Arbetsrapport SGC A22

CATALYTIC ABATEMENT OF CO- AND UHC-EMISSIONS FROM GAS-FUELLED ENGINES

Experimental study

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February 1999

SGC
Svenskt
Gastekniskt
Center AB

KATATOR

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Lund 981222, revised 990222

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Summary

An investigation concerning the utilisation of wire-mesh catalysts in an up-stream position of the turbo charger on gas fuelled engines has been performed on the request of SGC AB (Swedish Centre of Gas Technology AB).

Micro reactor tests state that it is possible to produce highly active wire mesh catalysts (Pd/PdO) for the combustion of unburned hydrocarbons (UHC) under exhaust conditions with respect to temperature, total pressure and gas composition in a position up-stream the turbo charger.

High concentrations of water vapour will decrease the catalyst's activity at low temperatures. The presence of SO_2 will lead to a more or less permanent deactivation. At temperatures below the decomposition temperature of palladium sulphate (≈550°C), we will experience a permanent deactivation whereas the deactivation is reversible at higher temperatures. Indeed, experiments with accelerated SO_2-deactivation only show weak tendencies of permanent activity loss after a time corresponding to several thousands hours of operation in exhausts of a gas-fuelled engine.

On-stream measurements of CO- and UHC-conversions verify the predictions of the numerical simulation model. It is thus possible to achieve a CO-conversion of 90% at a space velocity of around 1 000 000 h^{-1}. The UHC-conversion at this gas load is around 50%.

The long-time deactivation test unfortunately indicated a rapid and severe deactivation of the catalyst. Careful examination of the deactivated catalyst by means of activity tests and characterisations let us conclude that the deactivation is caused by a fouling mechanism, where inorganic oxides have collected on the catalyst's surface. These dense layers of slag most probably originated from metal organic substances added to the combustion air in previous experiments. It was possible to restore the initial activity of the catalyst completely by means of mechanical and chemical treatment.

The study verifies the advantages of the wire-mesh concept and the choice of an up-stream position of the catalyst. The catalyst was completely intact after the tests and no evidences of mechanical ruptures causing debris was observable. Continued tests in co-operation with manufacturer of gas-fuelled engines are necessary to clearly demonstrate the potential of the wire-mesh concept in this application.

Sammanfattning

Föreliggande studie avseende möjligheterna att installera nätbaserade katalysatorer före turboladdaren i gasdrivna motorer har utförts på uppdrag av Svenskt Gastekniskt Center AB.

Studien verifierar de resultat som framkommit i en tidigare teoretisk förstudie inom området och som klart indikerar fördelar med nätkatalysatorer och den aktuella placeringen. Den ökade tryck- och temperaturnivån medför en väsentlig aktivitets-och stabilitetsförbättring hos katalysatorn, vilket leder till att extremt kompakta reaktorer kan utnyttjas. De genomförda experimenten visar att omsättningen av CO uppgår till ca 90% vid ett flöde motsvarande ca 1 000 000 reaktorvolymer per timme. Motsvarande omsättningsnivå för oförbrända kolväten (UHC) ligger kring 50%.

Mikroreaktorförsöken visar att det är fullt möjligt att framställa högaktiva nätkatalysatorer (Pd/PdO) för rening av avgaser från gasmotorer. Mikroreaktorförsöken indikerar att vattenånga och SO_2 har en negativ inverkan på katalysatorns aktivitet medan den ökade trycknivån positivt påverkar förbränningsförloppet. Effekterna av vattenånga är fullständigt reversibla medan SO_2-deaktiveringen kan vara såväl reversibel som irreversibel. Om deaktiveringen sker vid en temperaturnivå under sönderdelningstemperaturen för palladiumsulfat (ca 550°C) är deaktiveringen irreversibel medan processen är reversibel vid temperaturer över denna nivå. Forcerade försök avseende SO_2-deaktivering visar att katalysatorn klarar den aktuella avgasmiljön under en period av tusentals timmar utan att allvarlig aktivitetsförlust uppstår beroende på närvaron av svavel.

Tester avseende flödets inverkan på omsättningen av CO och UHC, utförda i en gasmotor (i samarbete med Danskt Gastekniskt Center a/s), är i överensstämmelse med existerande numerisk modell. Långtidsförsöket påvisade en oväntat snabb och svår katalysatordeaktivering. Aktivitetstester och katalysatorkarakterisering visar att katalysatorn deaktiverats till följd av påslag av oorganiska oxider på katalysatorns yta, en s.k. fouling-mekanism. De oorganiska oxiderna kan sannolikt härledas till försök som tidigare gjorts i motorn avseende tillsatser av metallorganiska föreningar till förbränningsluften.

Den genomförda studien har verifierat den numeriska modellens förutsägelser varför modellen fortsättningsvis kan användas vid dimensioneringsberäkningar.

Ytterligare studier avseende katalysatorns stabilitet bör genomföras i samarbete med lämplig motortillverkare

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1. Introduction

Katator AB has on the request of SGC AB (Swedish Centre of Gas Technology AB) performed a study concerning the installation of wire-mesh catalyst on lean-burn engines to reduce the emissions of carbon monoxide (CO) and unburned hydrocarbons (UHC).

The utilisation of gas fired engines for production of heat and electricity in Europe has increased greatly during the last decade. The implementation of gas engines in Sweden has, however, been slow, mainly due to the current tax legislation.

During the last years, environmental concern has been directed towards the hydrocarbon emissions from gas-fuelled engines. Since the combustion is performed at a high lambda value, the emissions of NO_x can be reduced to a relatively low level (1 - 2 g/kWh). The exhausts will, however, also contain between 1000 and 3000 ppm(v) of unburned fuel, which corresponds to a couple of percent of the supplied fuel. The UHC-slip will result in a decreased fuel economy and, perhaps even worse, to negative effects on the environment since methane effectively contributes to the greenhouse effect. Indeed, a UHC-slip of 2000 ppm corresponds to a CO_2-emission of 5.1 vol%, since methane is a much stronger greenhouse effect producer than CO_2 [1]. The normal exhaust concentration of CO_2 is around 5 vol%, which means that the UHC-emissions will double the specific greenhouse effects of gas-fired engines.

Another problem associated with gas-fuelled engines is the formation and emission of ill-smelling compounds. These compounds are probably partial oxidation products, e.g. aldehydes which may give rise to odour also at very low concentrations (ppb-levels).

In order to reduce the emission problems, tests have been conducted with oxidation catalysts installed in the exhaust gas flow [2]. The exhaust temperature in a position down-stream the turbo charger is normally between 380 and 450°C. The low temperature will cause problems with catalyst activity and stability. Methane is especially difficult to combust catalytically and the combustion process will demand temperatures above at least 500°C to be effective. It is well-known that the presence of water vapour will retard the catalytic combustion significantly and it is therefore necessary to increase the temperature further [3]. In addition to water the exhausts will also contain around 0.25 - 0.5 ppm of SO_2, which origin from the odorant present in natural gas. Small amounts of sulphur, phosphorus and metal organic compound may also be derived from leakage of lubricating-oil. Some trace elements present in the exhausts, and especially so sulphur, might give rise to catalyst deactivation (through sulphatisation of the carrier and the active phase). Indeed, several on-stream tests with combustion catalysts have failed due to sulphur poisoning [2].

