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Selective catalytic reduction of NOx in real exhaust gas of gas engines using unburned natural gas

Catalyst deactivation and advances toward long-term stability

J.A.Z. Pieterse, S. Booneveld, R.W van den Brink, H. Top, J.E. Westing, F. Vollink, K. Hoving

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Selective catalytic reduction of NOx in real exhaust gas of gas engines using unburned natural gas: catalyst deactivation and advances toward long-term stability

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Content

- ECN and ECN/Catalytic Emission Reduction
- NOx (and gas engines)
- NOx emission control technology
  - Selective catalytic reduction of NOx with methane (CH_4-SCR)
  - Results of tests with catalysts in synthetic gas and real exhaust gas of gas engines
    - *can we maintain high levels of NOx conversion at prolonged times-on-stream ?*
- Remarks / Ongoing research

Energy research Centre of The Netherlands

Mission

ECN develops knowledge and technology for the transition to a sustainable energy system

ECN Priority Areas

Solar Energy, Wind energy, Biomass, Fuel cells, Clean Fossil Fuels, Energy Efficiency

Key figures

staff: 650 fte

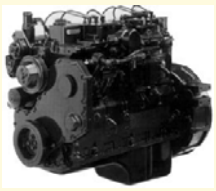
turnover: 70 M€

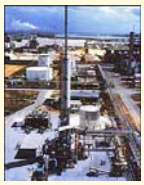
Catalytic Emission Reduction

(research group within Unit Clean Fossil Fuels)

Mission: Develop catalytic solutions to environmental problems

1. Techniques that prevent the emission of CO_2 during use of fossil fuels
2. Catalysts for the reduction of emissions of CH_4, NO_x, N_2O, soot, etc.





Products and Services

- Assessment of catalysts under realistic process conditions
- In-house development of catalysts and catalytic reactors
- Coating of catalysts onto substrates
- Characterisation of catalysts

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NOx (= NO + NO_2)

- *Fuel NOx* from nitrogen containing compounds in fossil fuels during combustion,
- *Thermal NOx* oxidation of N_2 at > 1000 °C
- *Prompt NOx* oxidation HCN in rich flames
  - Noxious effects: destroy ozone, acid rain, smog, emphysema, eutrophication

➢ Legislation: NOx limits more stringent

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NOx and gas engines

- In the Netherlands, emission NOx in 2002 ca. 12.2 kton: 7.8 kton (64 %) originates from 'older' engines (< 01-01-1994)[1]. Methane-slip 1 – 1.5 vol %
  - Engine management to lower NOx emission:
    - ca. 80 g/GJ possible but 2-6 % higher greenhouse gas emission (CH_4/CO_2)
    - *'the anticipated level of NOx reduction renders combustion modification alone insufficient as a control technology'*

1. Dijk G.H.J. van, *Inventarisatie NOx en CH4 emissie reductie voor aardgas motoren*, Gasunie Research Energy Innovation & Consultancy, 2004.

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NOx emission control technology

- Engines need to be equipped with NOx reduction technology (retrofit strategy):
  - after-treatment control ('End-of-pipe')
    - **Selective Catalytic Reduction (SCR)**
      - external supply reductant necessary
      - methane-slip left untouched

➢ Elegant solution: reaction of methane-slip and NOx, both present in the exhaust gas of gas engines, over a catalyst to remove the greenhouse gas and NOx simultaneously

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Selective catalytic reduction using hydrocarbons (HC-SCR)

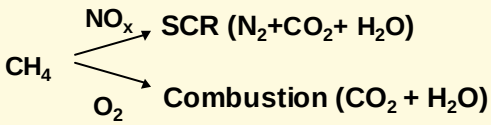
- Studies concern after-treatment for lean-burn **diesel engines** (C_2-Cn) hydrocarbon
  - Insufficient conc. HC in diesel engine exhaust may result in low conversion
  - If exhaust gas temperature below 200 °C, plasma-assistance necessary to boost activity (hydrocarbons traps,…)
  - Mobile applications: large temperature excursions, catalysts stability is issue

➢ **(stationary) Gas engine** :
  - Sufficient conc. HC (methane)
  - 'Stable' exhaust gas temperatures (350-500 °C)

Selective catalytic reduction of NOx with methane (CH_4-SCR)

➢ **What are the challenges from a catalytic point of view**

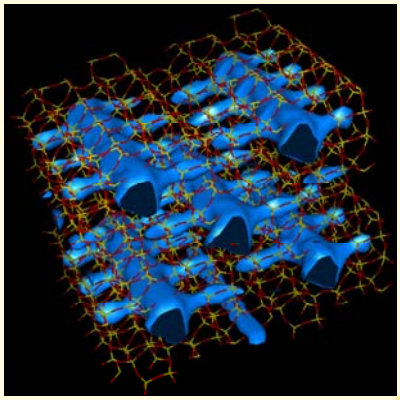
- Exhaust gas (lean-burn) engine: NOx and (surplus of) methane (water, oxygen, CxHy, S, CO, aldehydes……..)



