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Regeneration of S-poisoned Pd/Al_2O_3 catalysts for the combustion of methane

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Abstract

Regeneration of S-poisoned Pd/Al_2O_3 catalysts for the abatement of methane emissions from natural gas vehicles was addressed in this work. Investigations were devoted to determine the temperature threshold allowing for catalyst reactivation under different CH_4 containing atmospheres. Under lean combustion conditions in the presence of excess O_2, partial regeneration took place only above 750 °C after decomposition of stable sulphate species adsorbed on the support. Short CH_4-reducing, O_2-free pulses led to partial catalyst reactivation already at 550 °C and to practically complete regeneration at 600 °C. Also in this case reactivation was associated with SO_2 release due to the decomposition of stable support sulphates likely promoted by CH_4 activation onto the reduced metallic Pd surface. Rich combustion pulses with $CH_4/O_2 = 2$ were equally effective to CH_4-reducing pulses in catalyst regeneration.

These results suggest that a regeneration strategy based on periodical natural gas pulses fed to the catalyst by a by-pass line might be efficient in limiting the effects of S-poisoning of palladium catalysts for the abatement of CH_4 emissions from natural gas engine.

Keywords: Pd-catalysts; CH_4 emission abatement; CH_4 combustion; Sulphur poisoning; Catalyst regeneration

1. Introduction

Natural gas represents one promising alternative energy source for the future in automotive and heavy-duty vehicles. In comparison with traditional fuelled vehicles, lean burn natural gas vehicles (NGV) engender a lower impact on environment, thanks to smokeless exhausts and reduced nitrogen oxide emissions due to the lower combustion temperatures associated with the high air to fuel mass ratios (typically 20 or greater) at which the lean engine operates. At given combustion engine efficiency also tailpipe CO_2 emissions in NGV light-duty vehicles can be lower than in conventional fuelled vehicles by virtue of the higher hydrogen-to-carbon ratio of natural gas. Nevertheless, the "green" image of lean burn NGV risks to be compromised by emission of unburned methane, a potent greenhouse gas estimated to have a 20 years global warming potential more than one order of magnitude higher than that of carbon dioxide. Accordingly severe limitations on CH_4 emissions have been enforced [1].

The use of an exhaust oxidation catalyst is the currently adopted way to match CH_4 emission limits, but obstacles arise from the reaction conditions specific to lean burn engines. Typical exhaust gases are characterized by low temperatures (even below 400 °C), presence of water vapour (10–15%), large excess of oxygen and concentration of methane as low as 500–1000 ppm. Under such conditions Pd/alumina catalysts are widely recognized as the most active in combustion of methane [1–4], but suffer from deactivation problems. The loss in activity is mainly attributed to sulphur containing compounds naturally occurring in natural gas or added as odorants necessary for safety reasons, which result in SO_2 concentration of 0.5–1 ppm in exhaust gases [2,5–10].

Several studies focused on the critical effect of SO_2 poisoning on the catalytic oxidation of methane, showing a marked loss in activity related to formation of stable sulphate species [2,5–10] associated with a strong adsorption of SO_3 produced by SO_2 oxidation over palladium catalyst. Several studies evidenced also the influence of the support on the rate of

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poisoning of the PdO catalyst, deactivation being much faster for non-sulphating support like SiO_2 [11] and SiO_2–ZrO_2 [2] than for sulphating supports, like Al_2O_3 which slow down the deactivation rate by scavenging of sulphate species. On the other hand, catalyst reactivation via decomposition of sulphate species by thermal treatment under oxidizing atmosphere [2,6] or, more effectively, by H_2 reductive conditions [12] was found more difficult for catalyst dispersed over sulphating supports suggesting that decomposition of stable support sulphate species is required for partial or complete reactivation.

In this work, the regeneration of a S-poisoned 2% (w/w) Pd/Al_2O_3 catalyst was investigated by means of alternate pulses and temperature step experiments, in order to evaluate the temperature threshold to obtain catalyst reactivation under different CH_4 containing atmospheres including: lean combustion (excess of O_2); CH_4-reducing (O_2-free) and rich combustion (O_2 deficient) atmospheres. The effect of alternate lean combustion/CH_4-reducing pulses on unpoisoned catalyst was also addressed to better understand modifications of palladium catalyst during reduction/reoxidation cycles.

2. Experimental

Palladium catalysts supported on γ-Al_2O_3 (LaRoche Versal TD250) were obtained by incipient wetness impregnation using an aqueous solution of $Pd(NO_3)_2$ (Aldrich, 10%, w/w, Pd, 99.999%) of the supports calcined at 800 °C for 6 h. 2% (w/w) Pd was loaded in a single impregnation step. Catalysts were dried overnight at 110 °C and then calcined for 6 h at 800 °C in a 0.2 l/min air flow (heating/cooling rate 10 °C/min). The BET surface area of the catalyst was 122 m^2/g.

The fresh catalyst was submitted to accelerated SO_2 poisoning by treatment at 380 °C for 15 h in a stream containing 10 ppm SO_2, 0.5% CH_4, 2% O_2, He to balance at GHSV = 180,000 cm^3/g/h at STP, in the presence of H_2O as a CH_4 combustion product. Details on procedure and poisoning behaviour are reported elsewhere [13].