The basic idea of this study is the retard or eliminate the sulphur poisoning by placing the combustion catalyst up-stream the turbo charger were the exhaust temperature is around 600°C. The high temperature level together with the high total pressure (typically 2.5 bar[a]) will also result in a higher initial activity of the catalyst, thus making it possible to increase the gas load.

2. Aim of the study

The aim of the study might be expressed as: "To demonstrate the possibility of placing a wire-mesh catalyst in an up-stream position of the turbo charger and to correlate the catalyst performance to experimental ant theoretical predictions".

To improve the numerical model, complementary experiments with methane combustion are performed. The aim is to get a fundamental understanding of the effects of the total pressure and different environmental parameters (gas composition). Some studies are also directed to the procedure of catalyst preparation and to the choice of suitable carrier material and precursor of the active phase.

3. Background

3.1 Previous studies

A theoretical study concerning the possibility of installing wire-mesh catalysts in an up-stream position of the turbo charger has previously been performed [4].

According to the study there are a number of advantages associated to the up-stream position and the utilisation of wire-mesh catalysts:
- High exhaust temperatures, >600°C
- Increased pressure, ≈2.5 bar(a)
- Less sensitivity to pressure drop

Catalytically active wire meshes show an extraordinary high mass-and heat transfer capacity in combination with low pressure drops and a high mechanic durability. These features makes an installation in a position up-stream the turbo charger possible.

Theoretic estimations and physic inspection of co-generation plants show that it is possible to reduce the UHC-emissions with 60-90% through installation of wire mesh catalyst in existing exhaust manifolds. In cases where the dimension of the exhaust manifold can be increased slightly, it is possible to increase the degree of purification to 90% or more.

Commercial catalysts need to be installed down-stream the turbocharger due to space limitations and problems with mechanic stability. In that position, the flue gas temperature is lower and most catalysts will suffer from a rapid sulphur poisoning due to the odorant content of natural gas.

The wire mesh approach is also commercial interesting since a wire mesh installation will be cheaper compared to a monolith installation down-stream the turbo charger.

3.2 The wire-mesh concept

It is commonly known that the mass-and heat transfer characteristics in a bed of catalyst pellets are superior to those in a monolith catalyst. The pressure drop of a pellets bed is however significantly higher than the pressure drop of a monolith catalyst. Monolith catalysts are therefore used in applications where an inherent sensitivity against a high pressure drop exists, e.g. in automotive applications and in catalytic devices for combustion and flue-gas cleaning.

Wire-mesh catalysts combine the excellent mass-and heat transfer characteristics of a pellets catalysts with a relatively low pressure drop, mainly attributed to the high porosity of the wire-mesh structure. Wire-mesh catalysts are commonly used in the production of nitric acid from ammonia (Pt/Rh-catalyst) and formaldehyde from methanol (Ag-catalyst). In these cases the wire-mesh consists of homogeneous metal wires, which are woven together. Homogeneous wire-meshes are extremely expensive and rather inactive, due to the low specific surface area (only a few m^2 per kg of catalyst).

It is possible to add catalytic activity to a wire mesh by a conventional wash-coating procedure. The major drawback here is the poor mechanical strength of the ceramic layer. The ceramic layer may flake away under the influence of mechanical stresses and vibrations whereupon the catalyst is destroyed.

By depositing the ceramic material through a thermal spray-technique (e.g. flame spraying or plasma spraying) it is possible to obtain a ceramic layer with an excellent adhesion to the substrate. The bond strength (shear stress necessary for fracture) usually is between 15 and 60 N/mm^2. Thermal spraying has been utilised in catalyst preparation before, mainly for the production of Raney-nickel- and iron-catalysts for hydrocarbon processing. The porosity and the specific surface area of an as-sprayed ceramic layer are normally extremely low. It is therefore not possible to obtain a satisfactory catalytic activity by simply impregnating the ceramic layer with a solution containing catalytically active materials, e.g. precious metals. Some researchers have therefore used the thermally sprayed ceramic layer as a substrate for a wash coat and a catalytically active material, e.g. on details in internal combustion engines.

Our research has focused on the possibilities of obtaining an as-sprayed ceramic layer with a high porosity and a high specific surface area. The specific surface area of the porous ceramic layer may be increased further in a second step by treating it with different sols or through an in-situ precipitation method. Catalytic activity is added to the ceramic layer in a third step through an ordinary impregnation procedure.

The thin and shell-like design of the catalytically active layer enables an excellent utilisation of the active material, i.e. the effectiveness factor with respect to pore diffusion is rather high compared to a pellets catalysts. The combination of a relatively low catalyst weight and a high heat transfer number leads to a low thermal inertia of the wire mesh catalysts, which is of great interest in certain applications, e.g. in start-up catalysts in automotive applications.

Porous wire-mesh catalysts can be used in a number of interesting applications, where they may replace or complement existing pellets-and monolith catalysts. Examples of interesting applications are:

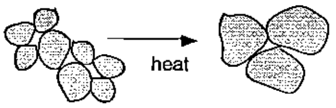
-Purification of flue gases with respect to CO and hydrocarbons
- Two-way catalysts in automotive applications
- Three-way catalysts in automotive applications (especially start-up catalysts)
- Catalytic combustion in energy production
- Catalytic devices for de-odourisation (ammonia, amines etc.)
- Purification of ventilation air with respect to VOC
- Ammonia oxidation
- Selective Catalytic Reduction of nitrogen oxides (SCR)
- Partial oxidation reactions like the ones used in formaldehyde- and acetaldehyde production
- Steam reforming
- Water-gas reactions

The mass- and heat-transfer characteristics of wire-mesh catalysts have been extensively studied by a number of researchers . These studies have focused on homogeneous wire-meshes, mainly Pt/Rh or Pt/Pd, for the production of nitric oxide (nitric acid production). In our case it is also necessary to take the effects of pore diffusion into consideration since our catalyst is porous and has a relatively high specific surface area. The effects of axial dispersion may decrease the conversion considerably, especially at low ratios between the flow rate and the cross sectional area of the package of catalytically active wire meshes. The effects of axial dispersion must thus be implemented in the numerical model.

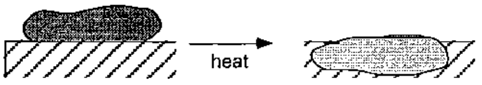
4. Deactivation

4.1 Thermal deactivation

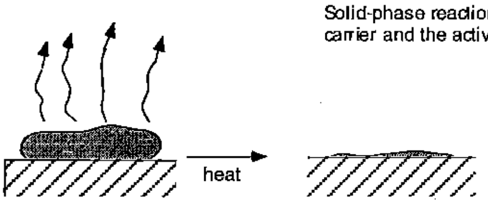
Thermal deactivation is certainly the most important deactivation process in catalytic combustion for energy production where the temperature reaches 1000°C or above (gas turbine applications). These high temperatures will influence the geometrical support as well as the carrier and the active material. The deactivation process will result in decreased catalyst activity and the combustion efficiency will drop during the course of deactivation. This will in turn result in increased emissions of CO and uncombusted fuel and increasing difficulties when starting the burner. The thermal deactivation is brought about by sintering processes resulting in decreased total and active areas, by solid-state reactions between the carrier material and the active phase, and through vaporisation of active material. These processes are illustrated below.



