

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

**Catalyst deactivation and advances toward long-
term stability**

J.A.Z. Pieterse and R.W. van den Brink

H. Top^{*}, F. Vollink^{*} K. Hoving^{*}
**Gasunie Engineering and Technology*

Submitted for publication in Chemical Engineering Journal, 2005

Abstract

Catalytic conversion of CH₄ and NO_x in synthetic gas and real exhaust gas of a lean-burn gas engine was investigated. Rare earth promoted Pd-MOR catalyst proved to be very active in selective catalytic reduction of NO_x by CH₄ under simulated tail gas conditions. Conversion of CH₄ with SCR was, however, incomplete. A dual bed configuration, in which an SCR and an oxidation catalyst are placed in series, could complete the conversion of CH₄. The high CH₄-SCR activity was also established in a real exhaust gas of gas engines: NO_x, CH₄, higher hydrocarbons, CO, and aldehydes were removed (in part) from the exhaust stream. However, the conversion of CH₄ at temperatures of 400°C and below was much lower than in the tests with synthetic gas: NO_x was mostly converted in reactions with higher hydrocarbons (and CO, aldehydes), which are present in the exhaust gas mixture.

Deactivation studies indicated that steam-dealumination and agglomeration of the active sites was significant at temperatures above 450°C. At 400°C, the catalyst showed initial deactivation in real exhaust gas during the first days on stream. At longer time on stream, the conversion persisted at a constant level. The initial decay of the activity, as indicated by a loss of NO_x conversion by 15 %, was caused by chemisorption of the sulphur species on the catalyst surface. The sulphur species originated from the odorant, which is added to the natural gas. TPR experiments indicated that temperatures above 500 °C were necessary to remove (hydrogenate) these sulphur species. Calcium, sodium, potassium and phosphorus, as present in the lubricant, did not have a significant influence on the catalyst deactivation.

Keywords: NO_x, methane, gas engine, catalyst, deactivation, stability

Contents

List of tables	3
List of figures	3
Introduction	7
Experimental	9
Results and Discussion	11
Conclusions	15

List of tables

Table 1: Exhaust gas composition of various types of gas engines currently in use in the Netherlands

Table 2: ICP/AES elemental analysis of fresh and used catalysts

List of figures

Fig. 1 Conversion of NO_x (open symbols) and methane (closed symbols), 500 ppm NO, 2500 ppm CH₄, 5% O₂, 5 % H₂O, W/F 4 mg.ml⁻¹.

Fig. 2 Influence of gas composition on the NO_x and CH₄ conversion, RE-Pd-MOR, W/F 4 mg.ml⁻¹, 390 °C.

Fig. 3 Concentration profiles of NO_x and CH₄ in a dual bed reactor with SCR and Oxidation catalyst placed in series.

Fig. 4 NO_x and CH₄ conversion with a dual bed reactor for which SCR and Oxidation catalyst (respectively RE-Pd-MOR and Pd-REO_x-ZrO₂) are placed in series: 500 ppm NO, 2500 ppm CH₄, 5% O₂, 5 % H₂O, W/F 4 mg.ml⁻¹ for both.

Fig. 5 Conversion of NO_x and CH₄ in the exhaust gas of a gas engine at ca. 500 °C, W/F 12 mg.ml⁻¹. Gas composition approximately: 800 ppm methane, 180 ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁₊ hydrocarbon, 9 ppm CO, 70 ppm oxygenate, 1 ppm SO₂.

Fig. 6 Hydrogen consumption (TCD) and H₂S desorption during temperature programmed reduction measurement with RE-Pd-MOR used in reaction.

Fig. 7 IR spectra of RE-Pd-MOR, calcined at 450 °C (fresh) and used in the reaction with gas engine exhaust gas (see Figure 5). The samples were dehydrated at 400 °C in nitrogen prior to IR measurements at 350 °C.

Fig. 8. Influence of the temperature on the durability of NO_x and CH₄ conversion, RE-Pd-MOR, synthetic gas 500 ppm NO, 2500 ppm CH₄, 5% O₂, 10 % H₂O, W/F 4 mg.ml⁻¹.

Fig. 9 Influence of SO₂ on the durability of NO_x and CH₄ conversion, synthetic gas 500 ppm NO, 2500 ppm CH₄, 5% O₂, 10 % H₂O, 0 and 1 ppm SO₂, RE-Pd-MOR, W/F 4 mg.ml⁻¹, 400 °C.

Fig. 10 Conversion of NO_x and CH₄ in the exhaust gas of a gas burner at 400 °C, RE-Pd-MOR, W/F 12 mg.ml⁻¹. Gas composition approximately: 800 ppm methane, 180

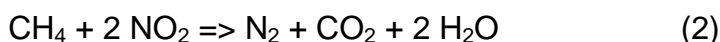
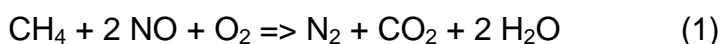
ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁+ hydrocarbon, 9 ppm CO, 70 ppm oxygenate.

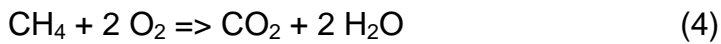
Fig. 11 Conversion of NO_x and CH₄ in the exhaust gas of a gas burner and gas engine at 400 °C, RE-Pd-MOR, W/F 12 mg.ml⁻¹. Gas composition approximately: 800 ppm methane, 180 ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁+ hydrocarbon, 9 ppm CO, 70 ppm oxygenate, 1 ppm SO₂.

Introduction

Gas engines are widely used for e.g. combined heat and power generation. Total yearly emission of NO_x by gas engines in the Netherlands is estimated to be 10 to 16 kton [1]. Catalytic methods to reduce NO_x have gained a great deal of interest over the last decade. Selective catalytic reduction (SCR) of NO_x with NH₃ as the reductant has found application in the industry [2, 3]. While high conversion (>95%) can be achieved at reasonably low temperatures, smaller and mobile applications are in need of an alternative DeNO_x technology. Here, selective catalytic reduction of NO_x with hydrocarbons (SCR-HC) is expected to be more cost-effective and safer than SCR with NH₃. The ideal situation would be to use the unburned hydrocarbon in exhaust gas to reduce NO_x instead of using (externally injected) ammonia or other reductant. In this respect, more stringent NO_x limits have also led to engine management that reduces NO_x emissions but increases the pool of the greenhouse gas methane in the exhaust gas. While conventional ammonia-based SCR has proved successful to reduce the NO_x, the methane-slip is left untouched. In contrast, the reaction of NO_x with methane (CH₄-SCR) annihilates two environmentally malignant gases at the same time, improving the environment and providing greenhouse gas emission credits.

