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

J.A.Z. Pieterse[a,*], H. Top[b], F. Vollink[b], K. Hoving[b], R.W. van den Brink[a]

[a] *ECN Clean Fossil Fuels, P.O. Box 1, Westerduinweg 3, 1755 ZG Petten, The Netherlands*

[b] *Gasunie Research, Energieweg 17, 9743 AN Groningen, The Netherlands*

Abstract

Catalytic conversion of CH_4 and NOx 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 NOx by CH_4 under simulated tail gas conditions. Conversion of CH_4 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 CH_4. The high CH_4-SCR activity was also established in a real exhaust gas of gas engines: NOx, CH_4, higher hydrocarbons, CO and aldehydes were removed (in part) from the exhaust stream. However, the conversion of CH_4 at temperatures of 400 °C and below was much lower than in the tests with synthetic gas: NOx 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 NOx 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: NOx; Methane; Gas engine; Catalyst; Deactivation; Stability

1. Introduction

Gas engines are widely used for, e.g. combined heat and power generation. Total yearly emission of NOx by gas engines in the Netherlands is estimated to be 10–16 kt [1]. Catalytic methods to reduce NOx have gained a great deal of interest over the last decade. Selective catalytic reduction (SCR) of NOx with NH_3 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 DeNOx technology. Here, selective catalytic reduction of NOx with hydrocarbons (SCR-HC) is expected to be more cost-effective and safer than SCR with NH_3. The ideal situation would be to use the unburned hydrocarbon in exhaust gas to reduce NOx instead of using (externally injected) ammonia or other reductant. In this respect, more stringent NOx limits have also led to engine management that reduces NOx 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 NOx, the methane-slip is left untouched. In contrast, the reaction of NOx with methane (CH_4-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 CH_4-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 to 500 °C, so the temperature available for end-of-pipe NOx and CH_4 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

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[*] Corresponding author.
E-mail address: pieterse@ecn.nl (J.A.Z. Pieterse).

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while leaving the NOx untouched. The stochiometric SCR and oxidation reactions (1)–(4) are listed below:

$$CH_4 + 2NO + O_2 \rightarrow N_2 + CO_2 + 2H_2O \quad (1)$$

$$CH_4 + 2NO_2 \rightarrow N_2 + CO_2 + 2H_2O \quad (2)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (3)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (4)$$

Selective CH_4-SCR catalysts, which activity is in favor of reactions (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 exists [5]. However, application of zeolites in the field of the 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 NOx with methane (CH_4-SCR) have been successfully developed [6,7]. However, deactivation of the zeolite-supported catalysts was observed. Detailed characterization including CO-chemisorption, H_2-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.

2. Experimental

2.1. 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 NH_4-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 NH_4-zeolite into H-zeolite with the release of NH_3. Pd-REOx-ZrO_2 (1 wt% Pd) combustion catalyst was prepared by impregnation of REOx-ZrO_2 with a solution of palladium nitrate.

REOx-ZrO_2 was prepared by co-precipitation: ZrO_2 (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 NH_3 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 8 h (25 °C/min) to obtain 15% REOx–85%ZrO_2. 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.

2.2. 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 CH_4, 5–8% O_2, 0–1 ppm SO_2 and 5–12% H_2O in nitrogen. The quantitative analysis of the gas-phase components was performed using a Bomen 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 under N_2 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 NOx was defined

$$\left(1 - \frac{(NO_2 + NO)_t}{(NO_2 + NO)_o}\right) \times 100\% \quad (5)$$

Conversion methane was defined

$$\left(1 - \frac{(CH_4)_t}{(CH_4)_o}\right) \times 100\% \quad (6)$$

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

$$\left[\frac{CH_4}{NOx}\right]_{consumed} \quad (7)$$

High methane combustion activity is reflected in a high $[CH_4/NOx]_{consumed}$.