Loss of specific surface area trough sintering



Solid-phase reactions between the carrier and the active material

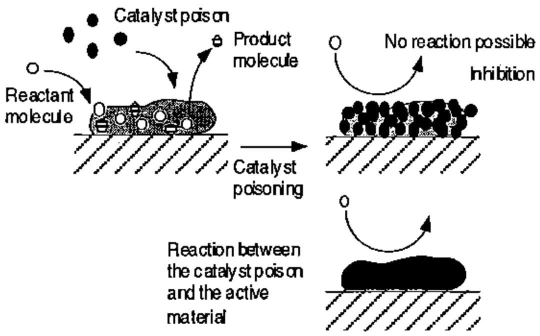


Vaporisation of active material

It is difficult to forecast the lifetime of a catalyst from deactivation data obtained during a short period of time. Complete deactivation tests are, however, extremely time-consuming. In some cases there is an analogy between time and temperature, which means that the deactivation tests may be accelerated by performing the test at a higher temperature.

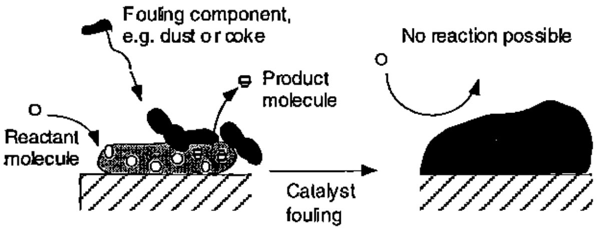
4.2 Poisoning

The active sites of the catalyst can be blocked by components which show a high affinity to the active material, thus preventing catalytic action from taking place. Such catalyst poisons may be present in fuels as well as in flue gases. Sulphur is a well-known catalyst poison which strongly deactivates most active materials, especially metal oxides. Precious metals are less susceptible to sulphur poisoning, at least at temperatures above 400°C. Other well-known catalysts poisons are phosphorus, alkaline and alkaline earth metals, halogenides and certain metals (e.g. Pb). The effects of poisoning may be more or less permanent. Metal oxides are generally difficult to regenerate as the catalyst poisons tend to be strongly bound to the active phase, in these cases through the formation of stable compounds (e.g. sulphates, phosphates etc). Precious metals generally do not form such stable compounds and are consequently easier to regenerate. The effects of poisoning are illustrated in the figure below.



4.3 Fouling

Mechanical deactivation or fouling implies that deposits of inert material are formed over the catalytically active surface, thus limiting or preventing access to the catalyst surface, as indicated in the figure below.



Such deposits may be formed through coking or gas-phase deposition of inert components. Coking may be a problem under oxygen-lean conditions where dense layers of coke may be formed due to cracking and polymerisation of hydrocarbons. Gas-phase deposition of inert components is a common problem in VOC-abatement when the gases contain silicon oil. The hydrocarbon content of the oil is easily combusted whereas the silicon content forms silica on the catalyst surface. The active combustion catalyst is gradually covered with dense layers of silica which deactivate the catalyst. Similar phenomena can be observed when treating flue gases which contain alkaline metals in the gas phase. The gaseous alkaline metals (especially K and Na) will deposit in the catalyst, thus producing dense deposits on the active phase. Deposits of alkaline metals can be removed by washing the catalyst with acidified water.

Deposits of ash and dust particles will produce a porous layer, normally on the outside of the catalyst. These porous layers will cause increased resistance to mass transfer but they are less detrimental to the catalyst performance than the dense layers described above.

5. Experimental set-up

5.1 Micro reactor system

The micro reactor tests were conducted in a tubular reactor with an effective diameter of 34 mm. A gas mixture containing methane and SO_x in compressed air was supplied to a pre-heater at a controlled flow rate. Water was supplied to the pre-heated gas mixture by means of an accurately calibrated syringe pump. The resulting wet gas mixture was led through the reactor and gas analysis was performed with a photo acoustic IR-technique (Brüel Kjær). The gas components of interest (SO_2, CO, CO_2, CH_4) could be analysed with ppm-accuracy down to levels below 5 ppm(v).

Pressurised combustion experiments were performed in a tubular reactor with an effective diameter of 20 mm. The absolute pressure of the reactor system was regulated by means of adjusting a control valve, fitted to the system.

5.2 Lean burn engine

The lean-burn engine has a power output of 40 kW_e. The total exhaust flow rate is around 200 kg/h. The experimental set-up is shown in Figure 1. A part of the total exhaust flow was led through the reactor at a total flow rate between 20 and 70 nm^3/h. The flow through the reactor was regulated by means of two butterfly valves, installed in the reactor line and the by-pass line respectively. The present flow rate was calculated from the pressure drop over the catalyst, corrected with the temperature and the absolute pressure of the reactor. The exhaust gas flow was then expanded in the turbo charger and emitted to the atmosphere.

Compressed air could be added to the exhaust gas flow to decrease the temperature and to increase the exhaust gas concentration of oxygen. Gas samples from positions up-stream and down-stream the reactor were led to the analysis train, containing equipment for analysis of CO, UHC, O_2 and NO_x. The absolute pressure and the pressure drop as well as the reactor temperature were continuously monitored.

During the tests the absolute pressure was 1.8 bar(a) and the reactor temperature around 600°C. The UHC-content of the exhausts was around 4000 ppm(v) whereas the CO-content was close to 700 ppm(v). The oxygen content of the exhausts was 8 - 9% by volume.

The reactor consisted of a tube with an inner diameter of 48 mm and a length of 200 mm. The reactor tube was connected to the flow system by means of flange connections. During the test, the reactor was supplied with 16 pieces of wire mesh catalyst in series. The wire mesh catalysts were corrugated with a top angle of 60°. The mesh number was 16 and the wire diameter was around 0.5 mm (including the catalyst layer).

Figure 2 show the pressure drop over the reactor as a function of the flow rate at ambient conditions. The measured pressure drop excellently correlates to the calculated values. The pressure drop will increase with temperature and decrease with pressure, as indicated by the simulation model. The simulation model enable us to determine the actual flow rate through the reactor from pressure-drop data with a high degree of accuracy.

The pressure drop will vary between 5 and 50 mbar at flow rates between 20 and 70 nm^3/h at 600°C, 1.8 bar(a).

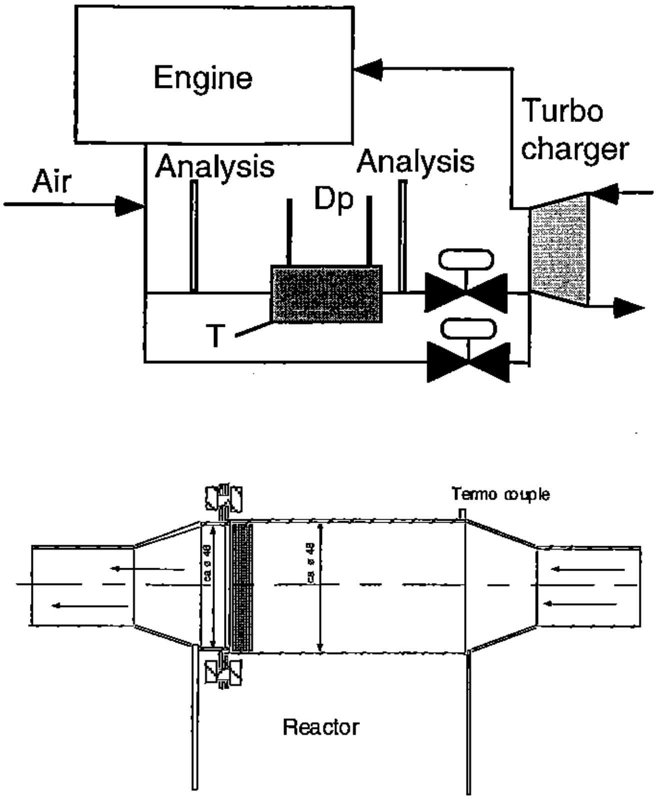


Figure 1 Experimental set-up during the lean-burn engine tests.