From a catalytic point of view the activity and in particular the selectivity in CH₄-SCR of catalysts pose major challenges. Methane is the least reactive alkane. In this respect, it is important to note that the temperature of the exhaust gas of gas engines ranges only from 350 °C to 500 °C, so the temperature available for end-of-pipe NO_x and CH₄ reduction catalysis is rather low. Also the selectivity of the catalysis is a matter of big concern: the tail-gas of lean-burn gas engines contains very high concentrations of oxygen. Using metal oxide supported noble metal catalysts like Three Way Catalysts (TWC) would mainly oxidise the methane while leaving the NO_x untouched. The stoichiometric SCR and oxidation reactions are listed below, 1-4.





Selective CH₄-SCR catalysts, which activity is in favor of reaction 1-3, are usually based on zeolite supports [4]. A well-known drawback is the limited hydro-thermal stability of most zeolites, which prohibits their use in mobile applications where large temperature excursions exist [5]. However, 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.

Zeolite-supported (cobalt-)palladium catalysts with high activity for catalytic reduction of NO_x with methane (CH₄-SCR) have been successfully developed [6,7]. However, deactivation of the zeolite-supported catalysts was observed. Detailed characterization including CO-chemisorption, H₂-TPR, DRIFT and activity measurements has indicated a temperature-induced mechanism of ion migration and sintering to be the ruling mechanism of deactivation. In addition, the process of steam dealumination in the presence of water might ease the sintering [6,7]. Zeolite MOR supported catalysts appeared most stable, albeit combustion activity (i.e., poor selectivity) lowered SCR activity [7].

In the present study, a Pd-MOR catalyst composition was modified with rare earth metals (RE) that increased (SCR-)activity, selectivity and durability. Catalysts were tested in synthetic feed gas that resembles exhaust gas composition of gas engines as well as in real exhaust gas of a gas engine and gas burner. Special attention was given to the elucidation of potential causes of catalyst deactivation in real exhaust gas. Therefore, the influence of sulphur and lubricant components in the gas together with the (hydro-)thermal stability, was explored.

Experimental

Materials

Mordenite (CBV21a, Si/Al 12) was obtained from Zeolyst. Pd-MOR (0.3 wt% Pd) SCR catalyst was prepared by wet ion exchange in air (24 h at 80 °C) from NH₄-zeolite powder and an acidified solution of palladium nitrate. Following the ion exchange, the catalyst was filtered, washed thoroughly with demineralised water and dried for 16 h at 80 °C. Rare earth metal (RE) was added to Pd-MOR by impregnation of the appropriate salt (RE-Pd-MOR). Finally, the catalyst was dried for 16 h at 80 °C and calcined at 500 °C in situ. This procedure ensured the transition of NH₄-zeolite into H-zeolite with the release of NH₃. Pd-REOx-ZrO₂ (1 Wt% Pd) combustion catalyst was prepared by impregnation of REOx-ZrO₂ with a solution of palladium nitrate.

REOx-ZrO₂ was prepared by co-precipitation: ZrO₂ (Gimex RC 100) was suspended with the rare earth metal nitrate salt under continuous stirring. The pH of the suspension was lowered from 5.2 to 4 with nitric acid. 0.125 M NH₃ was added to the suspension with 2 ml/min until a pH of 8 was reached. The suspension was filtered off, washed, dried at 80°C and calcined at 600 °C, for 8hr (25°C/min) to obtain 15 % REOx-85%ZrO₂. Catalyst powders were pressed at 5 bar and subsequently crushed and sieved. Sieve fractions of 0.25-0.5 mm were used for the experiments with synthetic gas and sieve fractions of 0.7-1.5 mm fraction were used for the experiments conducted with real exhaust gas.

Catalytic tests

The catalytic tests with *synthetic* feed gas were carried out in a computer-controlled flow set-up. The quartz reactor with an internal diameter of 0.6, 0.8 or 1 cm was placed in an oven. The catalyst sieve fraction (0.25–0.5 mm) was placed on a quartz grid. The catalyst bed height to reactor diameter ratio was kept constant to exclude axial dispersion effects. The feed consisted of 100-500 ppm NO, 800 - 2500 ppm CH₄, 5-8 % O₂, 0-1ppm SO₂ and 5-12 % H₂O in nitrogen. The quantitative analysis of the gas-phase components was performed using a Bomem MB100 Fourier transform infrared (FTIR) spectrometer equipped

with a model 9100 gas analyser. At the start of each activity experiment, the reactor temperature was increased to 175 °C at 3 °C. min⁻¹ under N₂ flow and flushed for 2 h. Subsequently, a background IR scan is made and the reaction gas mixture is then applied and fed to the catalyst. Preconditioning was set for 20 min at each temperature. Data were collected at ascending temperature using a ramp of 5 °C/min to maximal 500 °C. FTIR analysis averages 150 scans (resolution 1 cm⁻¹) and was performed twice at each temperature.

Conversion (based on dry flow) of NO_x was defined

$$(1 - (\text{NO}_2 + \text{NO})_t / (\text{NO}_2 + \text{NO})_o) * 100 \% \quad (5)$$

Conversion methane was defined

$$(1 - (\text{CH}_4)_t / (\text{CH}_4)_o) * 100 \% \quad (6)$$

The methane-based selectivity, in order to distinguish reaction with NO_x via SCR and methane oxidation by oxygen, is defined by means of consumed methane and NO molecules, i.e.,

$$[\text{CH}_4/\text{NO}_x]_{\text{consumed}} \quad (7)$$

High methane combustion activity is reflected in a high $[\text{CH}_4/\text{NO}_x]_{\text{consumed}}$.