The performances of fresh and S-poisoned catalysts were studied using a fixed bed tubular quartz micro reactor (i.d. = 7 mm) at atmospheric pressure, placed within an electrically heated furnace. Temperature was monitored by a K-type thermocouple located in the middle of the catalytic bed, consisting of 60 mg of powder catalyst (140–200 mesh) diluted by 60 mg of quartz with the same particle size. Reactant and product compositions including SO_2 and H_2S were monitored by a mass spectrometer with quadrupole detector (Balzers QMS 422). Analyses were periodically verified using a HP6890 GC system.

Different types of experiments were performed to monitor activity of fresh and S-poisoned catalysts.

2.1. Fresh catalyst

Temperature programmed combustion (TPC) tests were carried out feeding the reactor with 0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He at 150 cm^3/min at STP and GHSV = 150,000 cm^3/g/h. H_2O was always co-feed to reactants under all the investigated conditions in view of its well recognized effect on palladium combustion catalyst [14]. Temperature was ramped at 15 °C/min up to two different levels: 500 °C (TPC-500) or 900 °C (TPC-900); respectively, well below and above the threshold of PdO decomposition under the investigated conditions. The catalyst was cooled at the same rate down to room temperature.

Temperature programmed reduction (TPR) experiments were carried out at the same flow rate, GHSV and temperature range conditions with a feed composition of 0.5% CH_4, 2% H_2O, balance He. Temperature was ramped up to 500°C and down to RT at 15 °C/min.

The behaviour of the fresh catalyst at a constant temperature of 350 °C was investigated by the following alternate pulses experiments: (i) a series of alternate lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) and CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar) pulses; (ii) a series of alternate oxidizing (4% O_2, 16% N_2, 2% H_2O, balance He) and CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar) pulses. Alternate pulse experiments were performed according to the following modality. The catalyst was maintained for 30–60 min under lean combustion (or oxidizing) conditions, then the feed was switched to pure He for 40–50 s to favour the desorption of species adsorbed on catalyst surface and the purge of the dead volume. After the purge a reducing stream was fed to the reactor for 2 min. Then a helium purge was again carried out for 40–50 s and finally lean combustion (or CH_4-free oxidizing) conditions were restored. Ar tracer was always fed with CH_4 (CH_4/Ar = 10) to clearly identify the actual switch time between different atmospheres. During all the different phases the flow rate was kept at 150 cm^3/min at STP corresponding to a GHSV = 150,000 cm^3/g/h at STP.

2.2. S-poisoned catalyst

Only TPC-900 test was carried out over S-poisoned catalyst at the same feed composition, flow rate and GHSV adopted for tests over fresh catalyst. Also in TPR the temperature was ramped up to 900 °C.

Three types of temperature step experiments were performed. CH_4 conversion value under lean combustion conditions at 400 °C was initially registered. Temperature was then increased by 50 °C steps at 15 °C/min up to different levels: e.g. 450, 500, 550, 600, 650, 700, 750 and 800 °C. Depending on the type of experiment the following treatments were performed at each temperature step: (i) one hour aging under lean combustion conditions; (ii) a series of four alternate lean combustion/CH_4-reducing pulses according to the same procedure described above; (iii) a series of four alternate lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar)/rich combustion (1% CH_4, 0.5% O_2, 2% N_2, 2% H_2O, balance He–Ar) pulses.

After each thermal step the catalyst was cooled down to 400 °C and CH_4 conversion was measured under standard lean combustion conditions so to evaluate activity differences by comparison with the conversion determined at the beginning of the experiment.

Following a similar procedure an experiment with a series of four alternate CH_4 lean combustion/H_2-reducing (2% H_2, 2% H_2O, balance He–Ar) pulses according to the same procedure described above was carried out.

Standard TPC-500 tests were also performed upon completion of the regeneration treatment.

3. Results and discussion

3.1. Fresh catalyst

3.1.1. TPR experiments

TPR experiments performed over fresh catalyst showed a peak of CH_4 consumption in a temperature range between 345 and 365 °C accompanied by an increase of CO_2 outlet concentration likely associated with reduction of PdO to Pd by CH_4. At higher temperatures a marked CH_4 consumption was observed, accompanied by production of CO_2, CO and H_2 likely associated with steam reforming and shift reactions that occurred over metallic Pd.

3.1.2. Alternate lean combustion/reducing pulses

Several cycles of alternate lean combustion/CH_4-reducing pulse experiments at 350 °C were performed before achieving a stable catalyst behaviour, similarly to what was reported by Bell and coworkers [15] for a 10% (w/w) Pd/ZrO_2 catalyst. Such stabilization procedure resulted in a marked activation, with CH_4 conversion under lean conditions increasing from 10 to 50%. A similar reactivation/stabilization effect was observed upon one TPC-900 cycle.