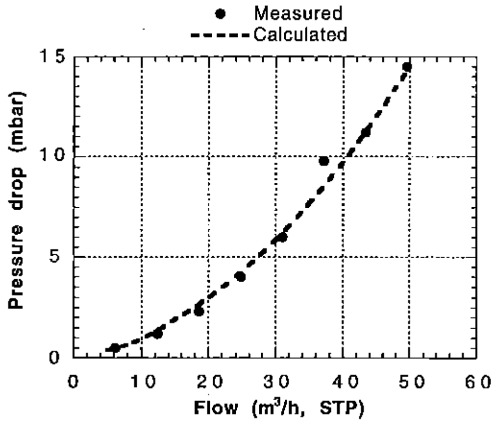


Figure 2 Pressure drop over the test reactor as a function of the gas flow at 20°C, 1 atm(a).

6. Micro reactor tests

6.1 Catalyst activity

Earlier investigations have shown that Pd/PdO is superior to other active phases in the combustion of methane [5]. The choice of carrier material and pre-cursor of the active phase may to some extent influence the activity of the catalyst. The interaction between the carrier and the active phase (MSI, metal-support interaction) can be either weak or strong. The interaction may influence the morphology of the active phase (dispersion) as well as the electronic neighbourhood of the active domains.

To find an active catalyst, we studied different pre-cursors of the active Pd-phase:

- Pd dissolved in agua regia
- $PdCl_2$ dissolved in diluted HCl
- Pd dissolved in aq. regia and chelated with EDTA at alkaline conditions (NH_3-addition)
- $Pd(NO_3)_2$ dissolved in acidified water
- $Pd(Ac)_2$ dissolved in ammonia
- $PdSO_4$ dissolved in acidified water

The Pd-loading was in all cases 10 g Pd per square metre of wire mesh. 10 pieces of wire mesh (16 mesh/0.5 mm) were treated with the different solutions, dried at 120°C for 1 h and then reduced at 800°C for 1 h. The catalysts samples were finally fired at 600°C for 1 h before the activity tests.

The activity tests were conducted at a space velocity of 300 000 h^{-1} and at temperatures between 300 and 700°C. The test gas contained 2000 ppm of methane in compressed air and gas analysis was performed with a photo acoustic IR-technique. Figure 3 summarises the experimental data obtained during the tests. From the figure it is obvious that the $Pd(Ac)_2$-solution is the most effective Pd-precursor, followed by the $PdSO_4$-

solution. These experiments thus demonstrate the possibility of producing effective catalysts for methane combustion with Pd as the sulphate, provided that the sulphur is removed by means of heat treatment.

The reason why $Pd(Ac)_2$ is especially effective as Pd-precursor might be explained in terms of the micro structure of the Pd/PdO-phase as well as the low concentrations of known inhibitors in this solution (Cl^-, SO_4^{2-}). The utilisation of extremely acid solution may cause corrosion whereupon the active phase may be contaminated by corrosion products.

It is believed that PdO is the active form of palladium and that methane adsorption occurs on the thin shell like metallic layer present on the PdO-phase [6]. The adsorption will proceed under dissociation and the molecule rests then diffuse into the PdO-phase where oxidation occurs. Reduced palladium then diffuses to the surface where re-oxidation will occur. Extensive investigations have shown that large Pd/PdO-crystallites are easier to reduce than PdO in a highly dispersed form [6].

All processes which retard the cyclic process between Pd and PdO will cause a drop in catalytic activity. Thus, the presence of contaminants in the palladium phase (e.g. S, P and metals), may give rise to a dramatic retardation of the cyclic redox-process of the palladium phase.

Indeed, at low reaction temperatures the palladium phase is poisoned by oxygen, which hinders the formation of metallic Pd where methane adsorption is believed to occur. In the presence of water vapour, the formation of palladium hydroxide has been observed. The presence of water will therefore strongly affect catalyst activity during methane combustion.

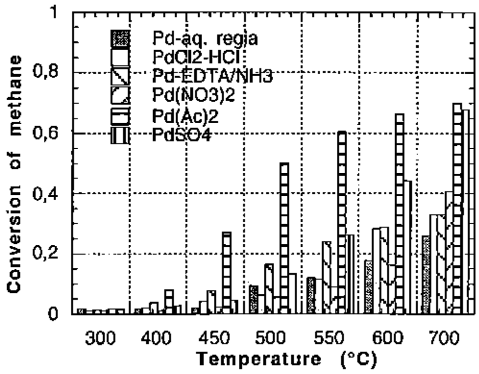


Figure 3 Methane conversion of different catalyst preparations at different temperatures. SV≈300 000 h^{-1}.

To demonstrate the effects of high and low dispersion of the palladium phase, experiments were conducted with materials giving different MSI. Titania is known to cause an extremely high dispersion of precious metals and should therefore not be chosen as a candidate for the carrier material in this case [7]. Alumina does not interact to such an extent with the active phase, which means that formation of larger crystallites is probable.

In Figure 4, the effects of different carrier materials have been investigated. From the figure it is clear that titania should be avoided in the catalyst preparation. The alumina- and the metal oxide-substrates are much better alternatives. Since the metal oxide carrier has a higher mechanical strength than the alumina carrier, the metal oxide alternative is chosen in this application, since catalyst debris can not be tolerated in an up-stream position of the turbo charger.

The activity of the PdO-MeO$_X$-catalyst is very high, also at temperatures below 500°C. This low-temperature activity is, however, not of interest in this application since inhibition with water and SO$_X$ will occur at these low temperatures.

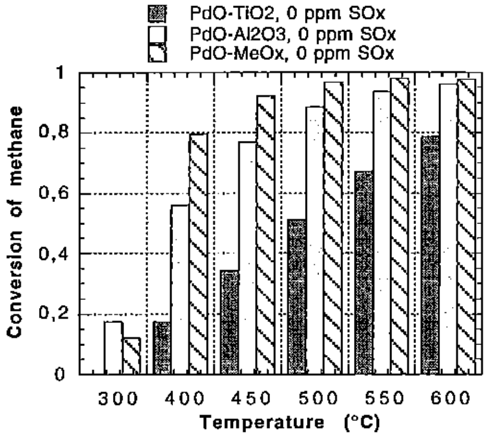


Figure 4 Methane conversion for different combinations of active phase and carrier.
SV≈150 000 h^{-1}.