The catalytic tests with *real exhaust* gas were conducted in a side-stream (controlled with valves to 100 NL/min) of the exhaust gas stream of the gas engine/burner. A Senertec mini-cogeneration gas engine (5 KWe) was used. A gas burner test facility (30 KWe), operated without lubricant, was also used in order to study the influence of the lubricant components. A gas flow that contained approximately 800 ppm methane, 150 ppm NO_x, 8 % O₂, 6 % CO₂, 1 ppm SO₂ and 12 % H₂O was passed over a reactor containing the catalyst. Trace elements from lubricant were also present in the exhaust gas of the gas engine. The exhaust gas composition was analyzed with NDIR (non-dispersive infrared spectroscopy), GC and a NO_x (chemiluminescence) analyzer.

Characterization

Fresh and used catalysts were characterized using ICP/AES chemical analysis, temperature programmed reduction (TPR) and desorption (TPD) techniques and Infrared spectroscopy (DRIFT). H₂-TPR spectra were recorded with an Altamira AMI-1 apparatus equipped with a TCD detector and a Balzers MS-detector, applying 30 ml/min flow of 10% H₂ in Argon at a heating rate of 20 °C/min. Infrared spectroscopic (IR) measurements were performed with diffuse reflectance spectroscopy (DRIFT) on a BIORAD FTS-175 spectrometer equipped with a Harrick HV-DR2 flow cell. Spectra were recorded in the Kubelka-Munk mode at 350 °C. The spectra were recorded with a spectral resolution of 4 cm⁻¹.

Results and Discussion

NO_x and CH₄ removal efficiencies

Figure 1 shows the NO_x and CH₄ conversions obtained with Pd-MOR, RE-Pd-MOR and Pd-REOx-ZrO₂ catalysts in a feed with 500 ppm NO, 2500 ppm CH₄, 5% O₂ and 5 % H₂O in nitrogen. As expected from a metal oxide-supported catalyst, Pd-REOx-ZrO₂ catalysts oxidised methane but left the NO_x largely unconverted. The MOR supported catalyst showed much higher NO_x conversion. NO_x removal with Pd-MOR was, however, limited at higher temperature due to excessive methane combustion (as concluded from increased [CH₄/NO_x]_{consumed} (not shown)). RE-Pd-MOR showed superior NO_x removal efficiency between 300 and 500 °C. Obviously, the RE in Pd-MOR increased both SCR activity and selectivity (lower [CH₄/NO_x]_{consumed} compared to Pd-MOR). The oxidation of NO to NO₂, which has been identified as an important step in the reaction mechanism of CH₄-SCR [5, 8], increased the SCR-activity in RE-Pd-MOR as compared to Pd-MOR.

Test conditions were also changed to approach more realistic exhaust-gas compositions of (lean-burn) natural gas engines currently in use in the Netherlands, denoted A, B and C (respectively A1, A27, M1 in reference [9]), see Table 1. Compared to results presented in Figure 1 (obtained with the conditions listed in the table under 'Reference'), the water content and the CH₄/NO_x ratios are higher. The NO_x and CH₄ conversion obtained with RE-Pd-MOR with the various gas conditions is compiled

in Figure 2 for the situation at 390 °C. From the results it follows that with the realistic conditions the NO_x conversion is higher than with the model (reference) conditions. Additional experiments in which the CH₄/NO_x ratio was varied while concentration O₂ and H₂O were kept constant (not shown) indicate that the high methane to NO_x ratios with conditions B and C caused the higher SCR-activity. In a similar way it was inferred that CO₂ concentrations up to 30 vol.% did not affect conversion levels. Unfortunately, the total methane removal efficiency remained very low under all conditions.

In order to abate the leftover methane, oxidation functionality should be included. From the results presented in Figure 1 it follows that palladium supported on REO_x-zirconia is not a good catalyst for CH₄-SCR. On the other hand, the catalyst oxidised methane with high efficiency. Therefore, this catalyst may be used to abate the methane that is left unconverted by the SCR unit. A plausible reactor configuration for this purpose is depicted in Figure 3: A gas flow containing NO_x and methane is passed through the CH₄-SCR catalyst bed where NO_x is converted but methane only in part. The unconverted methane is subsequently passed over a catalyst bed placed in series comprising the oxidation catalyst. In order to test this dual-bed reactor in practice the RE-Pd-MOR and a Pd-REO_x-ZrO₂ catalyst were placed in series and tested in synthetic gas. As shown in Figure 4, over 70 % conversion of both NO_x (to N₂) and CH₄ was obtained at temperatures from 400 °C and up. No other nitrogen-containing compounds than N₂ were detected.

Performance of CH₄-SCR catalyst with real gas engine exhaust gas

RE-Pd-MOR was tested in a side stream of a gas engine. NO_x and CH₄ conversions are shown in Figure 5 as a function of the time. The temperature of the catalyst was close to 500 °C. As can be seen the NO_x and methane conversion initially reached very high conversion of 80 % for both. However, these conversions decayed to values below 10 % within 24 hour on stream. Thus, severe catalyst deactivation is observed. Three well-known contributions to catalysts deactivation are likely to play a role here: 1) sulphur from the natural gas and from the lubricant poisons the catalysts [10], 2) alkali metal, phosphorus, Zn from the lubricant is deposited on the catalyst inhibiting the catalytic reactions [11] and 3) the catalyst support and/or the active sites change due to the high temperature in the presence of high concentrations of water and oxygen [12]. In order to assess the significance of these three to catalyst deactivation the catalyst was characterised for both deposits and structural changes. Elemental analysis results

are compiled in Table 2. From the table it follows that some alkali metals have deposited on the catalysts during its use in the exhaust gas stream of the gas engine. Some phosphorus is found and also significant amounts of sulphur but no zinc.

