



Regeneration of palladium based catalyst for methane abatement

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Abstract: The exhaust gas of lean burn gas engines contains significant amounts of unburnt methane gas. Since methane is a strong greenhouse gas, reducing methane emissions would greatly improve the environment and provide greenhouse gas emissions credits. Oxidation catalysts containing platinum are commonly used for the elimination of non-methane hydrocarbons (all hydrocarbons except methane). The problem with platinum based catalysts is that methane is the most stable of the hydrocarbons. Because of this, platinum based catalysts are not very effective with methane and only eliminate a small fraction of methane contained in the exhaust gases under normal lean burn operating conditions. Since these platinum based oxidation catalysts are not very efficient, another method is desired and this paper will discuss another type of catalyst that can provide high methane conversion. It has been reported in the literature that oxidation catalysts containing Palladium are very

efficient in converting methane (typically greater than 80%). However, these palladium based catalysts are extremely sensitive to sulphur poisoning and their activities toward CH₄ destruction deteriorate very quickly in the presence of SO₂ or SO₃. Since lean burn gas engines always contain a small amount of SO₂ from lubricating oil or the natural gas itself (1-5 ppm SO₂), it is very difficult to use palladium catalysts for methane abatement. In the first section, this paper will explain the deactivation mechanisms for palladium-based catalyst in the presence of SO₂. In a second section, the paper will discuss methods for maintaining high CH₄ activity with palladium catalysts over a long period of time and in the presence of SO₂ by means of continuously regenerating the catalyst. The paper will describe various methods for regenerating palladium-based catalyst. There are basically two ways for regenerating palladium-based catalysts. The first method is thermal regeneration and the paper will discuss



the boundary conditions with its advantages and disadvantages. The second method is similar to what is being currently done with NO_x adsorber catalysts. In order to regenerate the catalyst, the exhaust must periodically be in a rich condition with little to no oxygen present. The paper will

discuss in detail what are the preferred operating conditions for successfully regenerating catalysts with rich conditions. With proper regeneration, it is believed that palladium based catalysts are an effective method for greatly reducing methane emissions from lean burn engines.

INTRODUCTION

Exhaust clean up of methane in lean burn natural gas engines is a big challenge. Since methane is the most stable component, it is therefore the most difficult component to catalytically oxidize. Many researchers have investigated the viability of palladium-based catalysts for natural gas exhaust clean up (1-11). They report that trace amounts of sulphur in the natural gas feed severely deactivates the catalyst and reduces its ability to convert methane. We have investigated the possibility of regenerating the catalyst using possible engine management scenarios. These are discussed in this paper.

EXPERIMENTAL PROCEDURE

1. Model Gas Reactor Testing

A catalyst for exhaust gas methane oxidation was tested for its sulphur poison resistance in a model gas reactor (Figure 1). Exhaust gas conditions and catalyst dimensions are presented in Table 1. A thermocouple was placed 1 mm away from the outlet of the catalyst. The temperature recorded by this thermocouple was taken as the reaction temperature. Four gases (CH₄, O₂, SO₂ and balance N₂) were introduced to the reactor from four separate mass flow controllers. Prior to entering the reactor, the bulk-premixed gases were preheated to 130°C. Water was added using a peristaltic pump after the pre-heater. The length of tube from the pre-heater to the reactor was heated to 130°C using heating tape to prevent condensation of the water. The tubing from the reactor to the gas chromatograph was also heated to prevent water condensation.

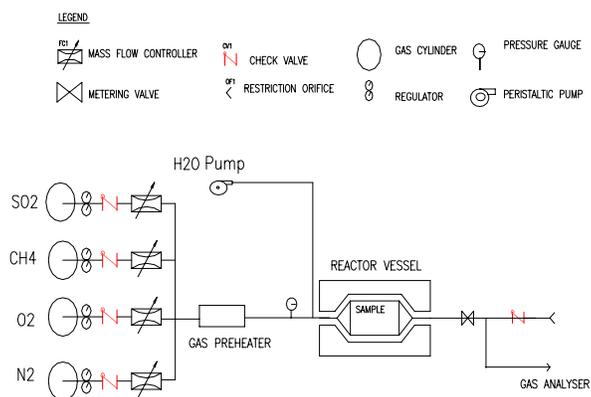


Figure 1 — Flow Diagram of Model Gas Reactor

Table 1 — Test conditions

Catalyst Dimensions	1 cm O.D. x 5 cm long	
Space Velocity	110,000 1/h	
Gas composition	CH ₄	112 ppm
	H ₂ O	6%
	O ₂	10.8%
	SO ₂	5 ppm
	N ₂	Balance
Temperature Range	250 °C to 550 °C	

The catalyst formulation used in this study is listed in Table 2. Detailed preparation and composition information is not provided due to its confidential nature.