6.2 Effects of water

To demonstrate the inhibiting effects of water vapour, experiments were performed with different concentrations of water in the gas mixture. Figure 5 shows the conversion of methane as a function of the temperature at different concentrations of water. From the figure, it is obvious that even small amounts of water strongly retard the performance of the catalyst. The inhibiting nature of water, excellently correlates to a classic adsorption isotherm. Also, the effects of water vapour are completely reversible. When turning off the water injection, the initial activity is completely restored.

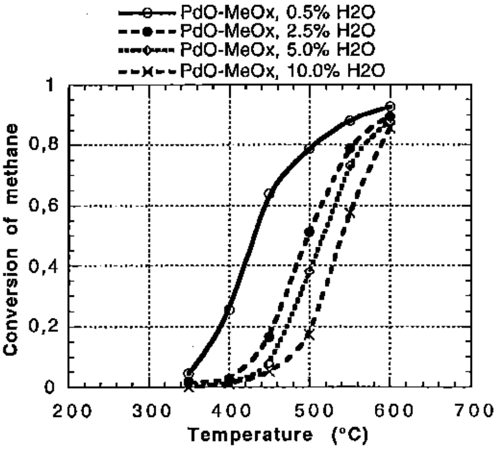


Figure 5 Effects of water on the conversion of methane. SV≈150 000 h^{-1}.

6.3 Effects of SO$_X$

Sulphur compounds give rise to a much stronger inhibition than water vapour. Among the precious metals, Pd has the highest sensitivity to sulphur poisoning. Platinum is rather insensitive to sulphur, provided that the temperature is above 300°C. Unfortunately, Pt can not be used in methane combustion since it has a rather low activity for methane combustion.

The reason for the rather strong sulphur deactivation found on palladium catalysts is the formation of palladium sulphates. Palladium sulphate is, however, decomposed into PdO and SO$_X$ at temperatures between 550 and 600°C and the catalyst's activity for methane combustion is restored.

To study the effects of sulphur poisoning, SO_2 was added to the gas mixture. Figure 6 show the strong inhibiting effects of 500 ppm of SO_2. From the figure it is clear that high concentrations of SO_2, will result in almost zero-activity at temperatures below 450°C, i.e. at normal exhausts temperatures down-stream the turbo charger.

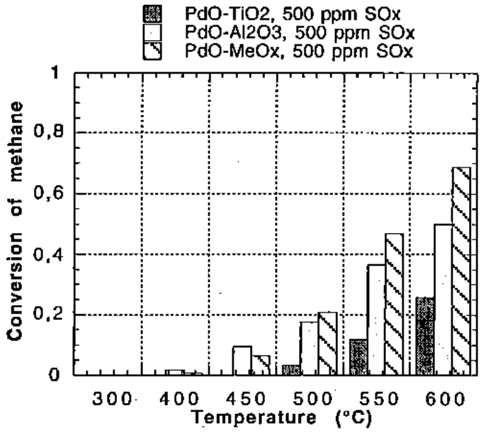


Figure 6 Effects of SO_x on the conversion of methane over different combinations of active phase/carrier. $SV \approx 150\ 000\ h^{-1}$.

Complementary tests at lower concentrations of SO_2, show a similar pattern, although the inhibition is slightly weaker, see Figure 7. It is of certain interest to study the effects of SO_x during a long time of operation. Since it is difficult to carry out long-time experiments in the micro reactor system, accelerated deactivation tests were performed by increasing the SO_2-concentration of the gas mixture. The results of these tests are summarised later in the report.

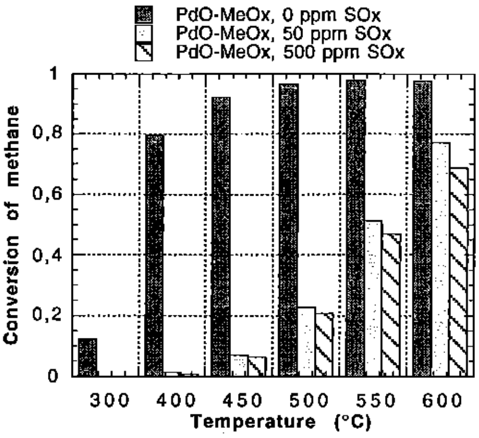


Figure 7 Effects of the SO_x-concentration on the conversion of methane over PdO/MeOx. $SV \approx 150\ 000\ h^{-1}$.

6.4 Pressurised combustion

According to the numerical simulation model, an increased total pressure should result in an increased methane conversion. To study the effects of pressurised combustion, combustion experiments were carried out at different total pressures, see Figure 8. As can be seen in the figure, an increased total pressure, will result in an increased conversion of methane. The effect is logarithmic in pressure and levels out at high pressures. The measured conversions are in good agreement with the calculated data, see Figure 9.

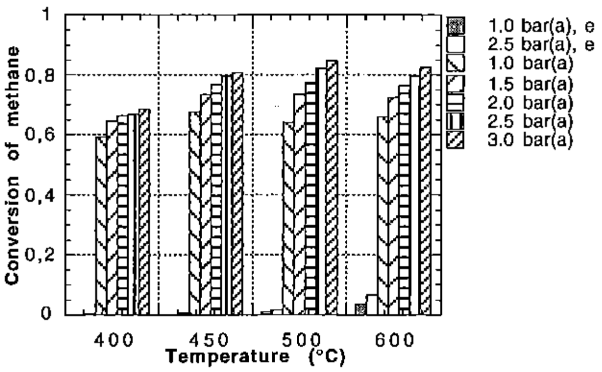


Figure 8 Effects of the pressure on the conversion of methane over PdO/MeOx. $SV \approx 400\ 000\ h^{-1}$. Tests performed with empty reactor are noted with an (e).

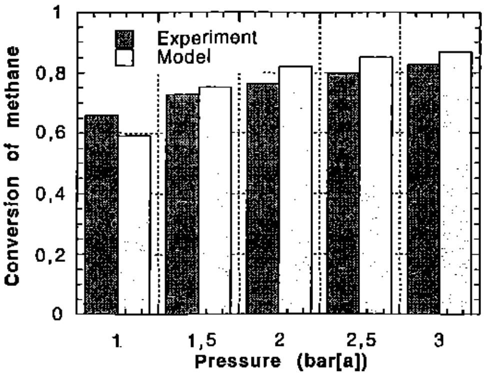


Figure 9 Comparison of measured and expected conversions at different pressures. SV≈400 000 h^{-1}.

The data let us believe that an increased total pressure will affect the catalyst performance in a positive manner, thus increasing the observable conversion. The total pressure up-stream the turbo charger of a lean-burn engine is normally around 2.5 bar(a).

6.5 Long-time tests

Accelerated long-time tests concerning sulphur deactivation were conducted in the micro reactor system by adding high amounts (10 - 500 ppm[v]) of SO_2 to the gas mixture. The tests are built on the fact that there exists an analogy between the concentration of the poison and the time on stream. This assumption is justified since parallel deactivation is postulated to follow an exponential decay in activity according to:

$$a_t = a_0 e^{-k_d p(SO_2)t}$$

a_t = Remaining activity at time=t

a_0 = Initial activity

k_d = Deactivation constant

$p(SO_2)$ = Conc. of SO_2

t = Time on stream

The product of $p(SO_2)$ and time is notified as the characteristic deactivation time with the unit [ppm · h].