Profiles of CO_2, CH_4 and H_2 outlet concentrations obtained in one cycle of alternate lean combustion/CH_4-reducing pulses performed over the Pd/Al_2O_3 catalyst after stabilization are reported in Fig. 1. Under lean combustion conditions deep oxidation of methane occurred reaching almost 50% conversion being only CO_2 and H_2O detected in the effluents. When the CH_4-reducing pulse was fed to the reactor, a sudden sharp increase in CO_2 concentration was initially detected followed by a decrease to a lower constant value. Following the initial CO_2 concentration peak H_2 production started. Concentration trends during the reducing pulse are consistent with an initial reduction of PdO to metallic Pd by CH_4 according to the following stoichiometry: $CH_4 + 4PdO \rightarrow CO_2 + 2H_2O + 4Pd$, as confirmed by quantitative evaluation of CO_2 release associated with the first peak. A significant contribution of desorption of CO_2 formed in the previous lean reaction pulse was excluded since no CO_2 evolution was observed during the He purge. Once Pd metal formed CH_4 steam reforming and shift reactions were likely responsible for H_2 production and the achievement of a plateau in CO_2 concentration [16]. The possible occurrence of CH_4 decomposition was revealed by experiments with alternate pulses of CH_4-free oxidizing (4% O_2, 16% N_2, 2% H_2O, balance He–Ar)/CH_4-reducing streams showing the presence of a small peak of CO_2 (0.6 μmol) at the beginning of the oxidizing pulse likely associated with combustion of coke formed during the CH_4-reducing pulse.

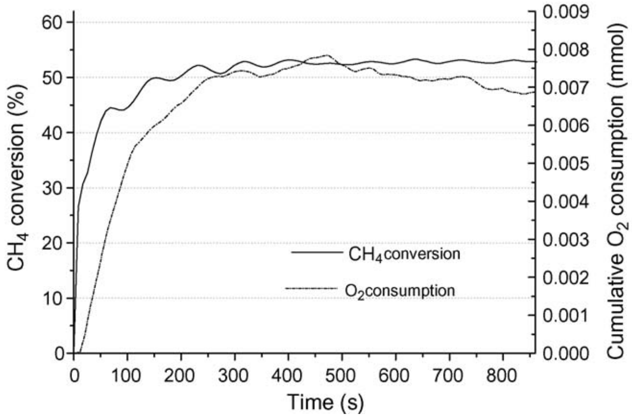

Fig. 2. Time evolution of CH_4 conversion after restoring lean combustion conditions ($t = 0$) and O_2 consumption associated with Pd oxidation in CH_4-free oxidizing pulses at $T = 350$ °C.

As shown in Fig. 2, upon restoring lean combustion conditions a marked increase in CH_4 conversion was observed during the first 100 s, followed by a more gradual reactivation, taking about 300 s to achieve a maximum activity level corresponding to a conversion slightly above 50%. In Fig. 3, such conversion trend is compared with the cumulative O_2 uptake curve obtained with a CH_4-free oxidizing feed following a reducing pulse and He purge. In correspondence with the

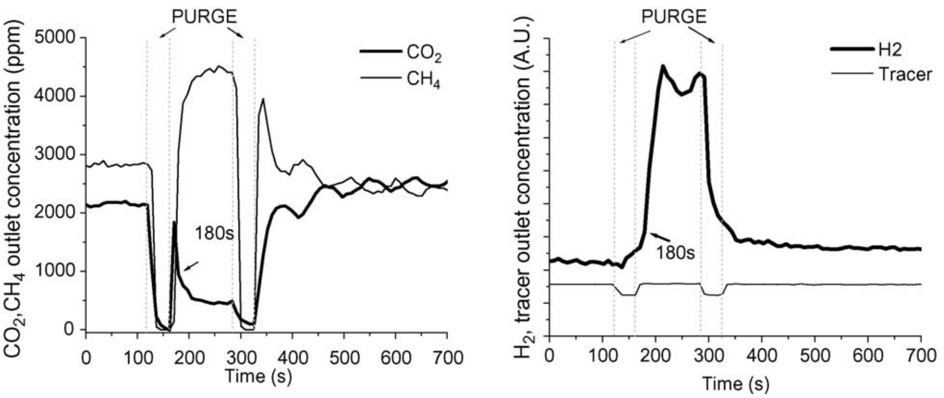

Fig. 1. CH_4, CO_2 (left) and H_2 (right) outlet concentrations during alternate lean combustion/CH_4-reducing pulses at $T = 350$ °C over fresh Pd-Al_2O_3 catalyst after stabilization.

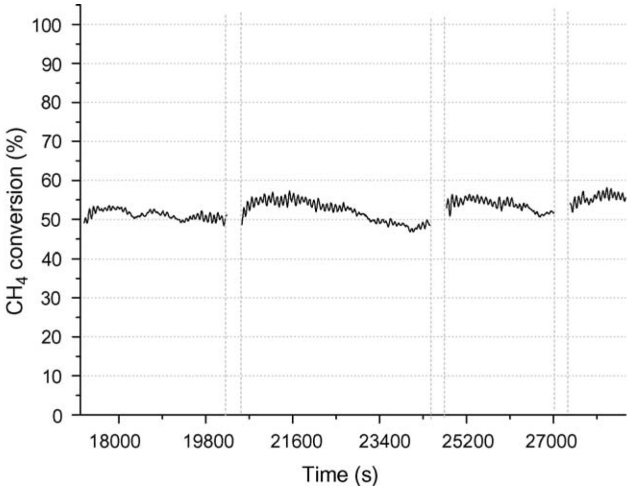

Fig. 3. CH_4 conversion in a sequence of alternate lean combustion/CH_4-reducing pulses at $T = 350\ ^\circ C$ over fresh Pd-Al_2O_3 catalyst after stabilization.

maximum in CH_4 conversion (300 s) the cumulative oxygen consumption achieved a plateau of about 7.0 μmol. Such a value, epurated from the contribution due to the combustion of coke (0.6 μmol) reasonably corresponds to the theoretical amount associated with complete Pd reoxidation (5.6 μmol).