The sulphur deposits were further characterised by means of TPR/MS analysis. Figure 6 shows hydrogen consumption by the reduction of sulphate and the concomitant formation of H₂S in the gas phase during TPR. At least two maxima as function of the temperature were observed. This indicates that the sulphur from the odorant and the lubricant is chemically bounded to the catalyst surface in at least two different ways. Temperatures over 500 °C are necessary to remove these sulphur species with hydrogen.

Infrared spectroscopy was used to study structural features of the zeolite-supported catalyst. High temperature in the presence of water is known to migrate aluminium from the tetrahedral environment in the lattice of zeolites (depending on the zeolite type, Si/Al, hydrophobicity), i.e. the process of steam dealumination. As a consequence, less charge compensating sites, as necessary for the stabilisation of metal(ions), are available, crystallinity is partly lost and surface area may increase [13]. Figure 7 shows the DRIFT spectra of fresh and used RE-Pd-MOR (the sample collected after the durability test presented in Figure 5). The bridging OH at 3600 cm⁻¹ became less intense and instead a new band evolved at slightly higher wavenumber, 3630-3660 cm⁻¹. This new band is attributed to extra-framework aluminium (EFAL) and indicates the removal of framework aluminium to locations in the zeolite pores [13]. It is clear that the crystallinity of the zeolite has been affected negatively by reaction at 500 °C. As a consequence, the electrostatic field stabilising the active metal [6,7] is partly lost, which in turn causes metal migration and eventually loss of dispersion. Therefore, loss of catalytic activity can be anticipated.

From the characterisation study covered by the Figures 6, 7 and Table 2 it becomes clear that all three factors that are in potential capable to cause catalyst deactivation are indeed present. However, in order to identify the relative importance of the three and to explore the possibility to improve durability, it is necessary to study each factor separately. The influence of thermal deactivation is easily studied by variation of the reaction temperature. Figure 8 shows the durability of the NO_x and methane removal efficiency at two different temperatures, i.e. 400 and 450 °C. The tests were conducted with synthetic gas, using 10 % water in the feed. At 400 °C stable conversion is obtained. However, at 450 °C some deactivation is already noticed. The same experiment at 400 °C was also repeated with 1 ppm SO₂ in the feed (Figure 9). The NO_x conversion first increased shortly, after which the NO_x conversion decayed to a 15 % lower value. Apparently, both temperature and sulphur contribute to the deactiva-

tion of RE-Pd-MOR in CH₄-SCR. The ruling contribution of both temperature and sulphur was also verified in a realistic test case: Figure 10 shows the time-on-stream behavior of RE-Pd-MOR in exhaust gas of the gas burner. Here, the gas burner was fed with odorant-free natural gas, i.e. any contribution of sulphur and lubricant-deposits to deactivation was excluded. The exhaust gas composition of the gas burner test facility and the gas engine was identical apart from the absence of lubricant components. Moreover, the catalyst temperature was kept at 400 °C during the course of the experiment. As shown in Figure 10, at 400 °C, in the absence of lubricant-components and sulphur and thermal deactivation, stable NOx and methane removal efficiency was obtained.

In order to identify the influence of lubricant components, time-on-stream behavior with gas engine exhaust gas was compared with the behavior with the gas burner exhaust gas. Both the engine and burner was fed with odorant-containing natural gas but the temperature of the catalyst was kept at 400 °C to exclude the contribution of thermal deactivation. The results are shown in Figure 11. It shows that the time on stream behavior obtained with gas engine exhaust gas was similar to that obtained with gas burner exhaust gas, i.e. the contribution of lubricant components to CH₄-SCR catalyst deactivation is not evident (within the time span of the experiments). From the Figure 11 it also follows that at 400 °C sulphur compounds, from odorant in the natural gas, cause some 15 % 'initial' deactivation during the first days on stream. After this period the conversion remained stable. However, the conversion of methane at 400 °C is much lower as was envisioned from the tests with synthetic gas: NOx is partly converted by reaction with higher hydrocarbons, CO, formaldehyde and methanol that are also present (respectively, 60, 9, 40 and 40 ppm) in the exhaust gas. In this respect, it was reported by Lampert et al. [14] that 1 ppm SOx present in the exhaust of a lean burn natural gas engine strongly inhibits the reaction of CH₄ over a Pd containing catalyst. The reaction of NOx with non-methane emissions, such as C₂H₆, C₃H₈ and CO, was also inhibited by low SOx concentrations, but to a lesser extent than CH₄.

The limited thermal stability of RE-Pd-MOR decreases practical feasibility. If the catalyst could be operated at a higher temperature it would increase the overall applicability of the technology with engines, increase NOx and methane removal efficiency by CH₄-SCR, thereby limiting the need for a dual bed SCR-oxidation reactor. Moreover, higher temperature could limit the extent of sulphur poisoning. Sulphur poisoning is mostly associated with the formation of sulphate species under oxidising conditions. The pool of activated methane (and thus formed hydrogen) expands with increasing temperature reducing NOx and (simultaneously) hydrogenating sulphate species. As is inferred from Figure 6, hydrogenation of the sulphate species removes sulphur from the

catalyst surface. Recently, it was shown that the higher temperatures indeed tremendously decrease the extent of deactivation by sulphur for supported Pd catalysts [15].

Conclusions

Catalytic conversion of methane and NO_x in synthetic gas and real exhaust gas of a lean-burn gas engine was investigated. MOR-supported palladium catalysts seem more suitable for use in selective catalytic reduction with hydrocarbons than ZrO₂ supported palladium catalysts. Rare earth promoted Pd-MOR catalyst proved to be particularly active in selective catalytic reduction of NO_x by CH₄ (CH₄-SCR) under simulated tail gas conditions. Conversion of methane with SCR was, however, incomplete below 500 °C. A dual bed configuration, in which an SCR and an oxidation catalyst are placed in series, could complete the conversion of CH₄. The high CH₄-SCR activity was also established in a real exhaust gas of gas engines: NO_x, CH₄, higher hydrocarbons, CO, and aldehydes were removed (in part) from the exhaust stream. However, the conversion of methane at temperatures of 400°C and below was much lower than in the tests with synthetic gas: NO_x was mostly converted in reactions with higher hydrocarbons (and CO, aldehydes), which are present in the exhaust gas mixture.

