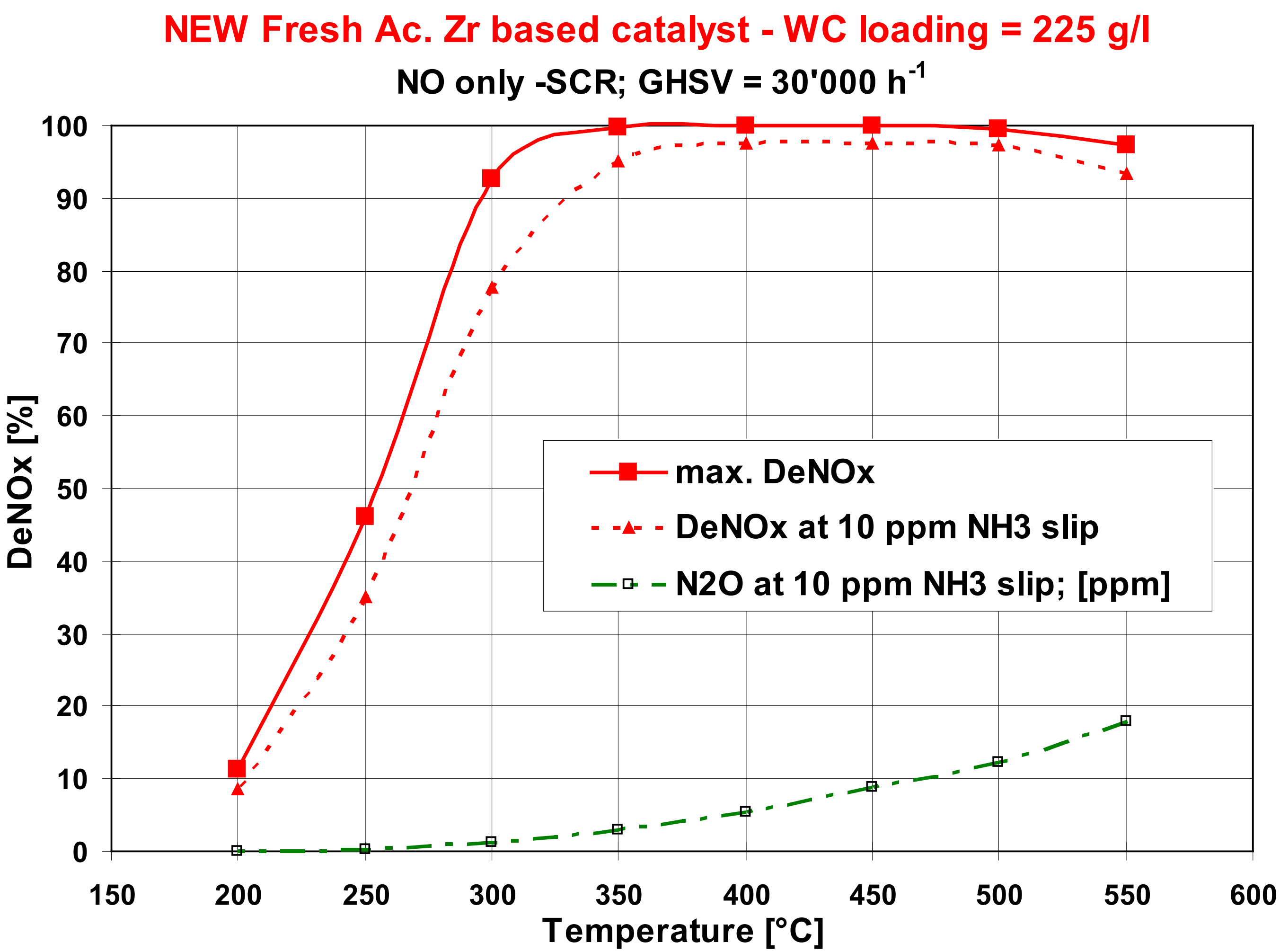
1000 ppm NO, 10 % O_2, and 5 % H_2O in N_2, NH_3 variable.