These results evidenced the strong dependence of catalyst activity from the oxidation state of palladium [14 and references therein], confirming that the oxide state progressively formed under lean conditions is the most active in methane combustion in the low temperature range, while the metallic state obtained upon reducing pulse is poorly active.

As shown in Fig. 3 after completion of the reoxidation/reactivation process, the catalyst underwent to a slow deactivation during the lean combustion phase, corresponding to 3–6% decrease of CH_4 conversion during 30–60 min. The activity was completely restored upon a CH_4-reducing pulse and the following reactivation/reoxidation process under lean combustion atmosphere, as evidenced also by CH_4 concentration profiles in Fig. 2. This activity trend was found very reproducible in many cycles after the initial stabilization treatment. Tests performed with H_2O-free oxidizing pulses following the reduction treatment indicated that H_2O poisoning is likely responsible for the observed deactivation in line with many literature reports [3,4,17–19]. Such behaviour was associated with different phenomena including formation of inactive $Pd(OH)_2$ species [18], smoothening of PdO crystallites with decrease of active surface [17] and sintering of palladium particles [3]. Our data showed that such poisoning is completely reversible upon reduction/reoxidation cycles which may results in decomposition of $Pd(OH)_2$ and/or in roughening of the newly formed PdO surface.

3.2. S-poisoned catalyst

3.2.1. TPC experiments

Comparison in Fig. 4 between the heating branches of conversion curves registered during TPC tests performed on fresh (solid line) and poisoned (dot line) catalysts confirmed the strong deactivation occurred following exposure to SO_2 under reacting atmosphere at 380 °C. The temperature at which a given conversion was observed over the poisoned catalyst during the heating ramp was shifted to higher values than that observed for unpoisoned catalyst in the second TPC-900 cycle (i.e. upon stabilization by one TPC-900 cycle). For instance, the temperature corresponding to 50% conversion increased of 90 °C (from 350 to 450 °C). Heating up the catalyst SO_2 release was observed occurring in two steps: a small peak with a maximum at 525 °C, followed by a major peak with a maximum at 810 °C.

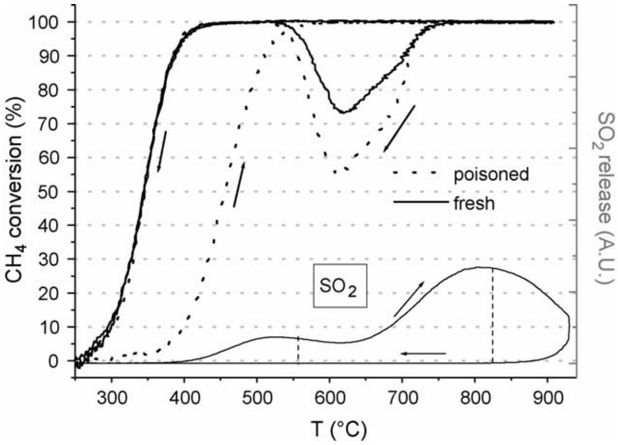

Fig. 4. TPC-900 tests over fresh and poisoned Pd-Al_2O_3 catalyst.

During cooling ramp the characteristic conversion hysteresis [20–23] associated with PdO decomposition/reformation process was observed. At temperatures below 450 °C the conversion curve of poisoned catalyst was practically overlapped to that of the fresh one, suggesting that catalyst exposure to lean combustion environment up to 900 °C results in the complete regeneration of the aged catalysts upon decomposition of stable sulphates species and palladium reduction/reoxidation cycle.

3.2.2. TPR experiments

TPR tests reported in Fig. 5 evidenced that under reducing atmosphere SO_2 release associated with decomposition of sulphate species was markedly anticipated, starting just above 400 °C, showing a maximum at 560 °C and being completed at about 700 °C. A broad peak of CO_2 release was evident in the 350–600 °C temperature range. Although the low level of signal to noise ratio prevented quantification of CO_2 amount, such a peak was likely associated with reduction of palladium which was severely hindered upon S-poisoning as evidenced by comparison with TPR over the fresh catalyst.

