

Sulfur Poisoning and Regeneration of Pd Catalyst under Simulated Emission Conditions of Natural Gas Engine

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ABSTRACT

Palladium-based catalyst can be employed for natural gas exhaust clean up due to its high activity for light hydrocarbon oxidation. Unfortunately, trace amounts of sulfur in the natural gas feed severely deactivate the catalyst.

In this paper, SO₂ adsorption over a monolithic Pd/Al₂O₃ oxidation catalyst is monitored in a time-resolved manner in the presence of 100 ppm SO₂ under simulated aging conditions of a natural gas engine, which is correlated with the oxidation activity for CO and hydrocarbons such as CH₄, C₂H₆ and C₃H₈. The SO₂ adsorption is saturated in 0.5 h at 400°C and 100,000 h⁻¹. The molar ratio of adsorbed SO₂ and Pd is about 2/1, indicating SO₂ molecules adsorbed, or transferred to the Al₂O₃ support. The oxidation activity gets stabilized upon saturation of sulfur adsorption, and the hydrocarbon oxidation activity cannot recover even when 100 ppm SO₂ is completely removed from the stream. The light-off temperatures (T₅₀) of hydrocarbons shift 50-100°C higher after SO₂ poisoning.

When the gas stream was switched to the fuel-rich mode, 15% of the adsorbed SO₂ molecules were released from the poisoned catalyst at 400°C. No H₂S was detected in the outlet stream in the reducing atmosphere. Only traces of SO₂ molecules were detected when the regenerating temperature increased to 550°C. The poisoned Pd catalyst was reactivated to some degree, but suffered from a significant deactivation in 30 min even in the absence of SO₂, regardless of regenerating temperature. The results revealed the existence of reversible and irreversible sulfur in the reducing atmosphere. A mechanism of sulfur poisoning and regeneration is proposed.

INTRODUCTION

Natural gas engines are in high demand and are used in many applications such as power generation, gas compression, and cogeneration. The driving forces include economical, political, and environmental factors. Natural gas used to be a relatively cheap primary energy source, always at a discount to crude oil (on a

comparative British thermal unit basis). It gradually evolved into a major resource during the 20th century — reaching a 24 per cent share of global primary energy in 1999. In the year 2000, natural gas prices in the USA rose to unheard-of highs of \$10/million Btu, ushering in a new era, with natural gas at a 120 percent premium to crude oil [1]. Due to the political instability in middle east and other oil-producing areas, the diversification of energy sources is encouraged by government. Furthermore, spark-ignited lean burn natural gas engines have significant environmental advantages over rivals of gasoline and diesel fuel, such as lower NO_x and SO_x emissions, fewer particulate matters. CO₂ emissions are also reduced because H/C ratio of natural gas is about double that of gasoline and diesel fuel [2].

The drawback of natural gas engines is the emissions of non-combusted methane and non-methane hydrocarbons (NMHCs). Methane is known to be a powerful greenhouse gas with about 20 times the greenhouse potential of carbon dioxide. The environmental impact of methane and NMHCs is being reflected in present and future regulations. At least 60% methane conversion is required to meet the most stringent current European regulations for THC limit values (Tier Euro IV, effective from October 2005) [2].

Palladium-based catalysts are discovered to be the most active for methane and NMHCs abatement [2]. The ease of oxidation of alkane hydrocarbons is related to carbon numbers, e.g. larger molecules are more vulnerable to attack by oxygen. Thus, methane is the toughest hydrocarbon molecule to activate. The additional factors of the presence of large amounts of water (5%-10%), low temperatures (400-450°C), and traces of sulfur dioxide (1ppm) in the engine exhaust create the greatest challenge to the Pd based catalysts [3]. Hydrothermal aging and phosphorous poisoning are contributors to catalyst deactivation. However, this paper focuses on sulfur poisoning. Phosphorous compounds are typically strong poisons and may be introduced from additives of lubricating oils used in pumps, blowers, fans and other machineries. Work by McCormick et al shows that Pd/Al₂O₃ catalyst deactivated in less than 50 hours in lean burn gas engine exhaust [4]. It is well known that the active site of hydrocarbon oxidation is PdO particles

[5]. SO₂ converts to SO₃ by PdO with excess oxygen in the gas stream, and PdO reacts with SO₃ to form less active PdO-SO₃. Complete poisoning of the PdO is retarded with the use of a sulphating support, such as Al₂O₃. The support is capable of adsorbing sulphur and buffering the poisoning onto the PdO particle. On the contrary, a non-sulphating support such as SiO₂ cannot act as a SO₃ reservoir, and PdO is poisoned rapidly and directly by SO₃. Sulphur-aged Pd catalysts can be partly regenerated under reducing atmosphere such as H₂ [5-8].

Few works have been published regarding the sulfur adsorption and desorption on Pd-based catalysts under lean burn natural gas engine conditions. Recently temperature programmed reduction (TPR) tests of SO₂-aged Pd/Al₂O₃ powder catalyst were conducted in flowing CH₄, 2% H₂O and He [7]. SO₂ release was observed between 400-700 °C by mass spectrometer.