- **Cu-ZSM-5 very active at T ≤ 300 °C.**
- **Fe-ZSM-5 very active at T > 400 °C.**
- **V_2O_5/WO_3-TiO_2 active at intermediate temperatures.**

NO-only SCR: AcZr REV3

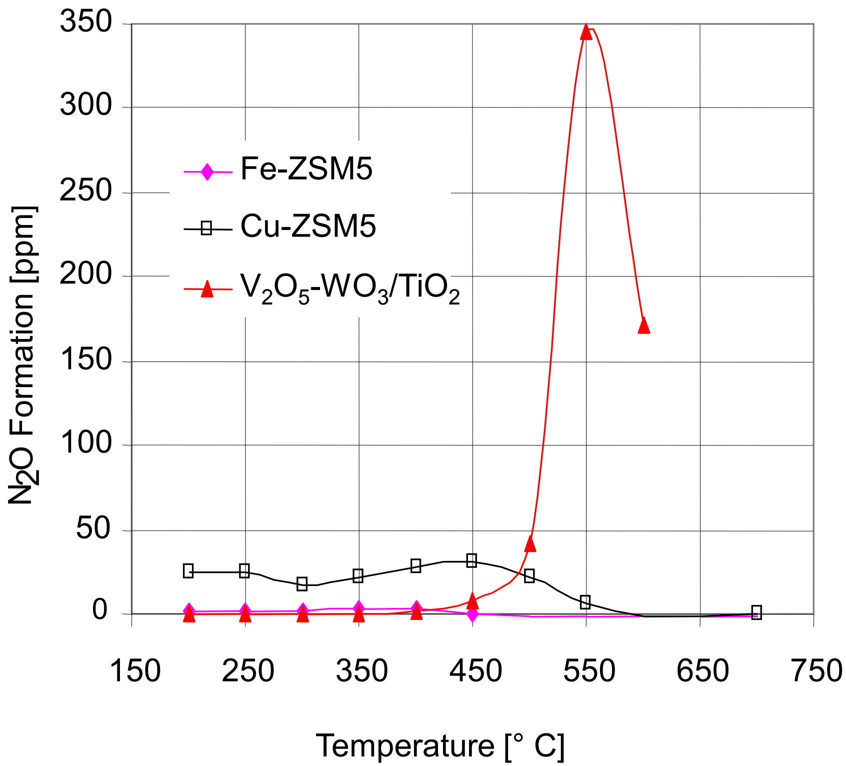
1000 ppm NO, 10 % O_2, and 5 % H_2O in N_2, NH_3 variable.