No marked consumption of CH_4 was observed below 600–620 °C possibly due to poor sensitivity. Above 620 °C a progressive decrease of CH_4 outlet concentration was observed which was paralleled by an increase of CO_2, CO and H_2 (not shown in the figure) likely due to steam reforming, water gas shift and CH_4 decomposition reactions occurring at high temperature over metallic Pd. However, also at high temperature CH_4 consumption rate was always markedly

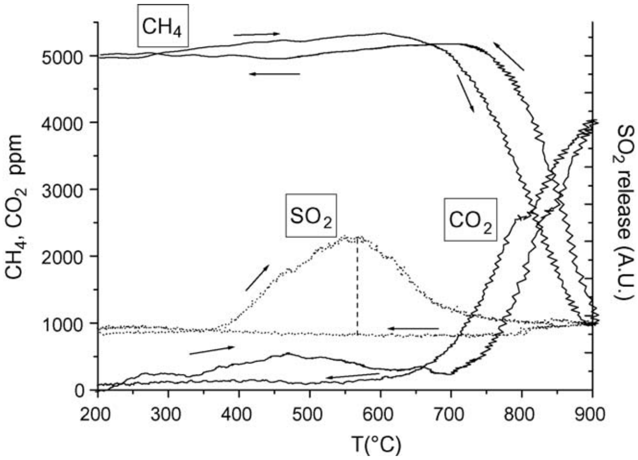

Fig. 5. CH_4 conversion, CO_2 production and SO_2 release during TPR test over S-poisoned Pd-Al_2O_3 catalyst.

lower than over the fresh catalyst. Besides following exposure at high temperature, methane conversion during cooling branch was significantly lower than in the heating branch. It is worth noting that a small increase in H_2S outlet concentration was observed above 730 °C in correspondence with significant production of H_2. It is possible that the presence of H_2 at high temperature was responsible for reduction of sulphates to sulphides either directly [24] or via H_2S intermediate resulting in catalyst deactivation. Nevertheless, at high temperature it cannot be excluded a blockage of active sites by coke deposition, which can be enhanced by an increase of surface acidity associated with the presence of sulphates [25].

It is worth noting that degradation of catalyst performances was not observed in TPC-900 which is consistent with both the hypotheses above. In fact, the presence of excess O_2 would prevent formation of both coke and reduced sulphide species.

3.2.3. Temperature step experiments

Following results of TPC and TPR tests, temperature step experiments were performed to identify the minimum temperature threshold required for catalyst regeneration under different atmospheres. Thermal regeneration under lean combustion conditions was investigated first. Fig. 6 shows that no changes in catalytic activity occurred up to 700 °C. Partial regeneration was obtained after treatment at 750 °C. After a thermal step at 800 °C about 60% conversion was obtained upon cooling at 400 °C to be compared with about 90% conversion obtained at the same temperature over the fresh catalyst upon stabilization (see Fig. 4) indicating that significant but not complete regeneration occurred.

These results are partly in agreement with those of Lampert et al. [2] who observed only a very small recovery of activity upon treatment in lean process stream at 650 °C for palladium catalyst dispersed onto a sulphating support like Al_2O_3. On the other hand, the same temperature was sufficiently high to obtain almost complete regeneration of a Pd catalyst dispersed onto a non-sulphating support (ZrO_2–SiO_2) [2], confirming previous results of Hoyos et al. [11] for a Pd/SiO_2 catalyst. Indeed while decomposition of Pd sulphate species occurs already below 650 °C [11], more stable alumina sulphate species remain onto the catalyst and can spill back to the palladium surface preventing complete decontamination. As shown in Fig. 4 decomposition of stable support sulphates under the lean condition herein investigated occurs only above 700 °C which explain why partial regeneration is observed only above this temperature. Noteworthy complete regeneration was obtained only upon TPC at 900 °C possibly due to both practically complete sulphates decomposition and to the occurrence of a palladium reduction/reoxidation cycle.

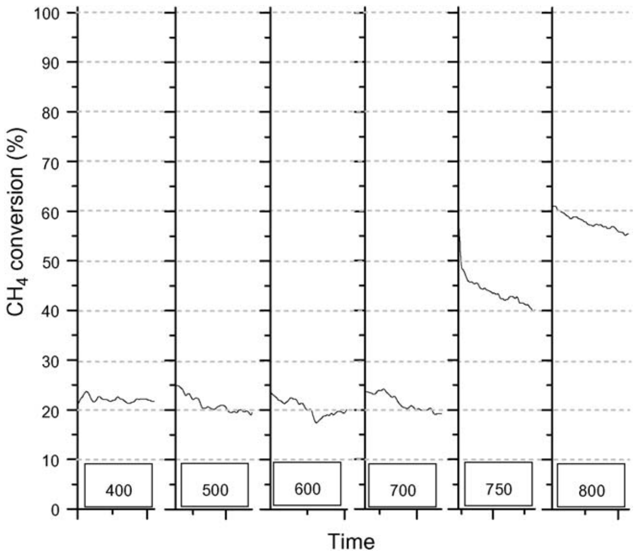

Fig. 6. CH_4 conversion at 400 °C after steps at different temperatures under lean combustion conditions.

In line with the lower temperature of SO_2 release observed under reducing atmosphere, Fig. 7 shows that upon a series of alternate CH_4-reducing pulses regeneration of Pd-Al_2O_3 catalyst occurred at relatively low temperature. Indeed marked

