

Selective catalytic reduction of NO_x in real exhaust gas of gas engines using unburned gas

Catalyst deactivation and advances toward long-term stability

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Oral presentation

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

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Introduction

Gas engines are widely used for e.g. combined heat and power generation. More stringent NO_x limits have led to engine management that reduces NO_x emissions but increases the emission of greenhouse gas methane. While conventional SCR with ammonia as the reductant has proved successful to reduce the NO_x, the methane-slip is left untouched. The ideal situation would be to use the unburned hydrocarbon in exhaust gas to reduce NO_x instead of using ammonia. The Energy Research Centre of the Netherlands has successfully developed zeolite based catalysts with high activity for catalytic reduction of NO_x with methane [1]. Limited hydro-thermal stability of most zeolites does not favor their use in mobile applications where large temperature excursions exist [2]. Application of zeolites in the field of stationary pollution control, i.e., without large temperature excursions, seems less challenging. The high activity that can be accomplished with zeolites lowers the (required) minimum temperature of operation and therefore poses fewer demands with regards to (hydro)thermal stability of the material. Recent modification of the catalyst composition has also led to increased stability in real exhaust gas of a gas engine. In the present study, special attention is given to the elucidation of potential causes of catalyst deactivation in real exhaust gas.

Materials and Methods

A side-stream of the exhaust gas of the gas engine containing ca. 800 ppm methane, 150 ppm NO_x, 8 % O₂, 6 % CO₂, 1 ppm SO₂ and 12 % H₂O was led over a reactor containing the catalyst. Trace elements from lubricant were also present in the exhaust gas. Gas engines involved in this study were Senertec -and Waukesha engines of respectively 5 KWe and 312 KWe. A gas burner test facility (30 KWe), operated without lubricant, was also used in order to study the influence of the lubricant components. The exhaust gas composition was analyzed with NDIR, GC and a NO_x (chemiluminescence) analyzer. Fresh and used catalysts were characterized using temperature programmed reduction and desorption techniques and Infrared spectroscopy (DRIFT). Catalyst deposits were analyzed by ICP/AES chemical analysis.

Results and Discussion

Promoted metal-zeolite catalysts remove NO_x, methane (partly) and higher hydrocarbons, CO and aldehydes completely from the exhaust gas. Deactivation due to steam-dealumination of the zeolite with the 11-15 vol.% H₂O present in the exhaust gas is significant when exhaust gas temperature exceeds 723 - 773 K. At temperatures below 673 K this contribution to catalyst deactivation is insignificant. Below 673 K sulfur compounds, from odorant (in the natural gas) and lubricant, cause some 15 % 'initial' deactivation. After this period conversion levels of NO_x and methane are stable (see Figure 1). The conversion of methane at temperatures below 673 K is very low: NO_x is partly converted by reaction with higher hydrocarbons (and CO, aldehydes) that are also present in the gas.

The sulfur from the odorant and the lubricant is chemically bounded to the catalyst surface in at least two different ways. Temperatures over 773 K are necessary to remove these sulfur species. No indications have been found for the contribution of calcium, sodium, potassium

and phosphor from the lubricant to catalyst deactivation to any significant extent. Limited misfiring does not effect catalyst performance negatively: the excess of methane increases the SCR activity and removal efficiency. Ongoing research is devoted to definition of the relations between catalysts composition and stability (activity) of the catalysts.

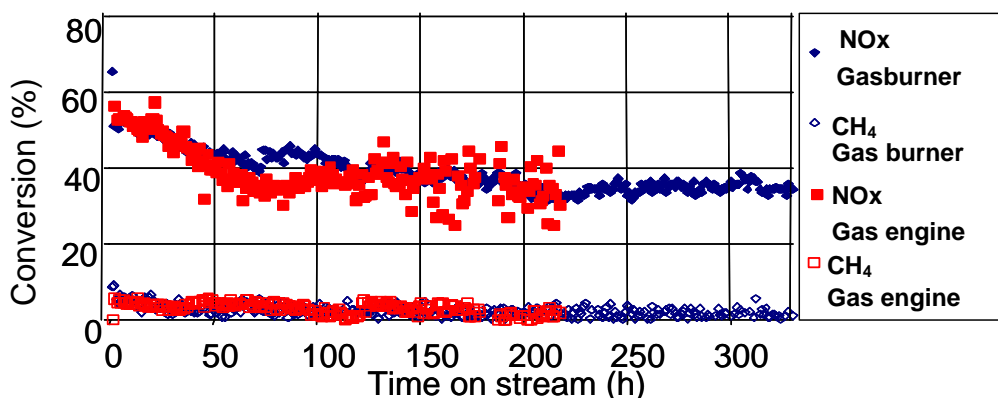


Figure 1. NOx and methane conversion over promoted pd-zeolite catalyst, $T_{\text{catalyst}} 673 \text{ K}$, natural gas driven engine (5KWe) and gas burner (30KWe), in the presence of ca. 800 ppm methane, 150 ppm NOx, 8 % O₂, 6 % CO₂, 1 ppm SO₂ and 12 % H₂O.