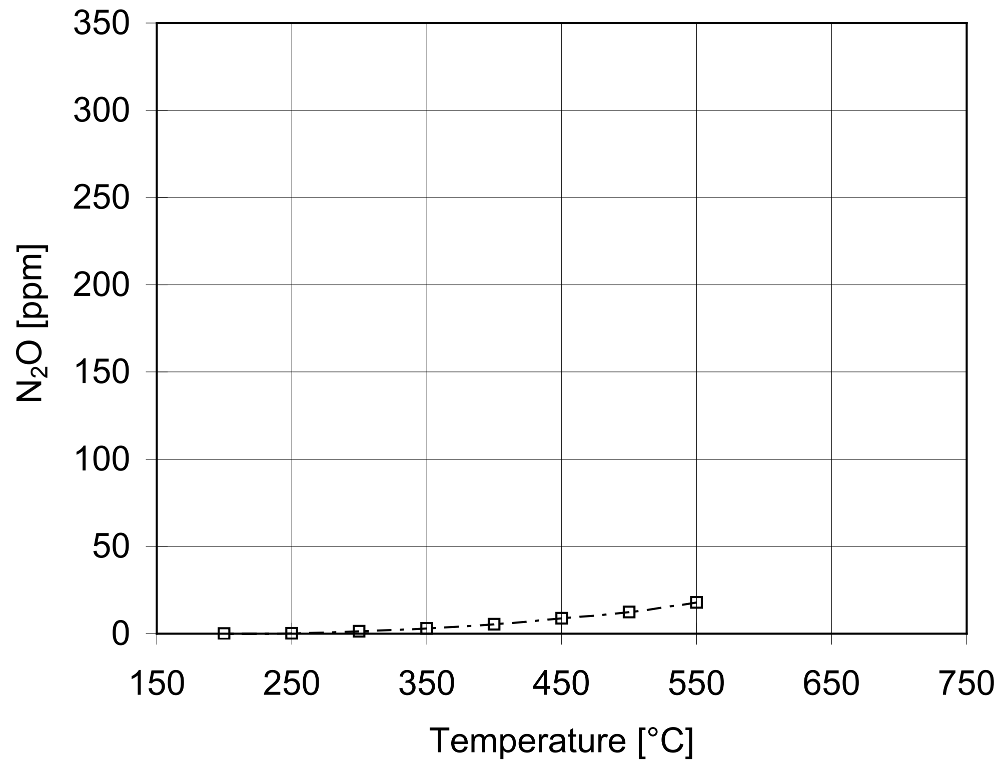


N_2O selectivity of V-cat., Fe-ZSM-5, Cu-ZSM-5 and Ac Zr REV3

N_2O formation at 10 ppm NH_3 slip

1000 ppm NO, **10 % O_2, and 5 % H_2O in N_2, NH_3 variable**

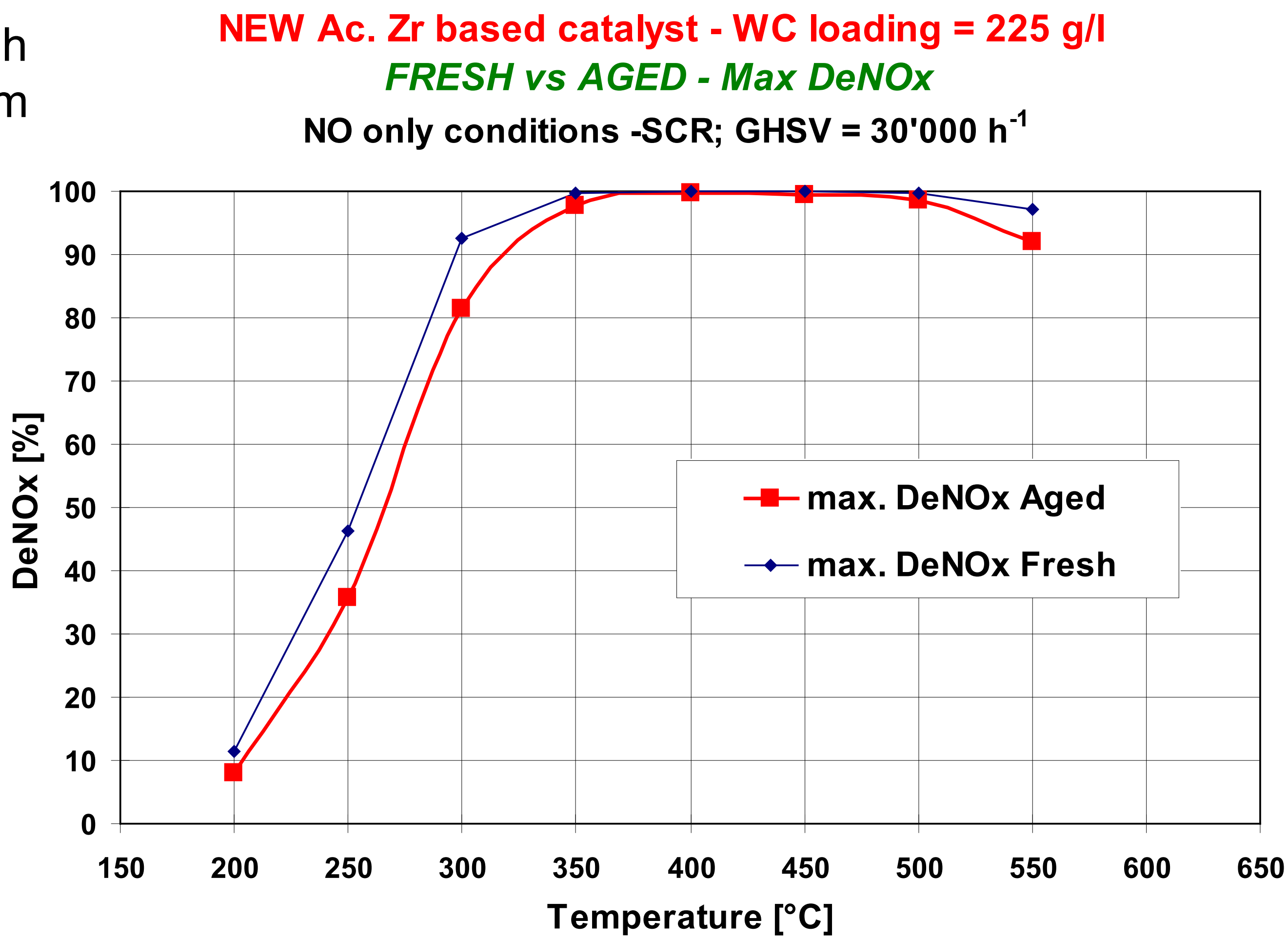




- Only small amounts of N_2O produced over Ac Zr REV3.