Table 2 — Catalyst Compositions

Catalyst A	10 g/l Pd/Pt 3:1 on Al ₂ O ₃
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Analysis was performed using a Varian CP-3800 Gas chromatograph (GC) equipped with an FID and TCD. The columns used on the GC for the separation are a CP-Sil 5CB, Hayesep T, Hayesep R and Molsieve 13X.

Samples were tested under fresh conditions and after exposure to the gas composition in Table 1 with 5ppm SO₂ for 10+ hours to determine methane conversion efficiency.

Regeneration of the catalyst after sulphur poisoning was attempted by manipulating the model gas composition to reflect potential engine management scenarios. These scenarios are discussed in detail later.

RESULTS AND DISCUSSION

Deactivation Mechanism

In order to understand the deactivation mechanism of Pd based catalyst under different lean burn engine operating conditions, we attempted to deactivate the catalyst with SO₂ under typical exhaust compositions but under different temperature conditions. Figure 2 shows a plot of

methane conversion as a function of sulphur exposure time and aging temperature. It shows that operating temperature affects the deactivation mechanism of the catalyst. At 240°C the deactivation of the catalyst is very rapid and a 30% drop in conversion is seen in 5.5 hours. On the other hand, the deactivation is much less at temperatures of 500°C. The conversion plateaus at 85% after four hours and the rate of deactivation of the catalyst reduces significantly. These observations can be explained by the deactivation mechanisms described by Farrauto (3,6), and Gelin (10). They propose that the deactivation of Pd based catalyst is through adsorption of SO₂ onto the Pd particle with eventual spillover of S onto the alumina support. At low temperatures (~240°C), the adsorption rate of SO₂ and SO₃ on the Pd particle and into the alumina support is maximized and thus the deactivation is very rapid. At the higher temperatures of 500°C, the SO₂ adsorption rate on the Pd particles is substantially lower, and any SO₂ adsorbed into the alumina washcoat begins to desorb resulting in a much slower deactivation of the catalyst.

Projecting forward the amount of deactivation at an operating temperature of 500°C, it is expected that the deactivation of the catalyst will take about 50 hours to reach 60% methane conversion. This temperature dependence is an important observation. It provides information on the practicality of regeneration schemes. Applications where the exhaust temperature at the catalyst is in excess of 500°C could be viable options for regeneration due to the longer times needed between potential regeneration events. Low temperatures applications are not practical. Regeneration of the catalyst would have to occur often and rapidly. In other words, the engine would be required to operate closer to a stoichiometric engine with a 3-way catalyst controller. This data shows that methane clean up of low temperature applications running under lean burn operation is not practical and impossible using the current Pd based technology.