Significance

The potential of selective catalytic reduction of NOx with hydrocarbons as a technology to abate NOx is widely recognized. This study shows that promoted zeolite supported metal catalysts reduce NOx in the presence of sulfur, water and other potential catalyst poisons. The catalysts can be used in exhaust streams containing NOx in the presence of hydrocarbons, aldehydes, CO and/or hydrogen to reduce the NOx.

References

1. Pieterse, J.A.Z., Brink, van den R.W. Booneveld, S. and Bruijn, de F.A. Appl. Catal. B: Environmental 46, 239 (2003).
2. Traa, Y., Burger, B. and Weitkamp J., Mic. Mes. Mat. 30 3 (1999).



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Outline

- NOx and gas engines
- CH₄-SCR model studies
- CH₄-SCR in the tail gas of gas engines

NOx and gas engines

- Gas engines are used with e.g. co-generation installations
- Gas engines emit yearly ca. 12 kton NOx and CH₄ 14 kton [CH₄-slip 1 – 1.5 vol %] in the Netherlands (2002)
- Engine management to lower NOx emission:
 - Limited and 2-6 % higher greenhouse gas emission (CH₄/CO₂)
 - *'the anticipated level of NOx reduction renders combustion modification alone insufficient as a control technology'*
 - *need for catalysis-based technology*

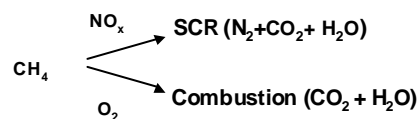
What catalysis-based technology can we use

- NO decomposition : Poor operation of catalysts under practical conditions (O_2 , H_2O)
- NH_3 - SCR : Complex operation with (small) gas engines
- Three-way-catalysis: Inadequate for *lean burn* (gas) engine
- CH_4 -SCR (HC-SCR):
 - Simultaneous reduction of NO_x and CH_4 emissions in tail gases of lean burn gas engines by *selective* reaction over a special catalyst

CH_4 -SCR

Challenges from a catalyst perspective:

- Tail gas (lean-burn) engine: NO_x , (surplus of) CH_4 , H_2O , O_2 , C_xH_y , S, CO, RCOH.....
- I. Activate CH_4
- II. Selectivity : combustion limits SCR



- III. Stability: Identify possible causes of deactivation

What catalyst do we need for CH₄-SCR

• Literature

Metals on metal oxide supports : poor to moderate (SCR -) activity (too much oxidation)

Metal on Zeolite support : high(er) activity

• History CH₄-SCR with metal-zeolites catalysts

Air Products (1992 - 1996) :

Cobalt-zeolite: active but loses activity in the presence of water

Gaz de France (2000), Ogura, Univ. Tokyo (2000) :

palladium (cobalt)-MOR and ZSM-5: very active

CH₄-SCR catalyst-testing at ECN

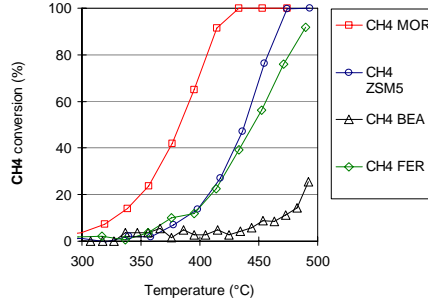
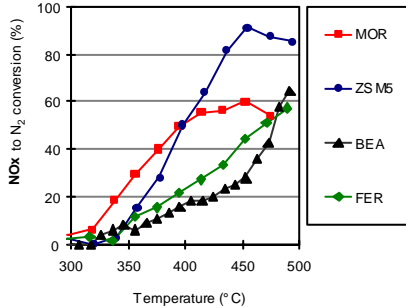
- Conventional micro-flow testing
- Pressure 1 atm.
- Flows up to 150 ml/min (STP)
- Synthetic gas mixtures to approach practical conditions of gas engines
- On-line IR gas analysis, NO_x chemiluminescence