Even if we are talking about pure inhibition, it will take some time for the inhibiting molecule to accumulate on the surface. During the accumulation period we will experience an exponential decay in catalyst activity. When turning off the supply of the inhibiting substance, the activity will rise to normal values in a short time. If the deactivation is permanent, however, we will experience no recovery in activity.

To demonstrate the nature of the SO_x-deactivation, 500 ppm(v) of SO_x was supplied to the PdO-MeOx catalyst for a couple of hours at 400°C. The remaining activity of the catalyst was determined after turning off the SO_2-supply. As can be seen in Figure 10, there are indications of permanent deactivation at 450°C after a characteristic deactivation time of 1500 h·ppm. At 600°C there is only a weak tendency of permanent activity decay, which also might be caused by thermal deactivation or increased by-pass effects during the long-time test.

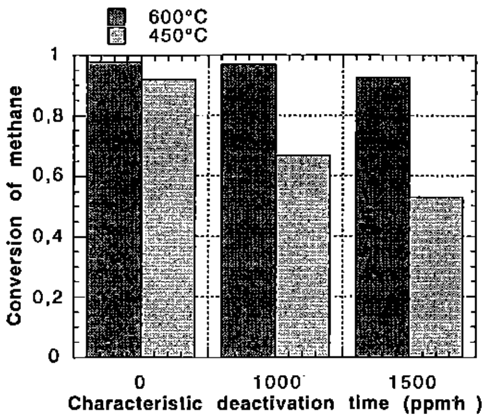


Figure 10 Long-term test performed with 500 ppm of SO_X in the gas mixture. The methane conversion is presented as a function of the characteristic deactivation time. Measurements were performed after turning off the SO_X-injection to reveal permanent deactivation..
SV≈150 000 h^{-1}.

Since exhausts from gas-fuelled engines will contain around 500 ppb of SO_X, the forced deactivation test should correspond to 3000 h on stream, clearly a very long time of operation.

It takes some time to accumulate the inhibiting molecule on the surface, as can be seen in Figure 11. At 1 ppm of SO_X in the exhausts, stable conditions are reached approximately after fifty ours of operation. Also, the accumulation time and the strength of deactivation increases when the temperature is decreased.

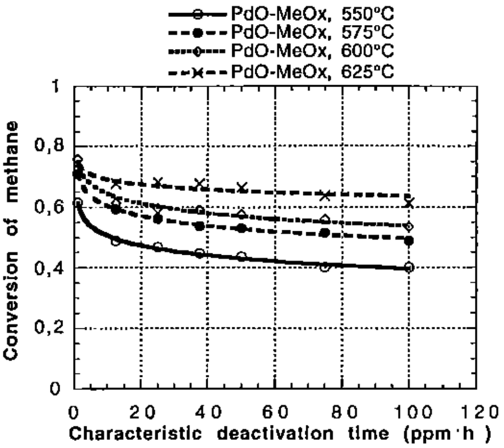


Figure 11 Long-term test performed with 50 ppm of SO_X in the gas mixture. The methane conversion is presented as a function of the characteristic deactivation time. SV≈150 000 h^{-1}.

Tests performed at a lower concentration of SO_X show a similar pattern. The accumulation time (ppm·h) at 600°C is approximately the same (≈50 ppm·h) in Figure 11 and 12, but the degree of deactivation is much less in Figure 12 due to the lower SO_X-concentration.

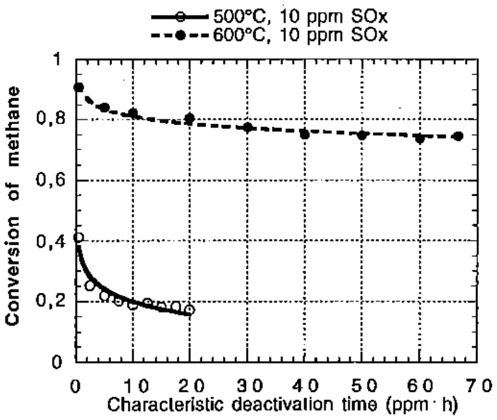


Figure 12 Long-term test performed with 10 ppm of SO_X in the gas mixture. The methane conversion is presented as a function of the characteristic deactivation time. SV≈400 000 h^{-1}, P_{tot}=2.5 bar(a).

The deactivating effects of SO_X will be rather weak at the exhaust conditions prevailing up-stream the turbo charger (only 500 ppm SO_X). The accumulation of SO_X will proceed during the first 100 h of operation, after which stable conditions with respect to sulphur deactivation is reached. Other deactivation phenomena might however cause further deactivation as time goes by.

6.6 Discussion

The micro reactor tests show that it is possible to prepare a highly active wire-mesh catalyst for the combustion of methane. Best results were obtained with $Pd(Ac)_2$ as pre-cursor to Pd/PdO. The active phase should be dispersed on a carrier which does not give rise to a strong metal support interaction.

The activity of the Pd-catalyst is strongly affected by high concentrations of water vapour and SO_x. The deactivating effects of water are completely reversible whereas the SO_x-deactivation is permanent at temperatures below the decomposition temperature of palladium sulphate. Accelerated experiments with SO_x-poisoning indicate that the catalyst will survive several thousands hours of operation in exhausts from lean-burn engines, provided that the exhaust temperature is above the decomposition temperature of palladium sulphate. Other deactivation phenomena, not investigated here, might however lead to further deactivation. Long-time experiments with different SO_x-concentrations also let us forecast the specific accumulation time of SO_x on the catalyst surface. The accumulation time is typically 100 h at exhaust conditions with respect to SO_x. During that period of time the catalyst will be severely deactivated if the temperature is below 550 - 600°C. At temperatures close to 600°C, we will only notice a very weak deactivation, mainly caused by inhibition phenomena of SO_x.

Tests performed with pressurised combustion indicate a nice agreement between the numerical simulation model and the experimental data. It may be concluded that the existing numerical simulation model can be used in further catalyst dimensioning.

7. On-stream tests

7.1 Effects of the gas flow

Before starting the long-time run, a test was performed to study the effects of the total flow. The total flow through the catalyst was varied in steps between 25 and 65 m^3/h (STP) through adjusting the two butterfly valves. The conversion of UHC and CO are given in Figure 13 at different flow rates together with expected conversions obtained with the numerical simulation model. There exists a rather good agreement between the measured and the calculated data. The CO-conversion decreases from 97% at flow rate of 25 m^3/h down to 90% at 65 m^3/h. Corresponding UHC-conversions are 67% and 51% respectively.

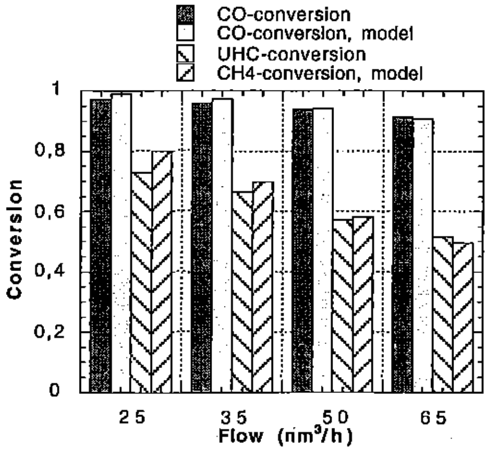


Figure 13 Effects of the gas flow on the conversion of CO and UHC on the lean-burn engine. The experimental data are presented together with calculated values according to the simulation model. The values were obtained at 600°C/1.8 bar(a).