Deactivation studies indicated that steam-dealumination and agglomeration of the active sites was significant at temperatures above 450°C. Below 400°C, the catalyst showed initial deactivation in real exhaust gas during the first days on stream. At longer time on stream, the activity remained stable. The initial decay of the activity, as indicated by a loss of NO_x conversion by 15 %, was caused by chemisorption of the sulphur species on the catalyst surface. The sulphur species originated from the odorant, which is added to the natural gas. TPR experiments indicated that temperatures above 500 °C were necessary to remove these sulphur species. Calcium, sodium, potassium and phosphorus, as present in the lubricant, did not have a significant influence on the catalyst deactivation.

Practical feasibility of HC-SCR of NO_x as a technology to abate NO_x should be increased by improving the hydro-thermal stability of the zeolite-supported catalysts. Ongoing research is devoted to this task.

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Table 1: Exhaust gas composition of various types of gas engines currently in use in the Netherlands

Gas engine	Reference	A	B	C
NO _x (ppm)	500	239	117	234
CH ₄ (ppm)	2500	1713	2259	881
H ₂ O (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

Table 2: ICP/AES analysis of fresh and used catalysts

(ppm)	P	S	Fe	Ca	K	Na
Fresh	11	0	790	55	60	5
used	24	450	700	76	95	55

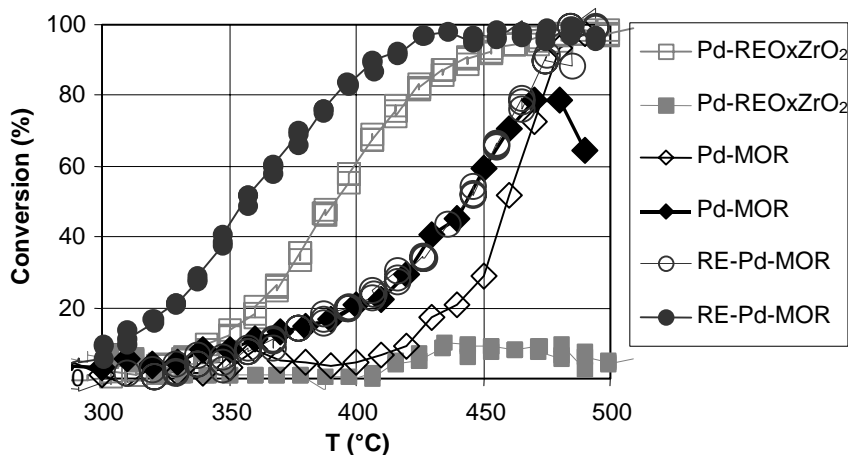


Fig. 1. Conversion of NO_x (closed symbols) and methane (open symbols), 500 ppm NO, 2500 ppm CH₄, 5% O₂, 5% H₂O, W/F 4 mg.ml⁻¹.

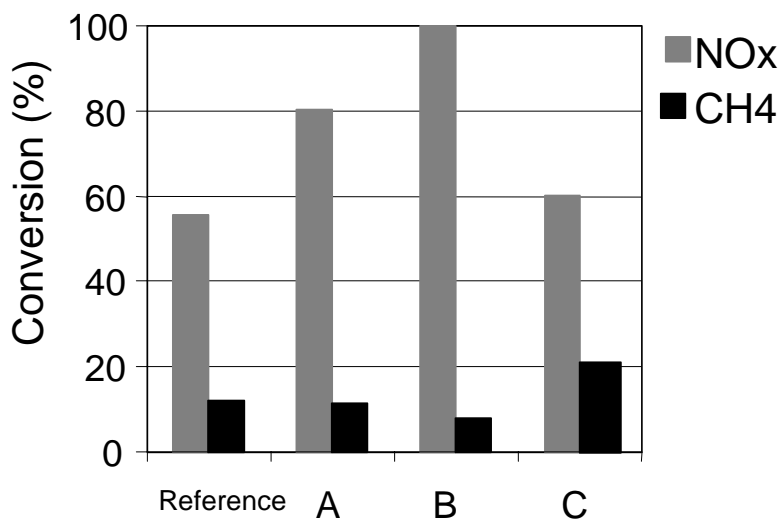


Fig. 2. Influence of gas composition on the NO_x and CH₄ removal efficiencies, RE-Pd-MOR, W/F 4 mg.ml⁻¹, 390 °C.

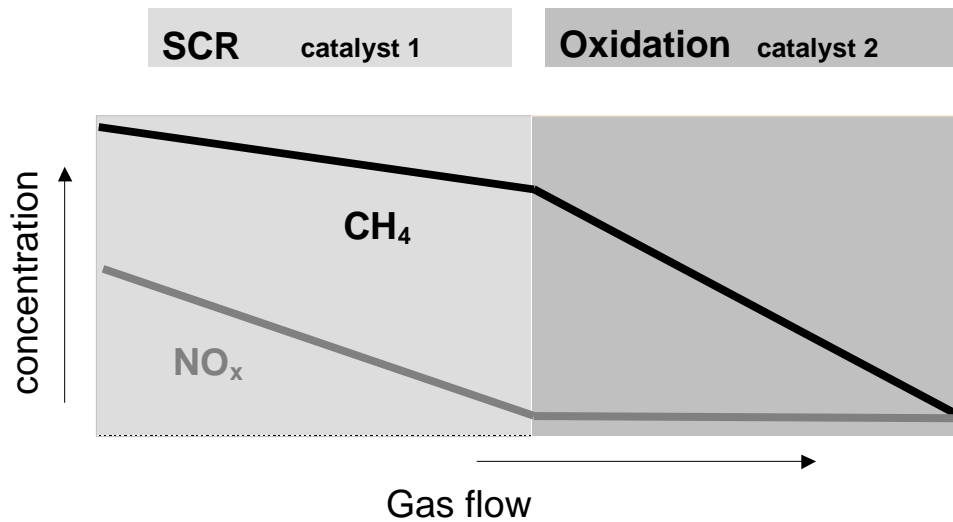


Fig. 3. Concentration profiles of NO_x and CH₄ in a dual bed reactor with SCR and Oxidation catalyst placed in series.