Effect of hydrothermal aging

750 °C/16h
10% steam



No effect under "Max deNOx" conditions

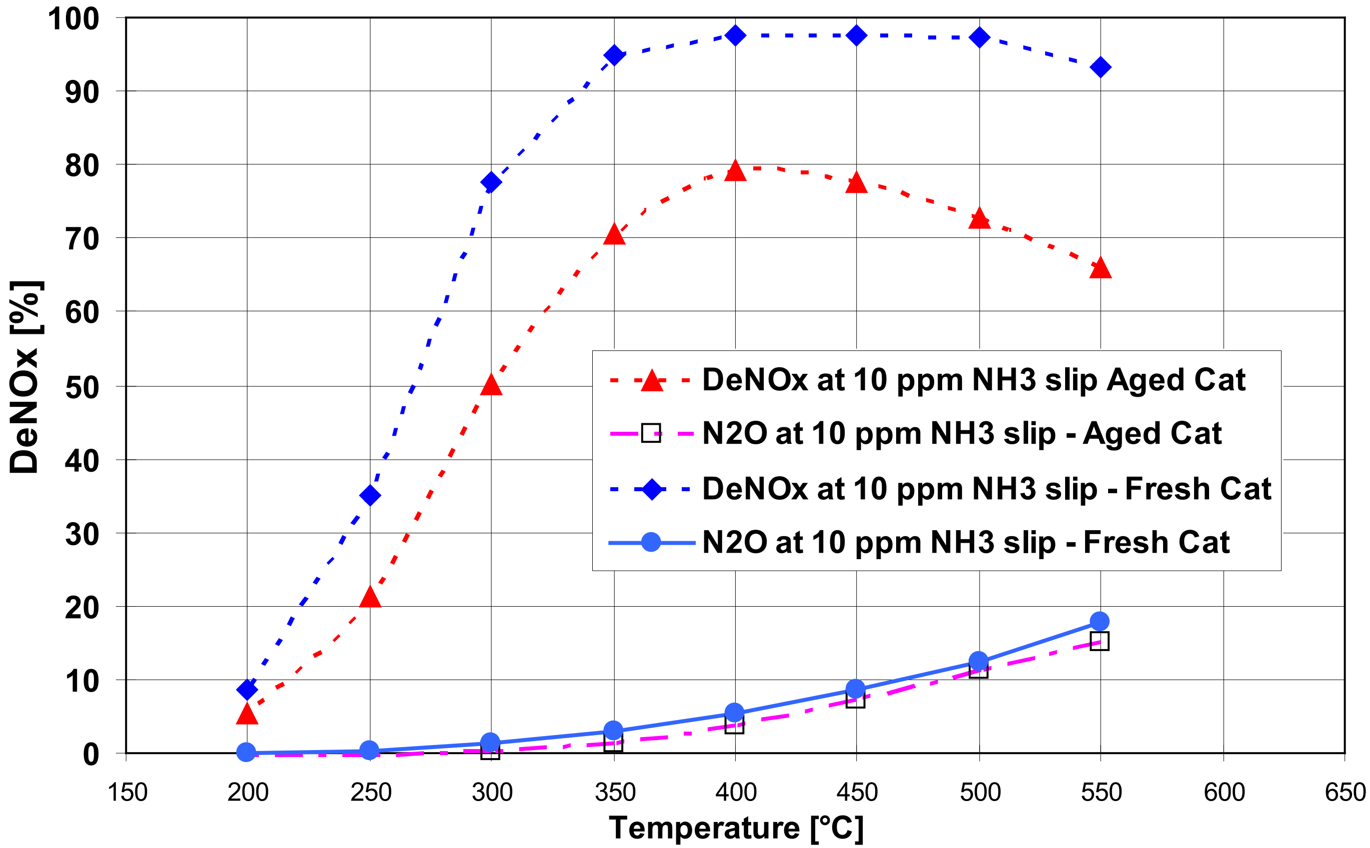
Effect of hydrothermal aging

750 °C/16h
10% steam