I. **activation of methane**
II. **selectivity : SCR limited by combustion at higher T**
III. **stability, durability: identification of potential causes of catalyst deactivation important**

ECN-catalysts for CH_4-SCR

- Zeolite (support)
- metal
- structure-stabilizer
- *additives to increase activity*



Catalyst-testing at ECN

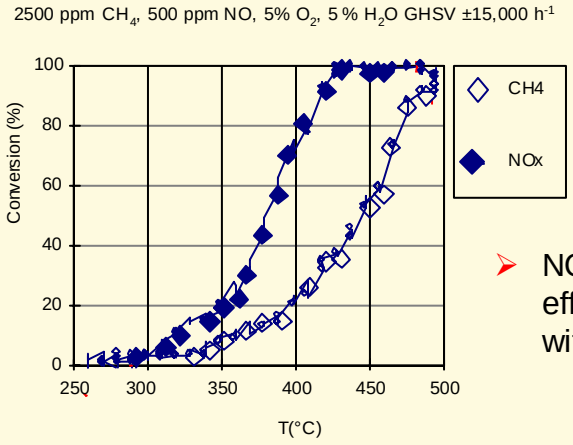
- Lab-scale tests of catalysts.
- Pressure 1 bar(a).
- Flows up to 150 ml/min (STP).
- Gas composition simulated to represent practical conditions
- On-line IR gas analysis

Catalyst-testing at GuR

- Senertec mini-WKK (5 kWe), Waukesha (312 kWe)
- Gas burner testfacility (30 kWe)
- Exhaust gas side-stream(100 l/min)
- Catalysts (pellets) in reactor placed in oven with temperature control
- On-line (IR, chemiluminescence) gas analysis and off-line GC analysis

ECN

Catalyst-testing at ECN with synthetic gas



- NOx and CH_4 removal efficiency increases e.g. with temperature

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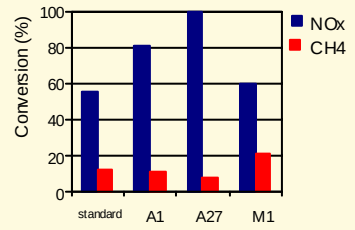
Catalyst-testing at ECN with synthetic gas

Gasengine	standard	A1	A27	M1
NO_x^* (ppm)	500	239	117	234
CH_4 (ppm)	2500	1713	2259	881
H_2O (vol.%)	5	10.9	10.6	12.8
O_2 (vol.%)	5	8.5	8.8	6.4
CO_2 (vol%)	0	5.7	5.6	6.7

*de Laat, 2001Gastec NO_xbased on gNO_2/GJ

promotor-metal-zeolite, T =385 °C, ±17,000 h^{-1}



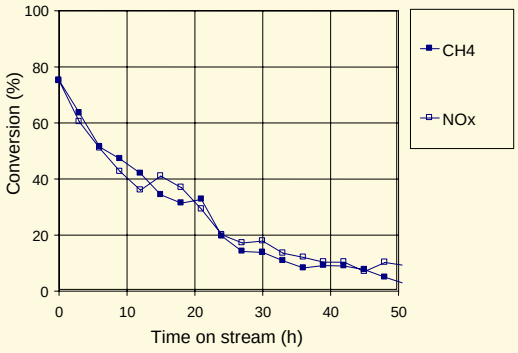
- CH_4/NOx >, SCR >
- CH_4 conversion incomplete

Also:

- **Stable conversion (tests >400 h)**

Testing catalysts at GuR in real exhaust gas of gas engines

- Gasengines 5Kwe ($T_{catalyst}$ ca. 500 °C) ± 800ppm CH_4, ±160 ppm NOx, ± 12 % H_2O, 0.5ppm SO_2, ± 8 % O_2 GHSV ± 3,500 hr^{-1}



- deactivation
- initial removal efficiencies similar to the ECN situation: no additional inhibition

What can cause catalyst deactivation in real exhaust gas?

1. Zeolite-structure ‘changes’ at high temperature in the presence of high concentration water
2. SO_3/SO_2 from lubricant and odorant (natural gas)
3. Ca, Na, K, P,(‘metal’)….. from lubricant

   - Active metal may ‘change’
   - structure-stabilizer (additives) may ‘change’

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Characterisation of the deactivated catalyst

1. Zeolite-structure ‘change’ ?: *Yes!*
2. SO_3/SO_2 ?: *Yes!*
3. Ca, Na, K, P,(‘metal’)…….?: *Yes!*

Are they all important for catalyst deactivation ?