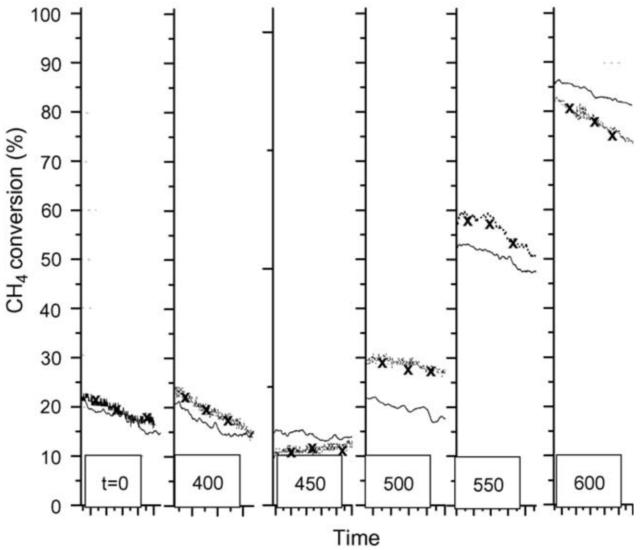

Fig. 7. CH_4 conversion under lean combustion conditions at 400 °C after: (i) alternate lean combustion/CH_4-reducing pulses (solid line) and (ii) alternate lean combustion/rich combustion pulses (-×-×-×-).

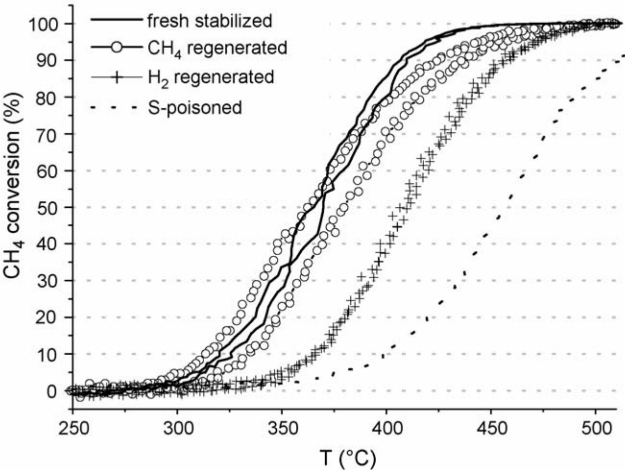

Fig. 8. CH_4 conversion values in TPC-500 test performed over: (i) fresh catalyst upon stabilization by repeated lean combustion/CH_4-reducing pulses, (ii) CH_4-regenerated catalyst, (iii) H_2-regenerated catalyst and (iv) S-poisoned catalyst.

reactivation was observed already after treatment at 550 °C and almost complete regeneration leading to 87% CH_4 conversion under lean conditions at 400 °C was observed after the treatment performed at 600 °C.

To better evaluate the regeneration extent a TPC-500 experiment was performed upon reducing treatment at 600 °C. Comparison of conversion curves reported in Fig. 8 confirmed that the regenerated catalyst exhibited an activity very close to that of the fresh one upon stabilization by repeated lean combustion/CH_4-reducing pulses.

Fig. 9 illustrates trends of SO_2 and CO_2 outlet concentration during the first CH_4-reducing pulses (and the following He purge) at each temperature step. From these profiles the regeneration mechanism sketched in Fig. 10 can be envisaged. At 400 °C no SO_2 and very small CO_2 release was detected confirming that palladium sites are almost completely blocked by sulphate species. At 450 °C a pronounced CO_2 peak was observed, which is likely associated with reduction of palladium. The absence of detectable SO_2 release suggests that only small amounts of adsorbed sulphate and not formation of bulk $PdSO_4$ were responsible for blocking palladium active sites under the adopted poisoning conditions. The absence of bulk $PdSO_4$ in the S-poisoned catalyst was confirmed by FT-IR spectra [13]. Besides at this temperature small amounts of SO_2 can be readsorbed onto the support surface. At 450 °C CH_4 is not able to activate the decomposition of stable support sulphates, thus regeneration does not occur likely due to spill of sulphate species back to the palladium surface when switching to lean combustion conditions. At 500 °C an even more pronounced CO_2 peak is observed at the very beginning of the CH_4-reducing pulse indicating that palladium undergoes to practically complete reduction. A small release of SO_2 is also observed suggesting that decontamination of the support has just started, which is consistent with the slight reactivation observed at 500 °C in Fig. 7. SO_2 release increases rapidly at 550 and 600 °C. Again this is consistent with the marked reactivation observed at these temperatures under the assumption that deep, although not complete, decontamination of the support is required to achieve effective catalyst regeneration. Noteworthy at 550 and 600 °C SO_2 release suddenly drops upon switching from CH_4-reducing stream to the He purge indicating that CH_4 plays a key role in reduction of support sulphates likely via activation onto the Pd metal surface.

Some apparent discrepancies arise from comparison between results of TPR and pulse tests that are likely related to the different transient nature of the experiments. In TPR the progressive temperature increase under CH_4-reducing condition may result in a more gradual evolution of PdO reduction and sulphate decomposition phenomena as suggested by broad CO_2 and SO_2 peaks in Fig. 5. On the other hand, during alternate pulse experiments, abrupt switch at constant temperature from lean combustion atmosphere to short CH_4-reducing pulses allows to clearly identify the temperature threshold at which PdO reduction and sulphate decomposition phenomena occur at a significant rate resulting in the well pronounced peaks which are evident in Fig. 9. It is also worthy to observe that no H_2S production was detected during alternate lean combustion/CH_4-reducing pulses up to 600 °C.