Performance with model tail gas of gas engines

Synthetic gas mixture: 2500 ppm CH₄, 500 ppm NO, 5% H₂O, 5% O₂ GHSV ± 20,000 hr⁻¹

Cobalt (2.5wt%)-palladium(0.3wt%)-zeolites



Very active

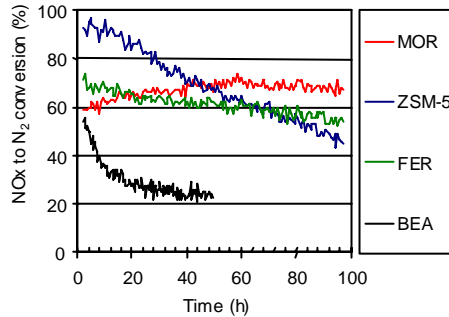
Stability ?

Pieterse et al. Applied Catalysis B: Environmental 46 (2003) 219
 Pieterse et al. Applied Catalysis B: Environmental 39 (2002) 167

Performance with model tail gas of gas engines

Synthetic gas mixture: 420 °C, 2500 ppm CH₄, 500 ppm NO, 5% H₂O, 5% O₂
 GHSV ± 20,000 hr⁻¹ (MOR and ZSM5), ± 10,000 hr⁻¹ (BEA and FER)

Cobalt (2.5wt%)-palladium(0.3wt%)-zeolites



Deactivation

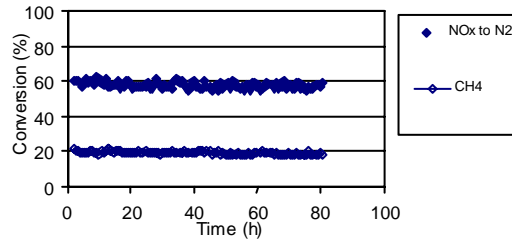
Pieterse et al. Applied Catalysis B: Environmental 46 (2003) 219
 Pieterse et al. Applied Catalysis B: Environmental 39 (2002) 167

Performance with model tail gas of gas engines

Synthetic gas mixture: 410 °C, 2500 ppm CH₄, 500 ppm NO, 10% H₂O, 5% O₂
 GHSV ± 30,000 hr⁻¹

Palladium-based zeolite with rare earth metal + additive

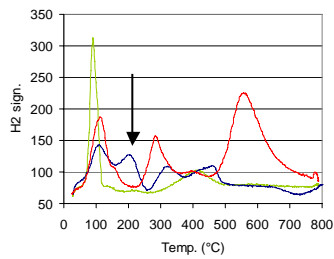
'Re - (pro) - Pd-zeolite'



Durability

Role of Re in stabilisation of palladium-zeolites

H₂-TPR



Fresh Pd-zeolite
 Used (deactivated) Pd-zeolite
 Used Re-pro-Pd-zeolite

General characteristic in deactivated Pd-zeolite is TPR-peak at ca. 200 °C

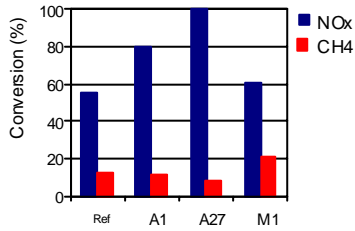
➤ Stable Re-Pd-zeolite catalyst does not show this peak

Performance with model tail gases of *various* gas engines

Synthetic gas mixture: A1, A27 and M1 refer to gas engines currently in use in the Netherlands

motor	Ref.	A1	A27	M1
NOx * (ppm)	500	239	117	234
CH4 (ppm)	2500	1713	2259	881
H2O (vol.%)	5	10.9	10.6	12.8
O2 (vol.%)	5	8.5	8.8	6.4
CO2 (vol%)	0	5.7	5.6	6.7

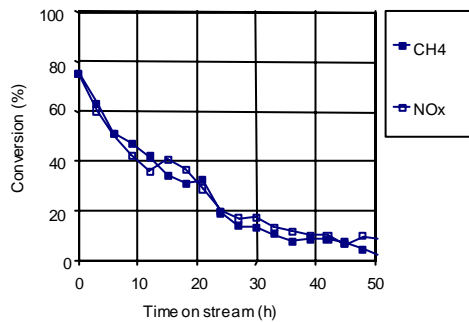
Re-pro-Pd-zeolite, 385 °C ±17,000 h⁻¹



➤ Catalyst *may* perform well in *real* tail gas of gas engines

Performance in *real* tail gas of gas engines

Side stream of Waukesha 312 KWe gas engine, ± 500°C, 800 ppm CH₄, 160 ppm NO_x, 12 % H₂O, 1 ppm SO₂, 8 % O₂



Initial activity very high but rapid deactivation

What causes catalyst deactivation in *real* tail gas of gas engines ?