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

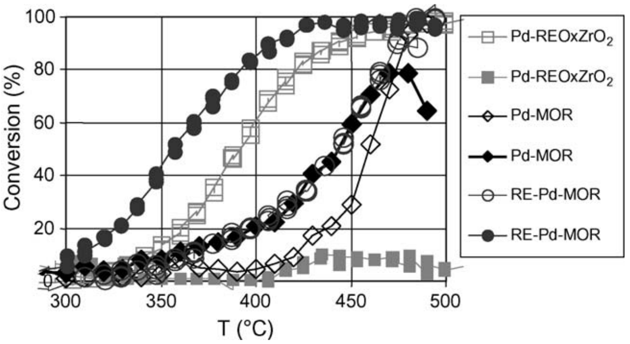

Fig. 1. Conversion of NOx (open symbols) and methane (closed symbols), 500 ppm NO, 2500 ppm CH_4, 5% O_2, 5% H_2O, W/F 4 mg ml^{-1}.

in order to study the influence of the lubricant components. A gas flow that contained approximately 800 ppm methane, 150 ppm NOx, 8% O_2, 6% CO_2, 1 ppm SO_2 and 12% H_2O 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 NOx (chemiluminesence) analyzer.

2.3. Characterization

Fresh and used catalysts were characterized using ICP/AES chemical analysis, temperature programmed reduction (TPR) and desorption (TPD) techniques and Infrared spectroscopy (DRIFT). H_2-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% H_2 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}.

3. Results and discussion

3.1. NOx and CH_4 removal efficiencies

Fig. 1 shows the NOx and CH_4 conversions obtained with Pd-MOR, RE-Pd-MOR and Pd-REOx-ZrO_2 catalysts in a feed with 500 ppm NO, 2500 ppm CH_4, 5% O_2 and 5% H_2O in nitrogen. As expected from a metal oxide-supported catalyst, Pd-REOx-ZrO_2 catalysts oxidised methane but left the NOx largely unconverted. The MOR supported catalyst showed much higher NOx conversion. NOx removal with Pd-MOR was, however, limited at higher temperature due to excessive methane combustion (as concluded from increased $[CH_4/NOx]_{consumed}$ (not shown)). RE-Pd-MOR showed superior NOx removal efficiency between 300 and 500 °C. Obviously, the RE in Pd-MOR increased both SCR activity and selectivity (lower $[CH_4/NOx]_{consumed}$ compared to Pd-MOR). The oxidation of NO to NO_2, which has been identified as an important step in the reaction mechanism of CH_4-SCR [5,8], increased the SCR-activity in RE-Pd-MOR as compared to Pd-MOR.

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_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

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 Fig. 1 (obtained with the conditions listed in the table under ‘Reference’), the water content and the CH_4/NOx ratios are higher. The NOx and CH_4 conversion obtained with RE-Pd-MOR with the various gas conditions is compiled in Fig. 2 for the situation at 390 °C. From the results it follows that with the realistic conditions the NOx conversion is higher than with the model (reference) conditions. Additional experiments in which the CH_4/NOx ratio was varied while concentration O_2 and H_2O were kept constant (not shown) indicate that the high methane to NOx ratios with conditions B and C caused the higher SCR-activity. In a similar way it was inferred that CO_2 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 Fig. 1 it follows that palladium supported on REOx-zirconia is not a good catalyst for CH_4-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 Fig. 3: a gas flow containing NOx and methane is passed through the CH_4-SCR catalyst bed where NOx is converted but methane only in part. The unconverted methane is subsequently passed over a catalyst bed placed in

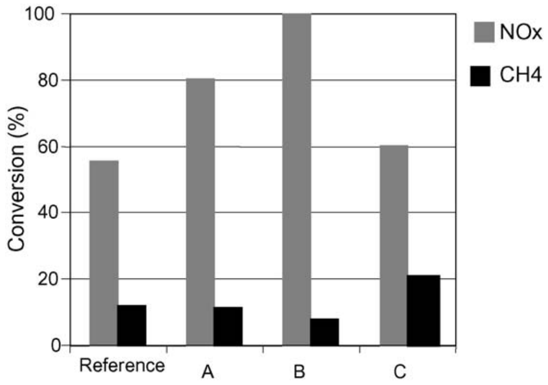

Fig. 2. Influence of gas composition on the NO_X and CH_4 conversion, RE-Pd-MOR, W/F 4 mg ml^{-1}, 390 °C.