Corrugated wire-mesh catalysts were used in this study. Complementary studies in the micro reactor and calculations indicate a possibility of decreasing the reactor size by a factor 2, by an optimisation of the corrugation, the mesh number and the number of wire-meshes in series. In Figure 14, the conversions of UHC and CO are given as a function of the space velocity for an optimal catalyst formulation with respect to geometrical parameters. It is thus possible to achieve CO-conversions as high as 90% at a space velocity of 900 000 h^{-1} (STP), clearly en extremely high value. The corresponding UHC-conversion at this gas load is around 50%.

A standard gas-engine of 1 MW_e, will give an exhaust flow of approximately 5000 kg/h (4200 m^3/h, 20°C, 1 atm). A catalyst volume of 5 l will, according to the experimental data, give a CO-conversion of 90% and an UHC-conversion of 50%.

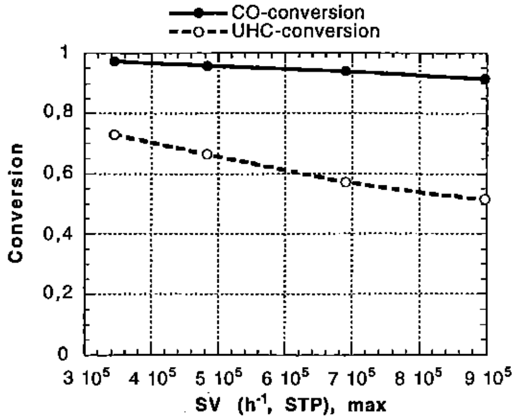


Figure 14 CO-and UHC-conversions presented as a function of the space velocity when using an optimised wire-mesh catalyst.

Since the volume effectiveness of the wire-mesh catalyst is so high, it is easy to install it in an up-stream position of the turbo charger.

7.2 Long-time tests

A long-time test was performed under steady state conditions with respect to the flow-rate and the temperature. The flow rate through the catalyst was 35 m^3/h (STP) and the reactor temperature was around 600°C. The UHC- and CO-emissions were rather stable during the course of deactivation and equalled 4000 and 700 ppm(v) respectively. The adiabatic temperature rise at 100% conversion of CO and UHC should be around 100°C.

The exhausts temperature in the manifold was around 650°C but decreased to a value between 550 and 600°C at the reactor entrance. During operation the reactor temperature was around 600°C, partly due to the adiabatic temperature rise associated with the combustion of CO and UHC.

The conversion results of the long-term test were unexpected and rather disappointing. The results indicated a rapid catalyst deactivation, both with respect to CO and UHC, as illustrated in Figure 15. The deactivation process followed a hyperbolical decay in catalyst activity. After a deactivation time of 60 h, the UHC-conversion had dropped from 70% to less than 20%. Corresponding values for the CO-conversion were 96% and 89% respectively.

It was unfortunately not possible to continue the long-term test more than 60 h, since the engine broke down.

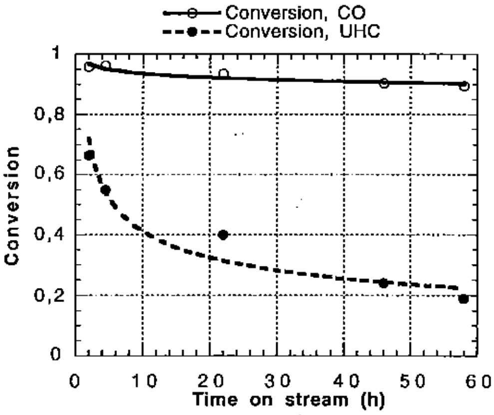


Figure 15 Catalyst deactivation during a long-time run.

The rapid deactivation process observed may have several reasonable explanations:

- Catalyst poisoning with S, P or other components
- Catalyst fouling with coke from the engine
- Catalyst fouling with inorganic compounds present in the lubricating oil
- Thermal degradation of the carrier or precious metal sintering
- Self deactivation through phase transformations and clogging of the pores
- Leakage in the reactor system (by-pass effects)

To be able to explain the deactivation in terms of physio-chemical processes, it is necessary to examine the deactivated catalyst carefully.

7.3 Catalyst characterisation

The activity of the deactivated catalyst was examined in the micro-reactor system. Samples were taken from the reactor entrance and the reactor exit, to investigate if the deactivation was homogeneous throughout the reactor. From the results, it is obvious that the deactivation is homogeneous which means that all parts of the reactor must have experienced the same strength of deactivation.

The catalyst activity has decreased by 75% (first-order rate coefficient) during the course of deactivation. This value very well agrees with the observed deactivation on-stream.

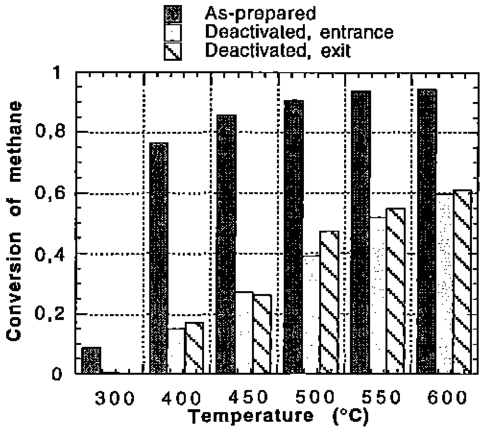


Figure 16 Micro reactor tests with as-prepared and deactivated catalyst, SV≈150 000 h^{-1}.

Thermal deactivation or sintering are not probable mechanisms since the temperature during the test was limited to 600°C. Heating the catalyst to 800°C gave no further decay in activity, which would be the result if thermal degradation was the reason to the deactivation observed.

Microscope investigations gave substantial information to suspect extensive catalyst fouling. Indeed, the catalyst was covered by a slag-like substance, rather strong bounded to the catalyst surface. When removing this layer by means of mechanical treatment, the greenish-black layer of PdO was restored. It is not possible to restore the catalyst activity simply by mechanical treatment, since the fouling component also has clogged the pore structure of the catalyst. The pore structure is not assessable for mechanical treatment.

Self-deactivation through phase-transformations might also explain the deactivation process and the formation of a slag-like layer. In order to exclude this explanation an as-prepared catalyst sample was treated in exhaust like conditions for 60 h. Visual examination and activity studies made it possible to exclude the hypothesis of self-deactivation completely.

Increased effects of by-pass during the deactivation is not the reason since it would affect the CO-and the UHC-conversion equally.

Catalyst coking may to same extent explain the deactivation observed. Indeed, heating the catalyst to high temperatures gave rise to a partial reactivation. Coking phenomena might arise if the rate of soot deposition is higher than the specific rate of soot oxidation. Coke/soot might also origin from the combustion of heavy hydrocarbon molecules, i.e. lubricating oil.

The colour of the fouling layer let us believe that it contains transition metal oxides (e.g. iron oxide). Through leaching the wire-meshes in a weak acid (citric acid) it was possible to remove parts of the fouling components. Tests were performed to qualitatively indicate the presence of iron and sulphate. Since no precipitation of $BaSO_4(s)$ was formed upon addition of $Ba(NO_3)_2$, it may be postulated that the catalyst contains only very low concentrations of sulphur. Addition of KSCN, on the other hand, yielded an intense red colour, thus indicating the presence of iron in the solution.