NEW Ac. Zr based catalyst - WC loading = 225 g/l

FRESH vs AGED - DeNOx at 10 ppm NH3 slip

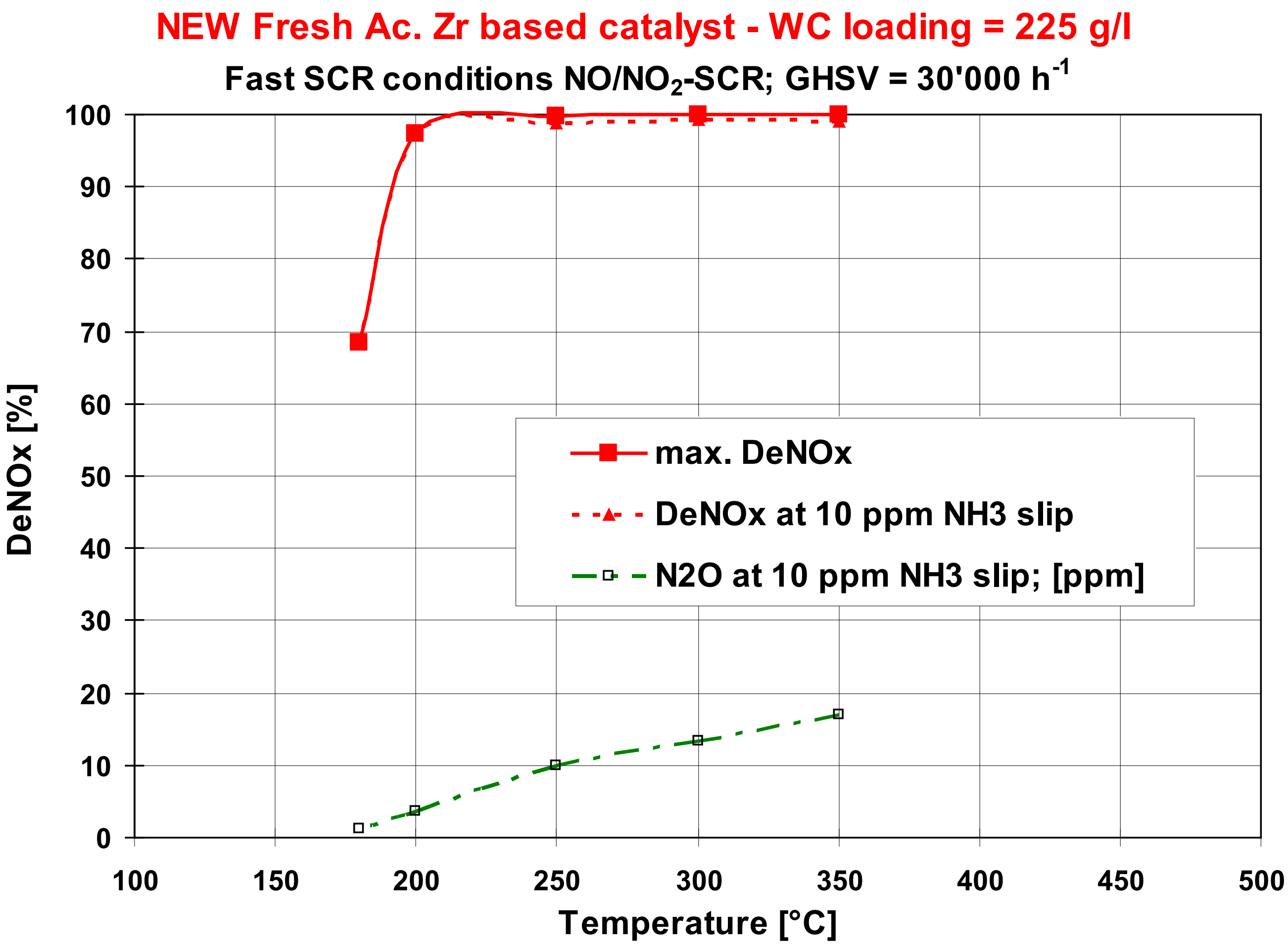
NO only conditions -SCR; GHSV = 30'000 h-1