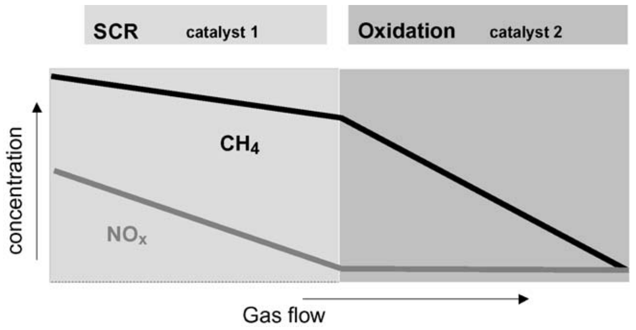

Fig. 3. Concentration profiles of NOx and CH_4 in a dual bed reactor with SCR and Oxidation catalyst placed in series.

series comprising the oxidation catalyst. In order to test this dual-bed reactor in practice the RE-Pd-MOR and a Pd-REOx-ZrO_2 catalyst were placed in series and tested in synthetic gas. As shown in Fig. 4, over 70% conversion of both NOx (to N_2) and CH_4 was obtained at temperatures from 400 °C and up. No other nitrogen-containing compounds than N_2 were detected.

3.2. *Performance of CH_4-SCR catalyst with real gas engine exhaust gas*

RE-Pd-MOR was tested in a side stream of a gas engine. NOx and CH_4 conversions are shown in Fig. 5 as a function of the time. The temperature of the catalyst was close to 500 °C. As can be seen the NOx and methane conversion initially reached very high conversion of 80% for both. However, these conversions decayed to values below 10% within 24 h 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. Fig. 6 shows hydrogen consumption by the reduction of sulphate and the concomitant formation of H_2S 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.

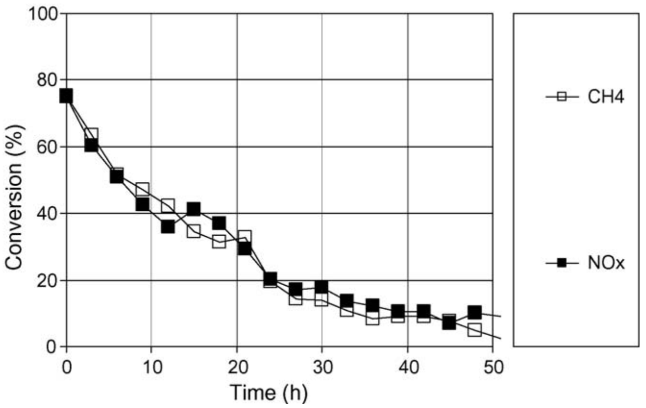

Fig. 5. Conversion of NOx and CH_4 in the exhaust gas of a gas engine at ca. 500 °C, W/F 12 mg ml^{-1}. Gas composition approximately 800 ppm methane, 180 ppm NOx, 12 vol.% H_2O, 8 vol.% O_2, 60 ppm C_1 + hydrocarbon, 9 ppm CO, 70 ppm oxygenate, 1 ppm SO_2.

Table 2
ICP/AES analysis of fresh and used catalysts

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

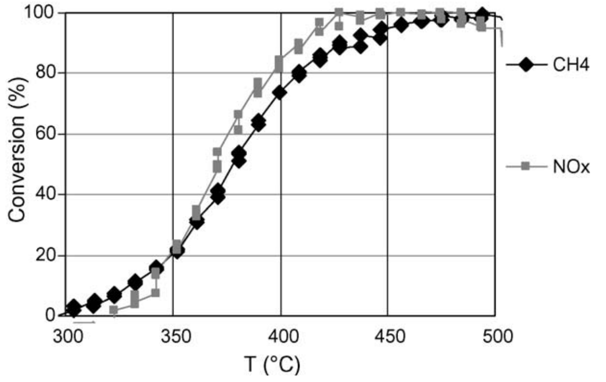

Fig. 4. NO_X and CH_4 conversion with a dual bed reactor for which SCR and Oxidation catalyst (respectively RE-Pd-MOR and Pd-REOx-ZrO_2) are placed in series: 500 ppm NO, 2500 ppm CH_4, 5% O_2, 5% H_2O, W/F 4 mg ml^{-1} for both.