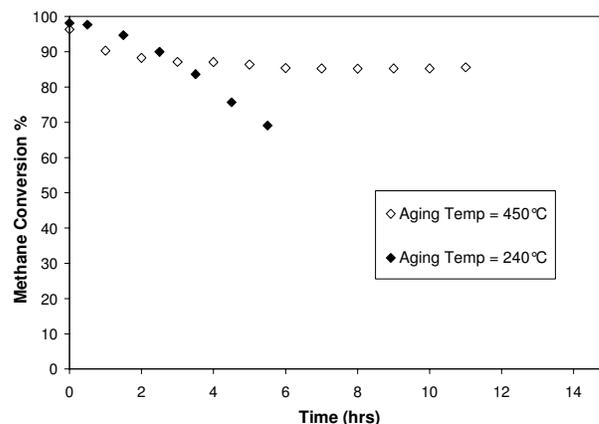


Figure 2 — Effect of SO₂ exposure and aging temperature on Methane conversion

In order to bring Pd type catalyst for methane abatement into the commercial arena, catalysts would have to meet extensive durability requirements such as 80%+ conversion for 8000 hours + operation. From preliminary aging data in the low temperature region, it seems difficult to meet this type of durability, hence the need for periodic regeneration. The most practical approach would be in-situ catalyst regeneration, thus eliminating the need for removing the catalyst. This type of approach is common in automotive catalyst industry where many examples can be found. The best-known example is the three-way catalyst, where the engine is designed to oscillate around the stoichiometric point so that the oxygen storage capacity is continuously replenished. Another example is the NO_x adsorber catalyst used in GDI cars (12, 13). Periodically, the engine is switched from lean-mode to rich-mode so that the adsorbed NO_x or SO_x is removed from the catalyst bed. An example is the PSA DPF filter system where the diesel particulate filter is thermally regenerated on a periodic basis using engine management and late cycle diesel fuel injection (14). In the next section, both avenues, thermal and chemical will be explored for methane catalyst regeneration.

The thermal approach for regeneration of Pd poisoned catalysts has been documented in the literature (10). This method is relatively easy to implement with secondary methane injection [either late-cycle or in-exhaust port]. Oxidation of hydrocarbons is exothermic, thus their oxidation will increase catalyst bed temperature. This is the basis for diesel particulate filter regeneration used by PSA and has been investigated in this study. Experimental set-up has been described in previous section. During regeneration mode, methane concentration is increased leading to an increase catalyst bed temperature of 650 °C. As illustrated in Figure 3, two regeneration events were conducted, one 2 hours and 10 hours long. Thermal regeneration events increase catalyst efficiency, but only for a short period of time. The

problems with this approach are that 1) regeneration times required are of the same order of magnitude as deactivation time, thus leading to high fuel penalty; 2) temperatures required for regeneration are high. In our example, 650 °C is not sufficient and higher temperatures would be required to improve regeneration. Gelin also reported that complete regeneration is not possible at 650 °C (10).

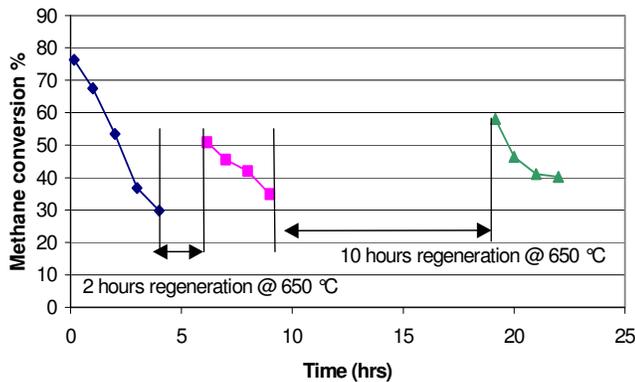


Figure 3 — Thermal regeneration

Another approach for catalyst regeneration is to change the chemistry of the exhaust gas with engine tuning. NO_x storage catalysts in gasoline direct injection engines are a nice illustration. Approximately 90% of the time, a GDI engine runs lean of stoichiometry and NO₂ is adsorbed onto the catalyst as barium nitrates or iridium nitrates. Once the NO_x storage catalyst is saturated with NO₂, the engine combustion mode is switched to slightly rich for roughly ten percent of total operating time. During this rich excursion period, the NO_x adsorber physically desorbs the NO₂ from the barium or iridium nitrates; Once released from the NO_x storage catalyst, the NO₂ molecules will then be reduced into N₂ as in a standard 3-way catalyst. GDI engines have the flexibility to run lean or rich so switching combustion modes is fairly easy. Today, there is a mix of rich-burn and lean-burn natural gas engines in the market place and it seems a reasonable assumption to have combustion mode switching on these engines especially at low-medium loads. On the other hand, switching modes at high loads may be impossible because of thermal load and stress on the engine.

From catalyst literature, using Lambda alone is not a good parameter for catalyst regeneration (6); rather one must look at the quality of the reductant itself. For NO_x storage catalysts, H₂ is the preferred reductant, followed by CO and then hydrocarbons. Amongst hydrocarbons, methane, being the most stable is the worst reductant. We have taken the assumption that this rule also applies to palladium based catalysts. In this next section, we are going to use various gas mixtures for our regeneration study. In Table 3, we look at three different mixtures.