Decrease in deNOx activity due to limited amount of NH_3 storage

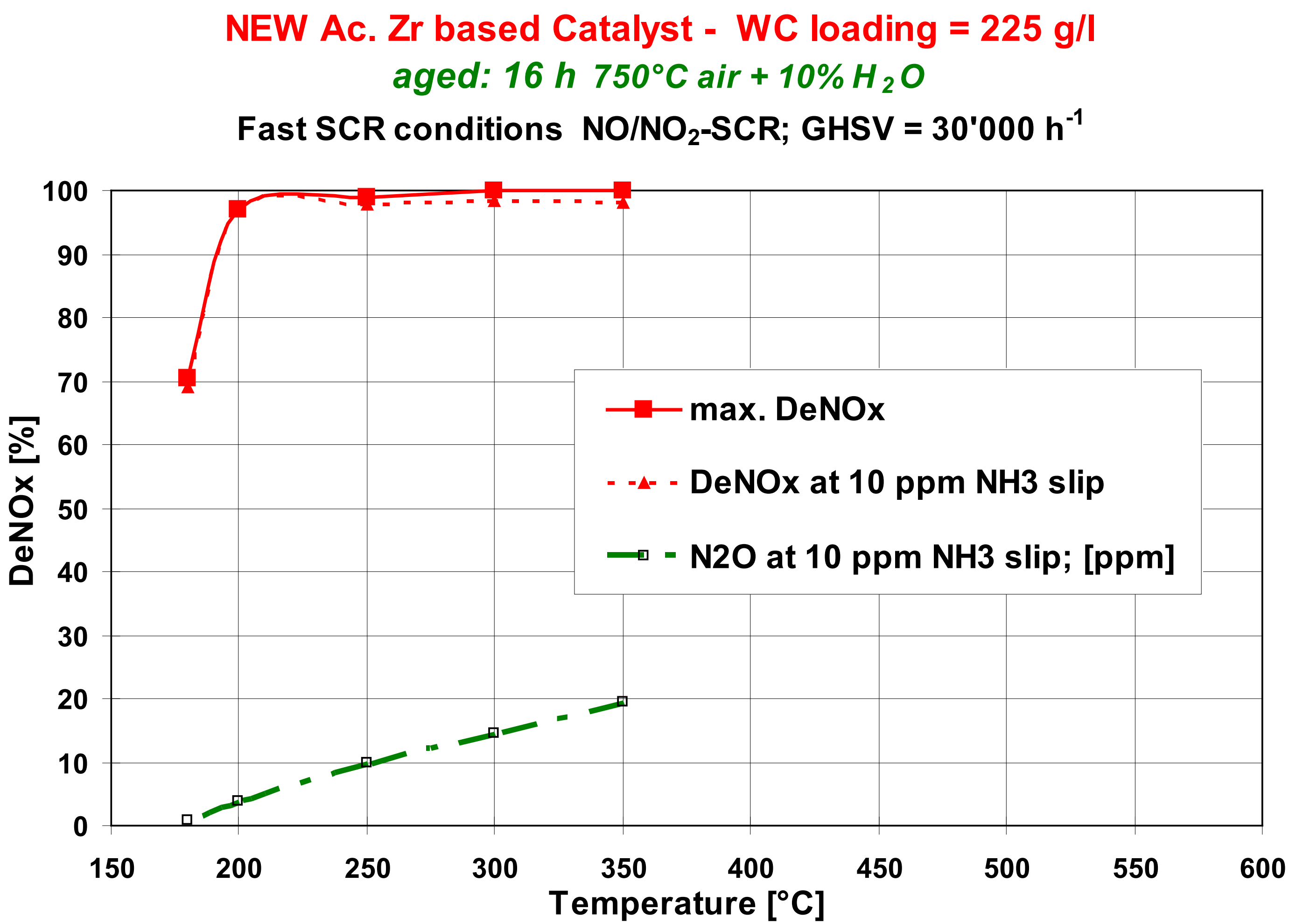
Fast-SCR over fresh AcZr REV3

500 ppm NO, 500 ppm NO_2, 10 % O_2, and 5% H_2O in N_2, NH_3 variable



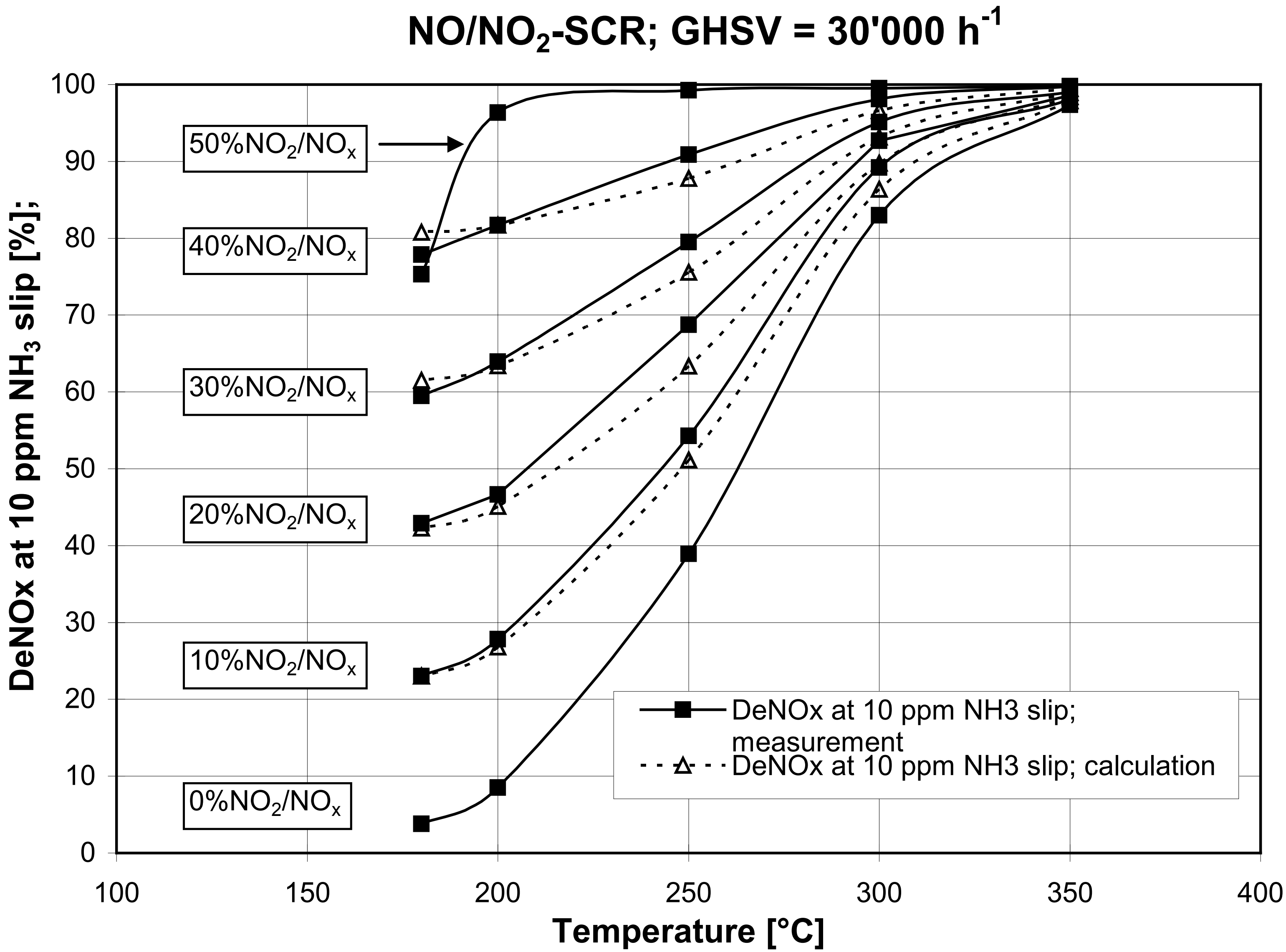
> 95% NOx conversion @ T>200 oC under fast-SCR conditions.