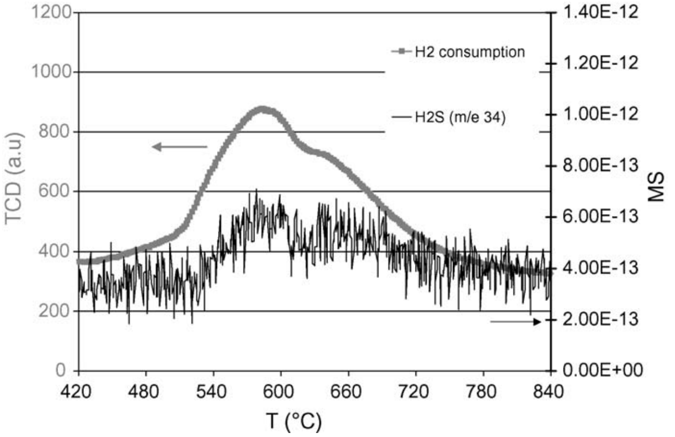

Fig. 6. Hydrogen consumption (TCD) and H_2S desorption during temperature programmed reduction measurement with RE-Pd-MOR used in reaction.

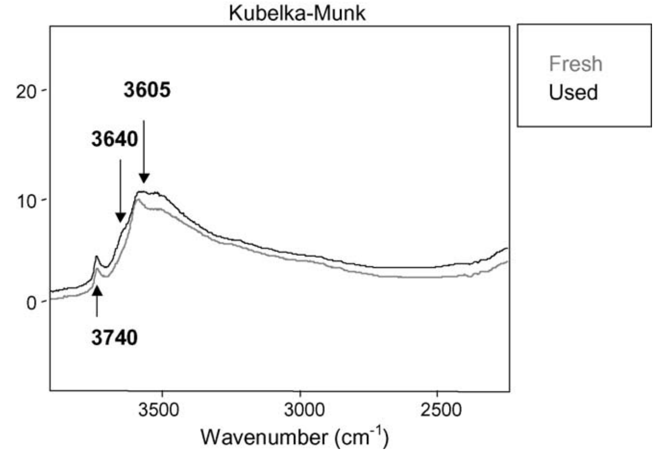

Fig. 7. IR spectra of RE-Pd-MOR, calcined at 450 °C (fresh) and used in the reaction with gas engine exhaust gas (see Fig. 5). The samples were dehydrated at 400 °C in nitrogen prior to IR measurements at 350 °C.

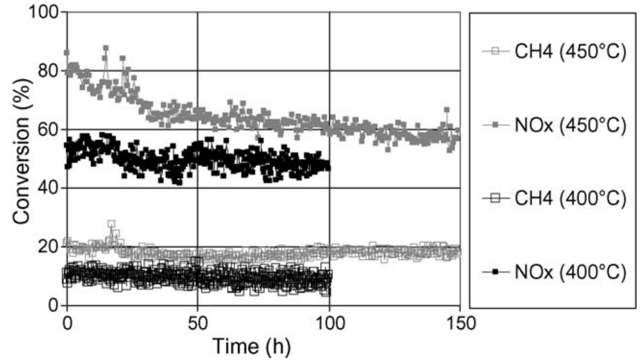

Fig. 8. Influence of the temperature on the durability of NOx and CH_4 conversion, RE-Pd-MOR, synthetic gas 500 ppm NO, 2500 ppm CH_4, 5% O_2, 10% H_2O, W/F 4 mg ml^{-1}.

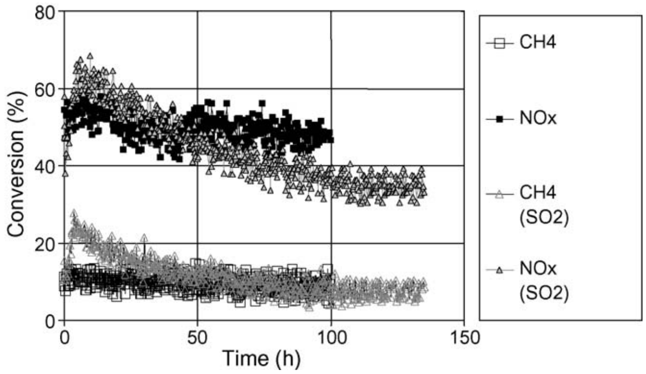

Fig. 9. Influence of SO_2 on the durability of NOx and CH_4 conversion, synthetic gas 500 ppm NO, 2500 ppm CH_4, 5% O_2, 10% H_2O, 0 and 1 ppm SO_2, RE-Pd-MOR, W/F 4 mg ml^{-1}, 400 °C.