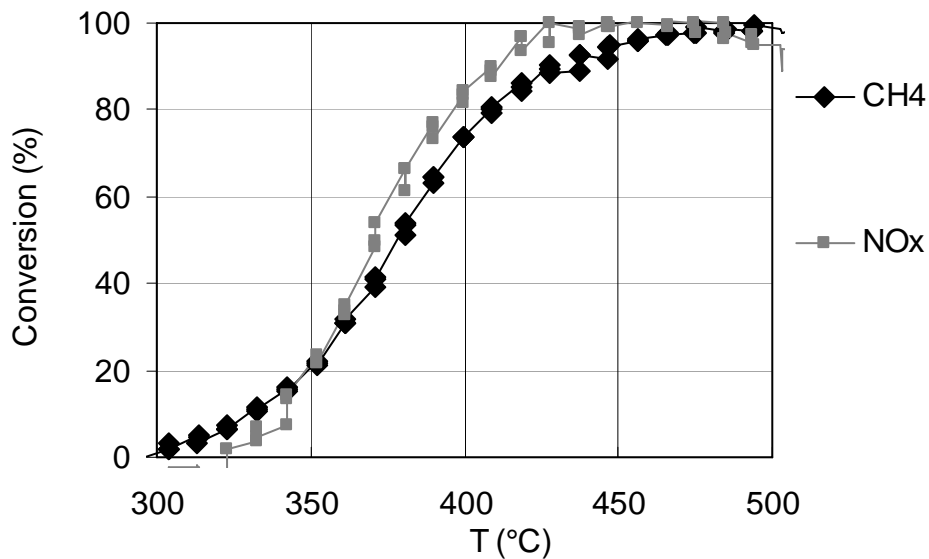


Fig. 4. NO_x and CH₄ conversion with a dual bed reactor for which SCR and Oxidation catalyst (respectively RE-Pd-MOR and Pd-REO_x-ZrO₂) are placed in series: 500 ppm NO, 2500 ppm CH₄, 5% O₂, 5 % H₂O, W/F 4 mg.ml⁻¹.

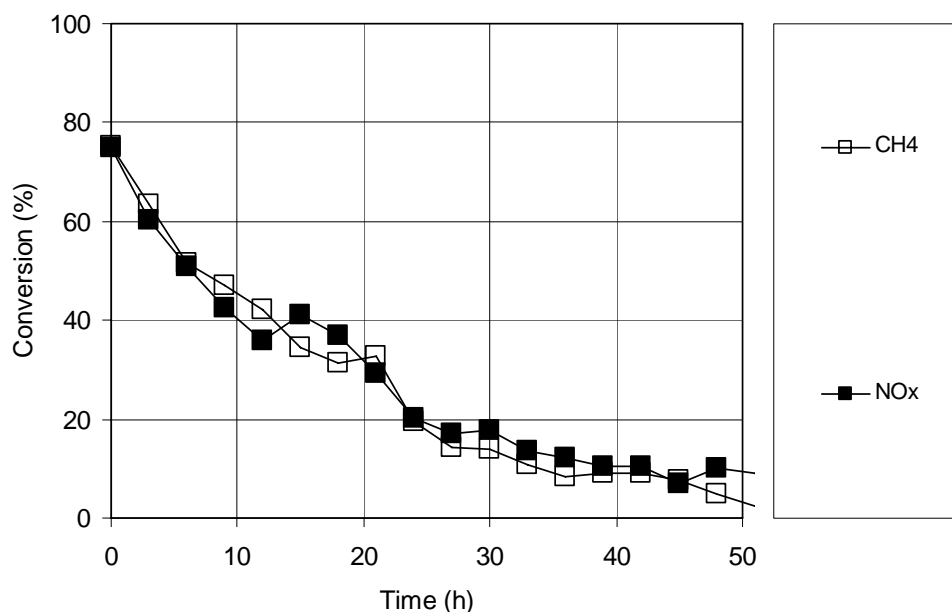


Fig. 5. Conversion of NO_x and CH₄ in the exhaust gas of a gas engine at ca. 500 °C, W/F 12 mg.ml⁻¹ Gas composition: 800 ppm methane, 180 ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁₊ hydrocarbon, 9 ppm CO, 70 ppm oxygenate 1 ppm SO₂.