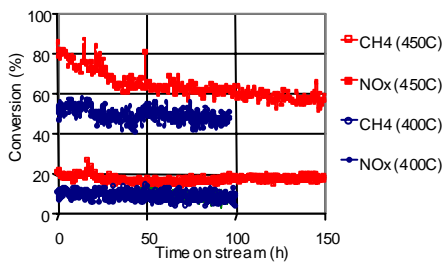
Possibilities:

- 1) Active metal, structure-stabilizer (zeolite structure) may 'change' at high temperature in the presence of high concentration water
- 2) SO₃/SO₂ from lubricant and odorant (natural gas)
- 3) Ca, Na, K, P, ('metal')..... from lubricant

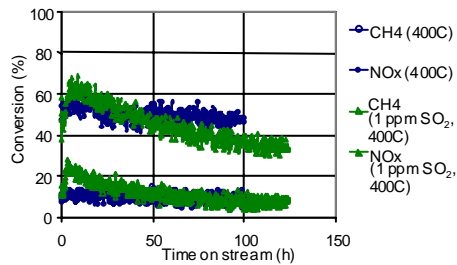
What causes deactivation

Synthetic gas mixture: 800 ppm CH₄, 200 ppm NO, 10% H₂O, 5% O₂

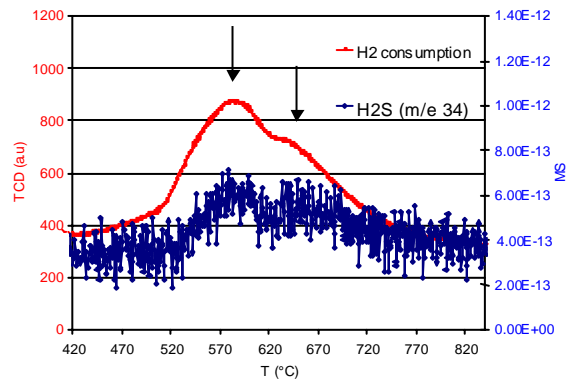
1) T + 10% H₂O (yes)



2) SO₂/SO₃ (yes)



TPR/MS



H₂S comes off at two different temperatures
Two SO_x species desorb at T > 500 °C

3) Ca, Na, K, P, ('metal')..... from lubricant

Real tail gas: 390°C, gas engine and gas burner, 800ppm CH₄, 160 ppm NO_x, 12 % H₂O, 1 ppm SO₂, 8 % O₂

1) **Keep temperature at 400 ° C**

2)

Gas **engine**: poisons
from lubricant (Na, K, Ca, P)

Gas **burner**: no 'poisons'
from lubricant (Na, K, Ca, P)

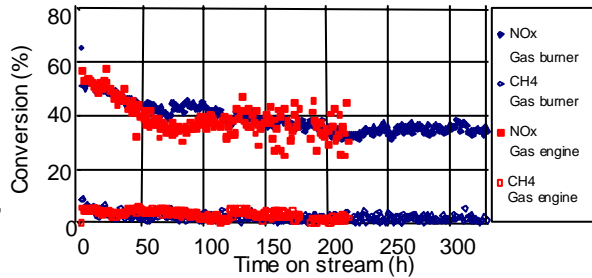
3) Ca, Na, K, P, ('metal')..... from lubricant

Real tail gas: 390°C, gas engine and gas burner, 800ppm CH₄, 160 ppm NO_x, 12 % H₂O, 1 ppm SO₂, 8 % O₂

1) Keep temperature at 400 ° C

2)
Gas engine: poisons from lubricant (Na, K, Ca, P)

Gas burner: no 'poisons' from lubricant (Na, K, Ca, P)



No apparent contribution of Na, K, Ca, P to deactivation

Poisoning with S is 'initial': **Stable NO_x conversion at prolonged times on stream in the presence of S**

Low conversion CH₄ / complete conversion traces C₂-C₆, HCOH, CH₃OH, CO

Conclusions

(Promoted) Pd zeolites give high NO_x removal efficiency

Temperature causes deactivation at >400 °C in the presence of >10% H₂O

Poisoning with S is 'initial': Stable NO_x conversion at prolonged times on stream

No apparent contribution Na, K, Ca.. from the lubricant to deactivation

Methane removal efficiency is low at <400 °C: NO_x is also converted by higher HC's, CO, aldehyde and alcohol

(Hydro-)thermal stability of catalysts should be improved for end-of-pipe use with gas engines