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]. Fig. 7 shows the DRIFT spectra of fresh and used RE-Pd-MOR (the sample collected after the durability test presented in Fig. 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 Figs. 6 and 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. Fig. 8 shows the durability of the NOx 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 SO_2 in the feed (Fig. 9). The NOx conversion first increased shortly, after which the NOx conversion decayed to a 15% lower value. Apparently, both temperature and sulphur contribute to the deactivation of RE-Pd-MOR in CH_4-SCR. The ruling contribution of both temperature and sulphur was also verified in a realistic test case: Fig. 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 Fig. 10, at 400 °C,

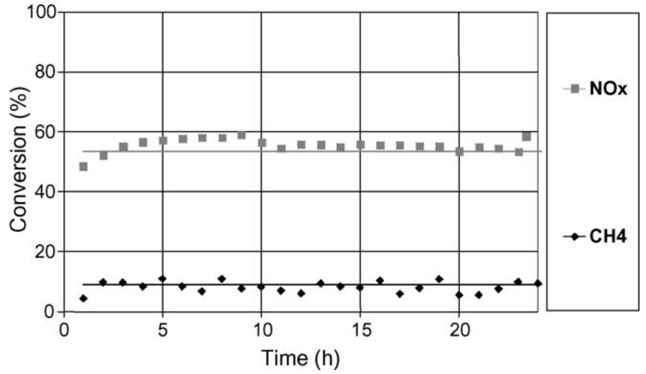

Fig. 10. Conversion of NOx and CH_4 in the exhaust gas of a gas burner at 400 °C, RE-Pd-MOR, W/F 12 mg ml^{-1}. Gas composition approximately 800 ppm methane, 180 ppm NOx, 12 vol.% H_2O, 8 vol.% O_2, 60 ppm C_1 + hydrocarbon, 9 ppm CO, 70 ppm oxygenate.

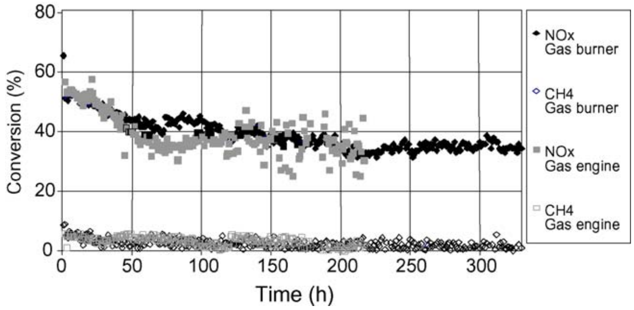

Fig. 11. Conversion of NOx and CH_4 in the exhaust gas of a gas burner and gas engine at 400 °C, RE-Pd-MOR, W/F 12 mg ml^{-1}. Gas composition approximately 800 ppm methane, 180 ppm NOx, 12 vol.% H_2O, 8 vol.% O_2, 60 ppm C_1 + hydrocarbon, 9 ppm CO, 70 ppm oxygenate, 1 ppm SO_2.

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 Fig. 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 CH_4-SCR catalyst deactivation is not evident (within the time span of the experiments). From the Fig. 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 CH_4 over a Pd containing catalyst. The reaction of NOx with non-methane emissions, such as C_2H_6, C_3H_8 and CO, was also inhibited by low SOx concentrations, but to a lesser extent than CH_4.

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 CH_4-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 Fig. 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].

4. Conclusions

Catalytic conversion of methane and NOx 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 ZrO_2 supported palladium catalysts. Rare earth promoted Pd-MOR catalyst proved to be particularly active in selective catalytic reduction of NOx by CH_4 (CH_4-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 CH_4. The high CH_4-SCR activity was also established in a real exhaust gas of gas engines: NOx, CH_4, 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: NOx 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 NOx 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 NOx as a technology to abate NOx 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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