Fast-SCR over aged AcZr REV3



No effect of hydrothermal aging under fast SCR conditions

NO_x conversion at different NO/NO_2 ratios



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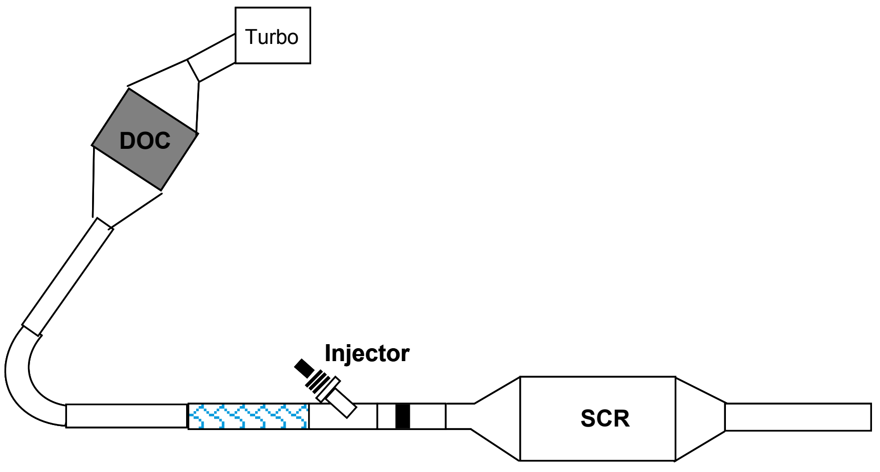
Engine bench test / Testing procedure