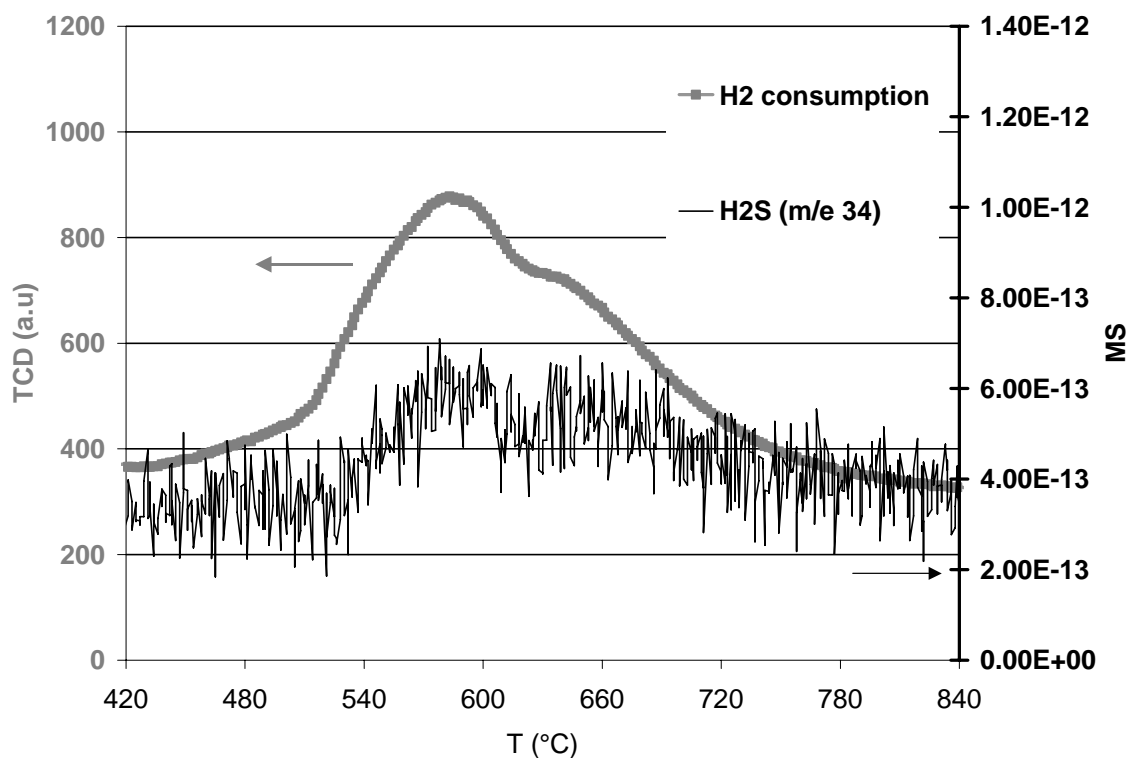


Fig. 6. Hydrogen consumption (TCD) and H₂S desorption during temperature programmed reduction measurement with RE-Pd-MOR used in reaction.

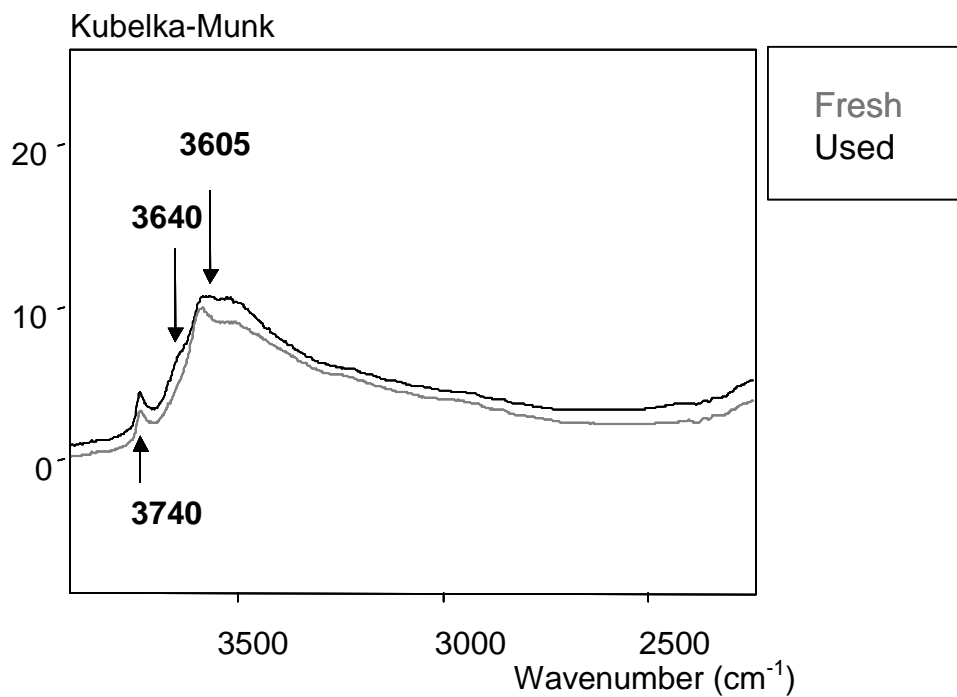


Fig. 7. IR spectra of RE-Pd-MOR, calcined at 450 °C (fresh) and used in the reaction with gas engine exhaust gas (see Figure 5). The samples were dehydrated at 400 °C in nitrogen prior to IR measurements at 350 °C.

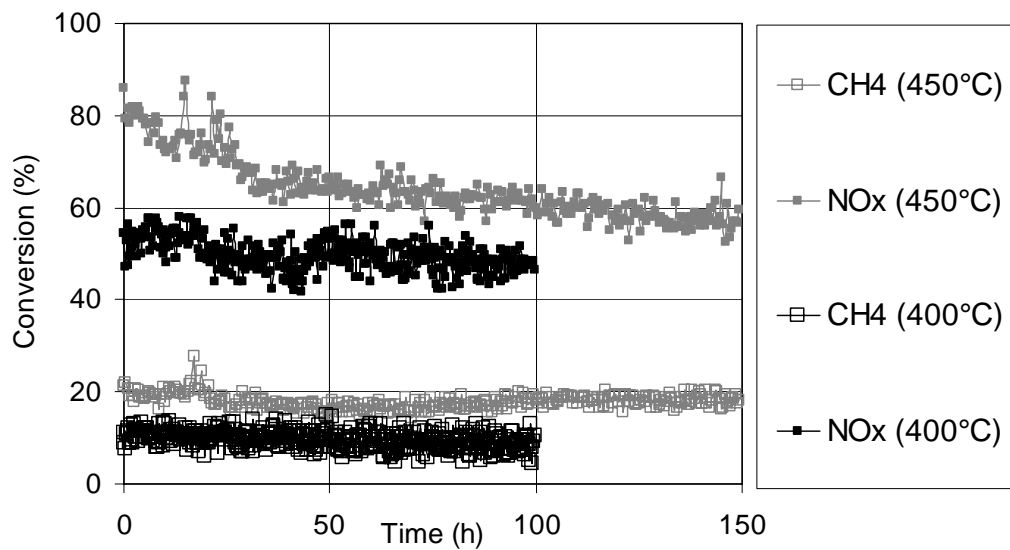


Fig. 8. Influence of the temperature on the durability of NO_x and CH₄ conversion, RE-Pd-MOR, synthetic gas 500 ppm NO, 2500 ppm CH₄, 5% O₂, 10 % H₂O, W/F 4 mg.ml⁻¹.