ICP-analysis (Inductively Coupled Plasma) of the solution also indicate the presence of different transition metals.

According to DGC a/s, the owner of the engine, the inorganic substances found in the fouling layer most probably origined from the lubricating oil. Test had previously been performed with additives (Dicyclopenta-dienyl-Fe and Methylcyclopentadienyl-Mn-Tricarbonyl) in the combustion air. It is therefore assumed that the lubricating oil contained small amounts of these substances, which have caused the fouling phenomena observed. Metal organic substances are indeed effective in producing catalyst fouling, since a dense inorganic layer of the corresponding oxides are formed upon combustion of the hydrocarbon content of the molecules. Also very small amounts of these components will cause extensive and rapid catalyst deactivation. Similar phenomena are observed in VOC-treatment when the ventilation air contains trace amounts of silicon oils.

The numerical model enable us to distinguish between parallel poisoning, which would be the case with palladium sulphatisation and catalyst fouling. Parallel poisoning will, in this case, follow an exponential decay in activity whereas fouling will demonstrate itself through a hyperbolical decay in activity, see Figure 17.

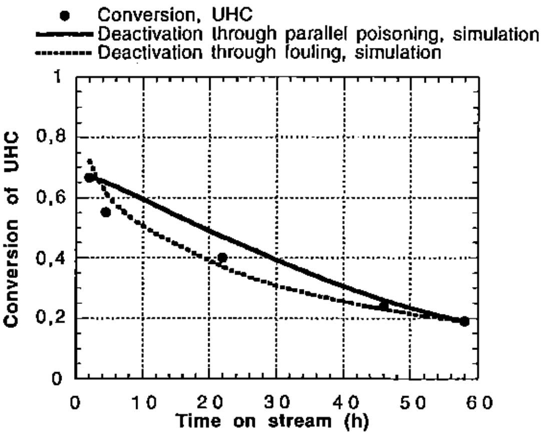


Figure 17 Observed trend of deactivation and simulated trendsof deactivation due to parallel poisoning and fouling.

The simulated deactivation trend of fouling is in perfect agreement with the experimental data. The exponential decay associated with parallel poisoning gives a slower initial deactivation. The CO-combustion is to a less extent affected by the deactivation than the UCH-combustion. This observation is explained by the fact that inorganic oxides like Fe_2O_3 and MnO_2 show a high activity in CO-combustion, especially at these high temperatures.

7.4 Catalyst reactivation

Different reactivation tests were performed to restore the catalyst activity. By simply heating the catalyst to 800° for 1 h in air it was possible to restore the activity to a great extent, see Figure 18. Citric acid treatment at room temperature gave a similar result and restored approximately 50% of the activity lost. The catalyst activity was completely restored by treating the catalyst with a citric acid solution at its boiling point. During the chemical treatment, the fouling components were dissolved.

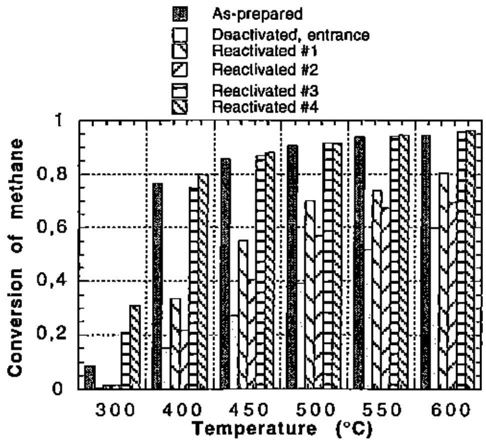


Figure 18 Results of catalyst reactivation tests.
#1 - Heat treatment, 800°C, 1h
#2 - Leaching in citric acid, 20°C, 1 h
#3 - Heat treatment + leaching at 100°C
#4 - Leaching at 100°C

7.5 Discussion

The conversions of CO and UHC, obtained during the initial phase of the deactivation test are in perfect agreement with the micro reactor data and the calculated data obtained with the numerical simulation model. It is thus possible to achieve high conversions at extremely high SV-values in an up-stream position of the turbo charger.

The catalyst was rapidly and severely deactivated during the long-time run. The deactivation observed is most probably caused by fouling with inorganic oxides, originating from additives (Dicyclopenta-dienyl-Fe and Methylcyclopentadienyl-Mn-Tricarbonyl) supplied to the combustion air in experiments previously performed in the gas engine.

8. Conclusions

8.1 Catalyst activity

The PdO/MeOx-catalyst shows a very high activity in the combustion of methane and carbon monoxide. Water vapour inhibits the combustion of methane through competitive adsorption. This effect is especially pronounced at temperatures below 500°C, where the rate of methane combustion is strongly limited by the desorption of water, which is formed during the combustion. Indeed, it has been observed that inactive palladium hydroxide is formed at high concentrations of water vapour and at low temperatures. At high temperatures the palladium hydroxide is decomposed into PdO and desorbing water, thus restoring the catalyst's activity.

Sulphur oxides give rise to strong inhibition phenomena at temperatures below 550°C, which corresponds to the temperature of palladium sulphate decomposition. In the presence of ever so small amounts of SO_X (<10 ppm(v)), the catalyst's ability to combust methane is more or less lost at temperatures below 500 - 550°C.

Increased total pressure influence the catalyst activity in a positive manner, thus increasing the conversion significantly. Initial measurements on the gas-fuelled engine show that it is possible to reach UHC-conversions of 50% at space velocities around 1 000 000 h^{-1}. The corresponding CO-conversion will be around 90% at this flow condition.

The initial catalyst activity is in very good agreement with the activity figures used in the theoretical calculations concerning catalysts in lean-burn applications previously performed [4].

8.2 Catalyst stability

The micro reactor tests indicate that the catalyst should survive gas engine conditions for several thousands hours of operation. On-stream tests, however, demonstrated a very rapid and strong deactivation under real operating conditions. Continued tests and catalyst characterisation made it possible to exclude different mechanisms of deactivation. We have certainly not experienced thermal degradation of the catalyst since extensive heat-treatment does not led to further deactivation but to a partial reactivation.

Careful examination of the catalyst show that a dense layer of slag is present on the catalyst surface. The shape and colour of the slag let us believe that inorganic ashes may have collected on the catalyst surface, thus giving rise to fouling phenomena. Through careful removal of this dense slag layers by means of mechanical and chemical measures, it was possible to restore the catalyst activity completely.

According to DGC a/s, the owner of the gas engine, tests had been performed with metal organic additives to the combustion air in previous experiments. This information together with the very rapid deactivation, the catalyst appearance and the results of ICP-analysis indicate that the catalyst was deactivated through fouling with metal organic compounds, which upon combustion formed dense layers of slag. The deactivation obser-ved, has nothing to do with sulphatisation or sulphur inhibition, which however, are important processes at low reaction temperatures.

8.3 Future outlooks

The study has verified the numerical model, which may be used in future dimensioning. Further studies directed to long-term stability of the catalyst should be performed, preferably in a real installation.

In addition to gas-fuelled engines used in co-generation, the problem of UHC-emissions is applicable also in automotive applications (gas-fuelled buses and trucks). Also in these applications, the wire-mesh catalyst will give clear advantages over conventional monolith catalysts installed in positions down-stream the turbo charger.

9 Literature

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