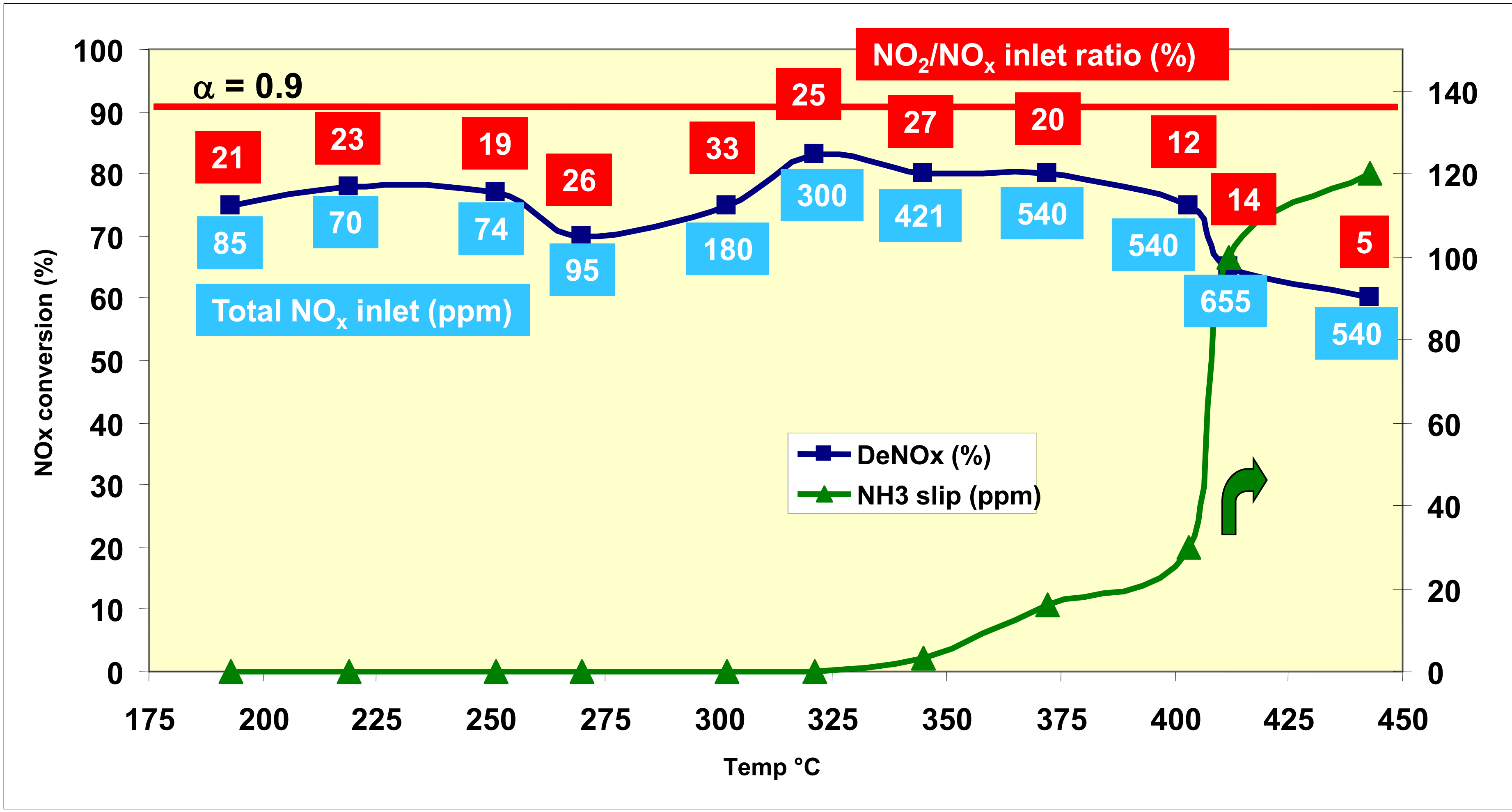
- **SCR prototype**
  - SCR catalyst based on Acidic Zirconia
  - SCR catalyst stabilised:
    4 h at 570°C then aged for 25 h at 800°C
  - Washcoat loading: ~120 g/L
  - Cordierite substrate (400 cpsi)
    - ∅ 5.66 in, length 7.00 in
      V = 2.9 L
- **DOC**
  - 400 cpsi
    ∅ 5.66 in, length 3.80 in
    V = 1.6 L



Engine test conditions:

- Engine speed: 1300 - 3500 min^{-1}
- T = 175 - 450°C
- NO_x measurement upstream and downstream of SCR catalyst
- $\alpha = NH_{3,in}/NO_{x,in} = 0.9$

AcZr SCR catalyst shows good light-off at the engine test bench even after aging



Conclusions / Perspectives

- Zirconia-based mixed metal oxide SCR catalysts show:
  - Good thermal stability
  - High NOx conversion
  - Good light-off
  - Low N_2O emissions
  - Low but constant NH_3 storage

- Catalyst compositions need to be optimized for improved light-off and ammonia storage

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Thank you for your attention