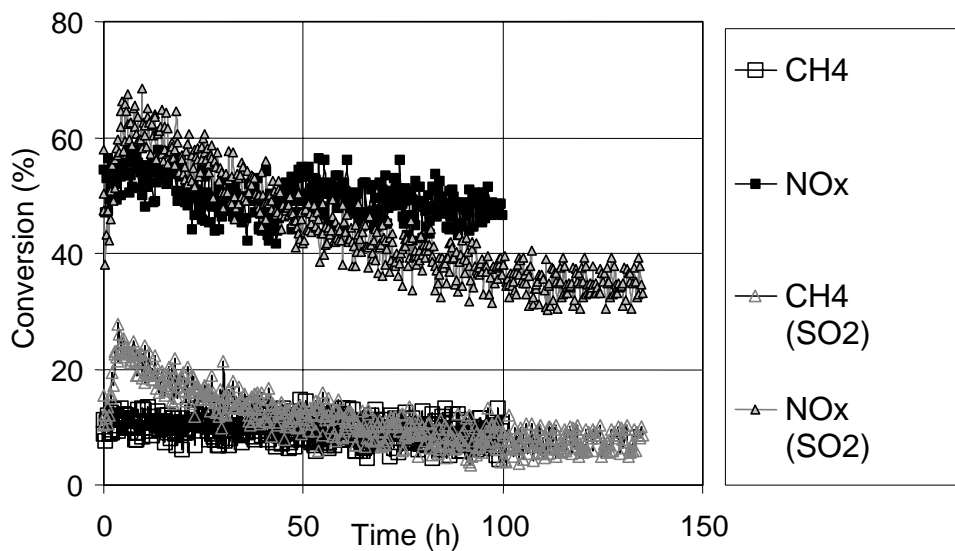


Fig. 9. Influence of SO₂ on the durability of NO_x and CH₄ conversion, synthetic gas 500 ppm NO, 2500 ppm CH₄, 5% O₂, 10 % H₂O, 0 and 1 ppm SO₂, RE-Pd-MOR, W/F 4 mg.ml⁻¹, 400 °C.

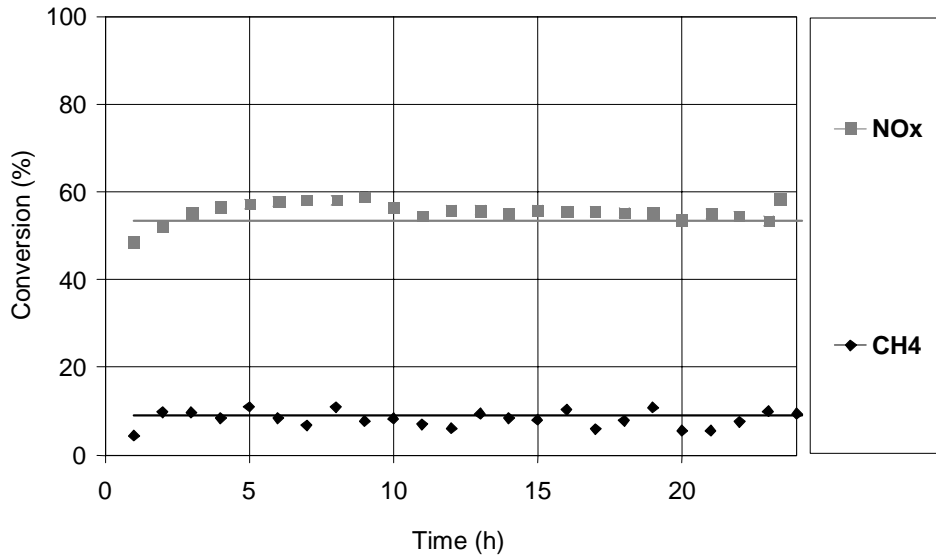


Fig. 10. Conversion of NO_x and CH₄ in the exhaust gas of a gas burner at 400 °C, RE-Pd-MOR, W/F 12 mg.ml⁻¹ Gas composition: 800 ppm methane, 180 ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁+ hydrocarbon, 9 ppm CO, 70 ppm oxygenate 1 ppm SO₂.

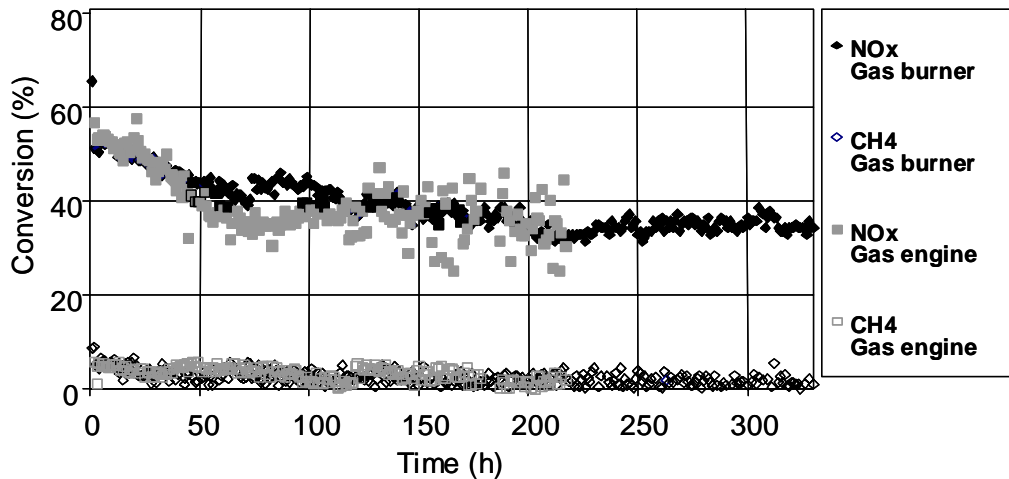


Fig. 11. Conversion of NO_x and CH₄ (conversion \pm 5 %, except for the period 120-220 hour on stream, gas engine: \pm 10 %) in the exhaust gas of a gas burner and gas engine at 400 °C, RE-Pd-MOR, W/F 12 mg.ml⁻¹ Gas composition: 800 ppm methane, 180 ppm NO_x, 12 vol.% H₂O, 8 vol.% O₂, 60 ppm C₁+ hydrocarbon, 9 ppm CO, 70 ppm oxygenate, 1 ppm S.