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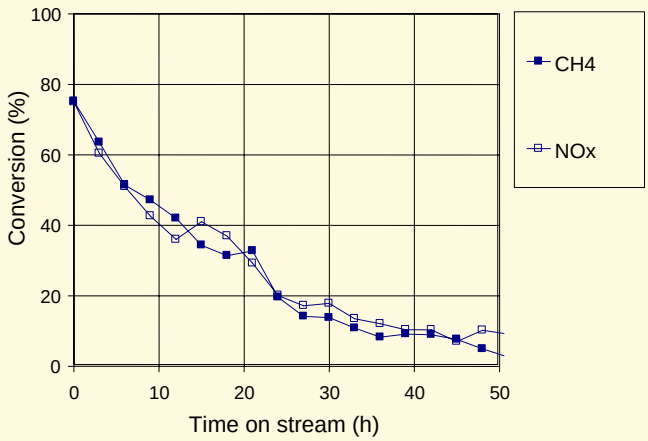
Identification of the causes of catalyst deactivation

- Study the influence of 1. (T&H_2O), 2. (S) and 3. (lubricant) independent from each other
  - ***Compare the catalyst performance with gas engine with gas burner with and without odorant-free gas***
  - Gas engine: presence of 'poisons' stemming from lubricant
  - Gas burner : absence 'poisons' stemming from lubricant
  - For both gas burner and engine: use natural gas (+S) and odorant-free gas (-S)

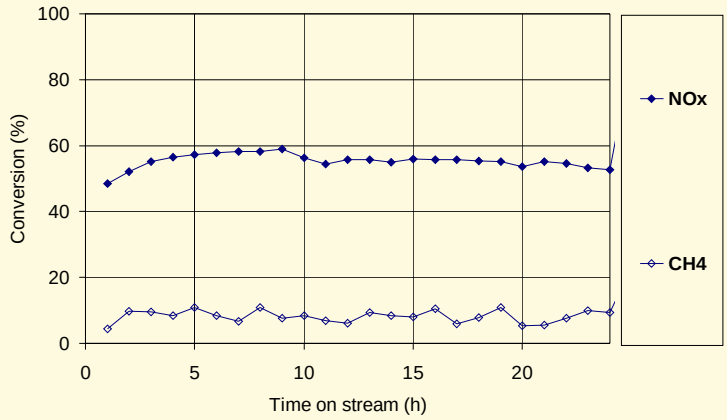
High T + 0.5-1 ppm SO_2 + [Na,K,Ca,….]

- **Gasengine 5 Kw, Tcatalyst ± 480 °C** ± 800ppm CH_4, ±160 ppm NOx, ± 12 % H_2O, **0.5-1 ppm SO_2**, ± 8 % O_2 GHSV ± 3,500 hr-1



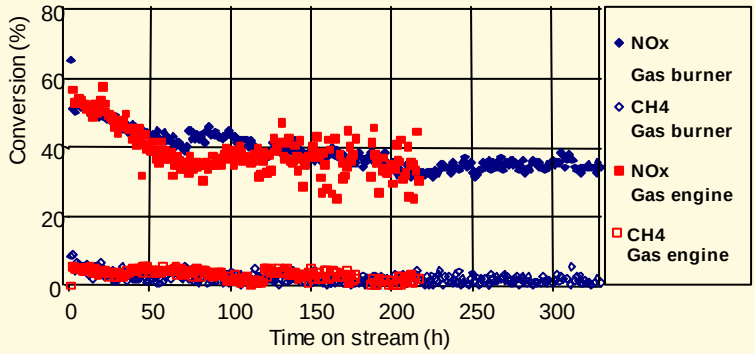
Low(er) T + 0 ppm SO_2 + 0 ppm [Na,K,Ca,….]

- **30 Kw 'Gasburner' fed with sulphur-free gas**
- T catalyst 380-400 °C, ± 800ppm CH_4, ±160 ppm NOx, ± 12 % H_2O, ± 8 % O_2 GHSV ± 3,500 hr-1



Low(er) T + 0.5-1 ppm SO_2 *+/- [Na,K,Ca,….]*

- 30 Kw "gasburner", 5 Kw gasengine: T catalyst 380-400 °C, ± 800ppm CH_4, ±160 ppm NOx, ± 12 % H_2O, 0.5ppm SO_2, ± 8 % O_2 GHSV ± 3,500 hr-1



Remarks

- Temperature cause deactivation at temperatures >400 °C
- At <400 °C, SO_2 causes ca. 30 % lower removal efficiency (X/X_0): 70 % removal efficiency retains
  - ***Remarkable stability NOx conversion (provided that the T<400 °C) !***
- No indication for contribution Na, K, Ca.. from the lubricant to deactivation
- Methane removal efficiency is low at <400 °C: NOx is partly converted by higher HC's (and CO, aldehyde)
- Removal of sulfur is recommended (absorbent, 'zero'-sulfur lubricant)

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Ongoing research

- Further improvement hydrothermal stability of catalysts is recommended
  - both NOx and methane removal efficiency increase at (somewhat) higher temperature
  - increase operating-window
    - It seems possible (*the chef's secret*)
- Increase activity in real exhaust gas (with sulfur-resistant) additive to catalyst with NO oxidation functionality : it is possible !
- Second catalyst to remove left-over methane-slip (?)
  - It is possible !
  - Improve cost-efficiency by integration of functionalities

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