Reactivation results showed in Fig. 7 were obtained upon four CH_4-reduction/lean combustion cycles at each temperature stage. However, SO_2 release under CH_4-reducing pulses at 600 °C was very limited already during the second pulse and drop to zero starting from the third pulse. Accordingly a fast regeneration treatment was tested consisting of a single CH_4-reducing pulse of 2 min at 600 °C. After such treatment 85% CH_4 conversion at 400 °C was achieved, confirming that one CH_4-reducing pulse is sufficient to obtain effective catalyst

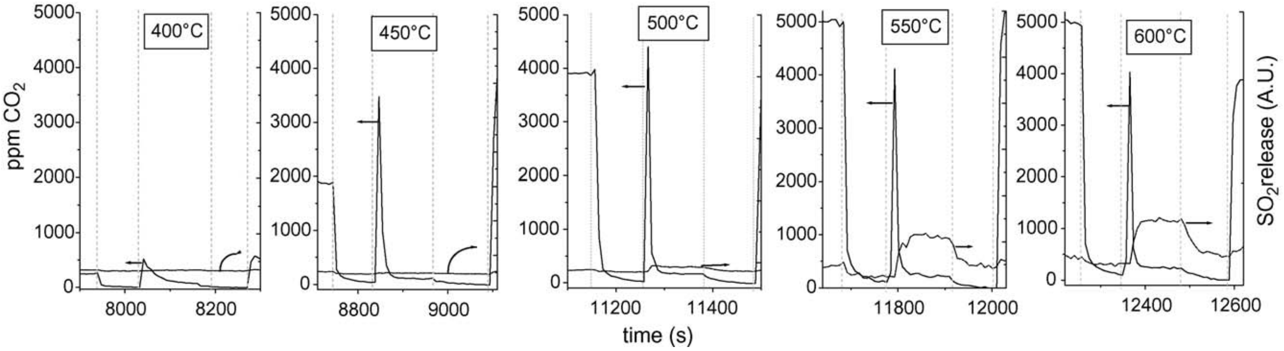

Fig. 9. Trends of SO_2 and CO_2 concentration during the first CH_4-reducing pulses and the following He purge at each temperature step.

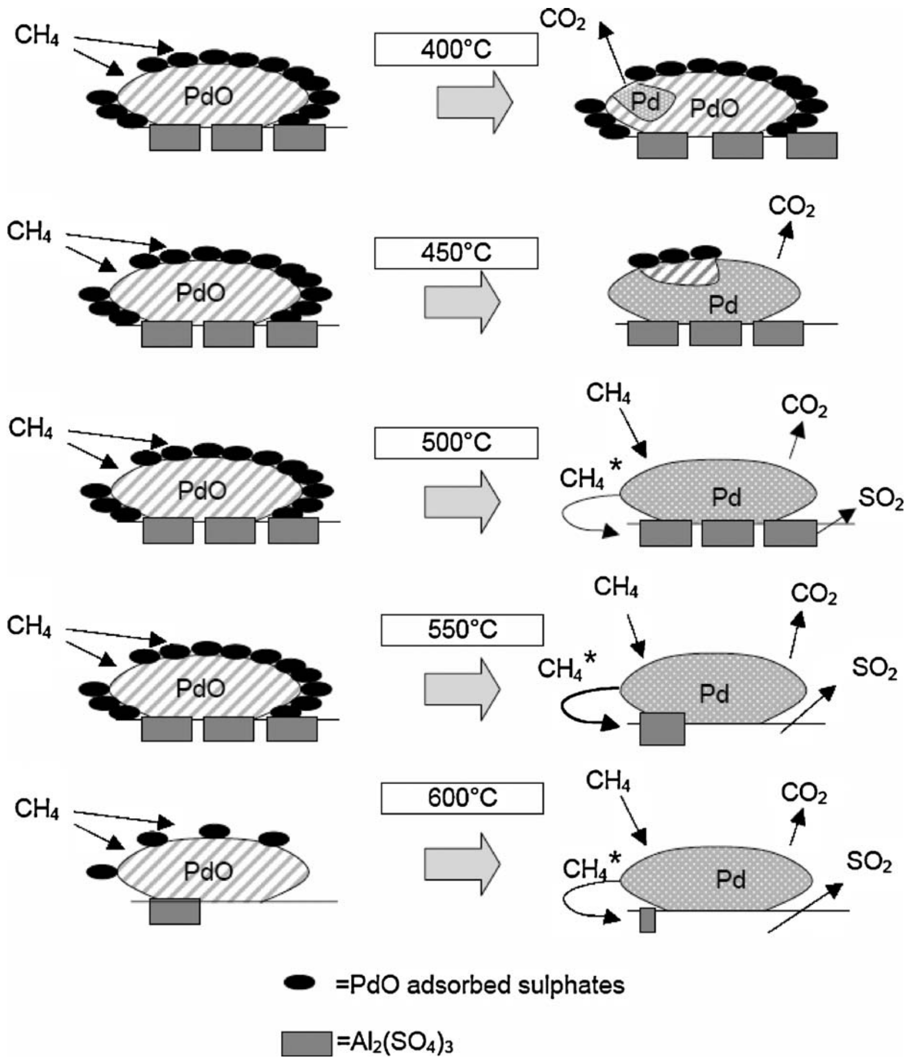

Fig. 10. Schematic behaviour of Pd/Al_2O_3 catalyst during reductive regeneration with CH_4.

reactivation. Note that one CH_4-reducing pulse followed by restoring lean combustion conditions also results in a complete reduction/reoxidation cycle of palladium which can play a significant role in the regeneration process. Results obtained for the unposoined catalyst indicate that decomposition/reformation of PdO enhanced catalyst stability under S-free reaction atmospheres possibly by decomposition of $Pd(OH)_2$ and/or by roughening of the newly formed PdO surface. The same regeneration mechanism may simply overlap with activity recovery associated with sulphate decomposition. However, more complex interactions between decomposition/reformation of PdO and transformation of S-species on the catalyst surface cannot be excluded and deserves further investigation.