Table 3 — Regeneration Gas Compositions

Mixture 1	Mixture 2	Mixture 3
1% H ₂ , Balance N ₂	0.25% H ₂ , 0.75% CO, Balance N ₂	70 ppm H ₂ , 200 ppm CH ₄ , 3 ppm SO ₂ , 500 ppm CO, 6% H ₂ O, Balance N ₂

Results in Figure 4 below clearly indicate that Mixture 1 is better than mixture 2 which is in turn better than mixture 3. The catalyst is almost completely regenerated after being exposed for 30 minutes to mixture 1 while 30 minutes under mixture 3 does not improve catalyst performance. These results confirm the similitude between NO_x adsorber catalysts and this type of catalyst.

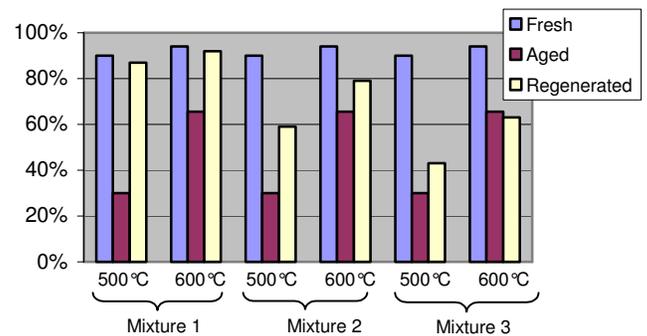


Figure 4 — Methane conversion at 500°C and 600°C using different gas mixtures in Table 3

We now need to investigate how often would we need to regenerate catalyst since different strategies may be used depending on the required frequency.

As discussed earlier, rate of deactivation is of function of exhaust temperature. In these conditions, it is fairly difficult to have accelerated aging. Hence, we have done some full size aging on a 2MW stationary gas engine and accumulated 2000 hours. Aging conditions were 540°C with North Sea Gas. Two samples, one Pt based and one Pd based technology were aged and results are shown (Figure 5). As expected, Pt based catalyst show very poor performance with 20% conversion at 600 °C while Pd based catalysts show surprisingly good results with 90% methane conversion at 500°C.

From these results, one can conclude that we would need catalyst regeneration every 2000 hours or more. In these conditions, hydrogen-based regeneration, which is the most efficient method could also be used during maintenance periods. Additional tests are still needed to optimize regeneration strategy.

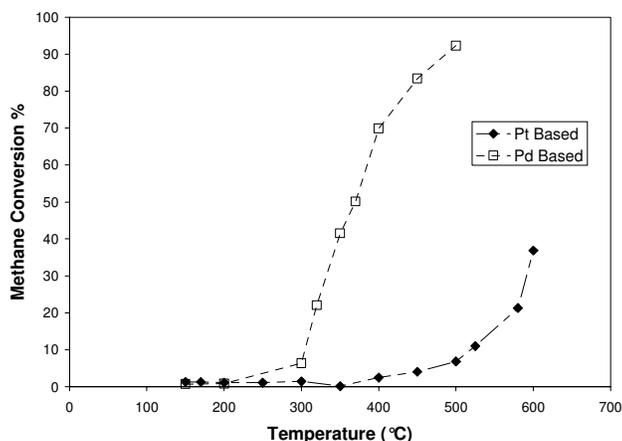


Figure 5 — Methane conversion after 2000 hours of field aging at 540°C using Pt and Pd based technology

CONCLUSIONS

It can be concluded that the application of Pd based technology for methane clean-up is a challenging task. The deactivation of the catalyst by sulphur in the exhaust is highly temperature dependent. At temperatures below 400°C, rapid deactivation occurs forcing the need for frequent regeneration at elevated temperatures (above 500°C). At temperatures above 500°C, deactivation appears to be very slow with a 10% loss of methane conversion on a catalyst with over 2000 hours of operation. This type of deterioration requires very little maintenance and regeneration of the catalyst could be achieved in-situ or by other external methods.

Regeneration of the catalyst using thermal and chemical means show mixed results. Thermal methods are not able to completely regenerate the catalyst. Hydrogen is shown to completely recover the catalysts activity, while gas mixtures are not as effective.

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