Regeneration of S-poisoned palladium catalysts under reducing conditions was already investigated in the literature. Hoyos et al. [11] reported that for catalyst dispersed onto a SiO_2 non-sulphating support regeneration at 600 °C with H_2 was less effective than thermal regeneration at the same temperature with inert N_2. These authors suggested that both treatments allowed to decontaminate the surface from sulphates, but H_2 treatment at high temperature resulted in secondary reaction between palladium and support, decreasing catalyst activity. On the other hand, Lampert et al. [5] reported that for palladium catalyst dispersed onto a sulphating Al_2O_3 support H_2 reduction at 600 °C resulted in a marked, although not complete, activity recovery. Similar results were reported by Yu and Shaw [12]. Jones et al. [8] suggested that sintering of palladium during H_2 reduction may limit the efficiency of regeneration treatment. Lampert et al. [5] also proposed and tested an operating strategy of NGV engines based on alternate long periods (14 min) under standard lean combustion conditions followed by short periods (0.5 min) under rich conditions. Rich combustion produced a reducing engine exhaust stream containing significant amount of H_2, CO and CH_4 which allowed a partial regeneration of the catalyst at about 650 °C.

In this work the effectiveness of a regenerating treatment by H_2 reduction was investigated by performing a series of alternate lean combustion/H_2-reducing pulses at 600 °C according to the typical procedure described in Section 2. In this case a marked SO_2 release was observed during the first reducing pulse, accompanied by a small H_2S production. In the following reducing pulses no SO_2 was detected, but a small production of H_2S was still observed. As shown in Fig. 8 where TPC curves of samples regenerated by different treatments are compared with that of the fresh/stabilized one, regeneration by H_2-reducing pulses was less effective than regeneration by CH_4-reducing pulses. This may be due to the formation of surface sulphide species associated with the stronger reducing action of H_2 also evidenced by significant H_2S production.

In view of the results reported above an operating strategy can be suggested that does not imply alternate lean/rich operation of the NGV engine but only periodically feeding of the catalyst with short CH_4-rich pulses using a by-pass line.

To gain further information about regeneration potential of such a procedure the efficiency of a treatment consisting of alternate lean combustion/rich combustion pulses was checked. As shown in Fig. 7, also in this case the treatment at 400 and 450 °C did not result in any catalyst regeneration. A slight reactivation associated with a small SO_2 release was observed after pulses at 500 °C, while pulses at 550 and 600 °C resulted in a large SO_2 release and, consequently, in marked recovery of activity. Indeed the O_2 containing, CH_4-rich combustion pulses were as effective in catalyst regeneration as O_2-free, CH_4-reducing pulses. Note that conversion of O_2 under rich conditions was already complete at $T \geq 450$ °C, whereas it was almost negligible at 400 °C, confirming that at 450 °C under CH_4-rich conditions desulphation of active sites occurs.

4. Conclusions

Temperature programmed, alternate pulses and temperature step experiments performed in this work allowed to investigate the effects of temperature and composition of CH_4 containing atmospheres on regeneration of a S-poisoned Pd/Al_2O_3 catalyst for CH_4 combustion.

The following main conclusions were pointed out:

(1) In unpoisoned catalysts PdO reduction/reformation processes occurring upon CH_4-reducing pulses and restoring of lean combustion conditions result in a complete recovery of activity losses that were observed during prolonged exposure under lean combustion conditions and were possibly associated with H_2O poisoning phenomena.
(2) Under lean combustion conditions partial regeneration of S-poisoned catalysts occurred only at $T = 750$–800 °C, following partial decomposition of stable support sulphates. Complete regeneration was observed only upon TPC tests up to 900 °C upon extensive decomposition of stable support sulphates and decomposition/reformation of PdO.
(3) Under reducing conditions decomposition of sulphates was markedly anticipated likely via CH_4 activation onto the previously reduced Pd metal surface. CH_4-reducing (and rich combustion) pulses led to marked reactivation already at $T = 550$ °C. Almost complete catalyst regeneration was obtained at 600 °C upon one single short (2 min) CH_4-reducing pulse. Such a treatment combines extensive sulphate decomposition with PdO reduction/reoxidation cycle.
(4) Comparison with results collected in this work and with literature reports indicates that reductive regeneration of S-poisoned catalysts with CH_4 containing atmosphere is more effective than analogous treatment with H_2 containing streams, possibly due to the milder reducing action resulting in minor formation of surface sulfides.
(5) On this basis it is suggested that operating strategies based on periodical feeding via a by-pass line of short CH_4 pulses directly to NGV mufflers can be effective in catalyst regeneration.

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