The objective of this work is to investigate the SO₂ adsorption and desorption under exhaust conditions of natural gas engines. This knowledge would help to better understand the mechanism of sulphur poisoning and regenerating of Pd catalysts. The sulphur adsorption over a monolithic Pd-based oxidation catalyst is monitored in a time-resolved manner in the presence of SO₂ under simulated emission conditions of natural gas engine, which is correlated with the oxidation activity for CO and hydrocarbons such as CH₄, C₂H₆ and C₃H₈. In order to regenerate the catalyst, the gas stream was changed to reducing atmosphere. The sulphur release was examined at different temperatures and correlated with effectiveness of the catalyst regeneration.

EXPERIMENTAL

The Pd-based catalyst is supported on 400cpsi cordierite substrate with an Al₂O₃ washcoat. The Pd loading is 5 g per litre substrate (142 g/ft³). Catalyst cores with a diameter of 1.0 cm and volume of 3.5 cm³ were used to fit the stainless steel reactor.

Catalytic performance was tested in a conventional stainless-steel tubular reactor that is described in a previous paper [9]. Gas compositions used are listed in Table 1 and the gas mixture was fed to the reactor with a space velocity of 100,000 h⁻¹ @STP based on substrate volume unless otherwise specified. The catalyst is located in the isothermal zone of the reactor. The gas temperature at the inlet was recorded as the reaction temperature. Light off curves were collected by increasing the reaction temperature from 100 to 500 °C. Gas composition was monitored in a time-resolved manner using a Fourier Transform Infra Red spectrometer (FTIR) manufactured by MKS Instruments.

SO₂ poisoning is performed by exposing the catalyst to 100 ppm SO₂. High concentrations of SO₂ are used to rapidly age the catalyst and simulate sulphur exposure of the catalyst to 1 ppm S for 100 hours. The fresh catalysts were poisoned at 400 °C by introducing 100 ppm SO₂ to

the lean gas composition reactant stream. The SO₂ poisoning generally takes less than 1 h for the oxidation activity to reach a steady state.

After SO₂ poisoning and light-off curve collection, the catalyst was regenerated in a reducing atmosphere. The gas composition of regeneration is listed in Table 1. During the regeneration, oxygen was switched to N₂ with the same flow rate. The regeneration continued until no sulphur dioxide was released from the catalyst, which generally takes half an hour.

Table 1. Model gas composition (SV = 100,000 h⁻¹).

Component	Lean	Regeneration
CH ₄	1000 ppm	1000 ppm
C ₂ H ₆	150 ppm	150 ppm
C ₃ H ₈	50 ppm	50 ppm
CO	1000 ppm	1000 ppm
NO	100 ppm	100 ppm
O ₂	10%	0
H ₂ O	5%	5%
CO ₂	5%	5%
SO ₂	0*	0
N ₂	Balance	Balance

Note: *SO₂ is around 100 ppm during poisoning. The regeneration was only performed in reducing atmosphere.

The fresh and regenerated catalyst samples were characterized with Transmission Electron Microscopy and Energy Dispersive X-Ray Spectrometry (TEM/EDS) in order to obtain Pd particle size information and sulfur content.

RESULTS AND DISCUSSION

Four catalyst cores (samples) were cut from the same piece of catalyst monolith and used in this work in order to characterize the samples with different conditions. The reaction conditions over various samples are listed in Table 2. The term 'light-off curve' in Table 2 means that a light-off curve was collected from 100 to 500 °C.

Table 2. Reaction conditions over various samples.

Steps	Sample 1	Sample 2	Sample 3
1	Fresh	Fresh	Fresh
2	Light-off curve	Light-off curve	1h SO ₂
3	1h SO ₂	1h SO ₂	1h/400 °C regeneration
4	Light-off curve	Light-off curve	1h/400 °C regeneration
5	39 h SO ₂	1h/400 °C regeneration	400-550 °C regeneration
6	Light-off curve	TEM/EDS	Light-off curve
7			TEM/EDS

The oxidation activity of Palladium catalyst was evaluated when fresh and after SO₂ poisoning. Figure 1

displays the light-off curves of methane, ethane and propane over the fresh and poisoned catalyst. The light-off curves were collected when the catalyst was fresh, after poisoning for 1 h at 400°C by 100 ppm SO₂, and after 40 h aging by SO₂ under the same conditions. During reaction conditions, the fresh catalyst sample is found to be deactivating slowly even in the absence sulfur dioxide, likely due to the presence of water in the stream [10]. The deactivation of the catalyst is greater after SO₂ poisoning. The catalyst was seriously poisoned by SO₂ during the first hour in the stream. The light-off temperatures of methane, (T₅₀) over aged catalyst are 100°C higher than fresh. Catalytic activity has reached steady state during the first hour, because no further deactivation is observed with longer exposure times (up to 40 hours) to high SO₂ concentrations.

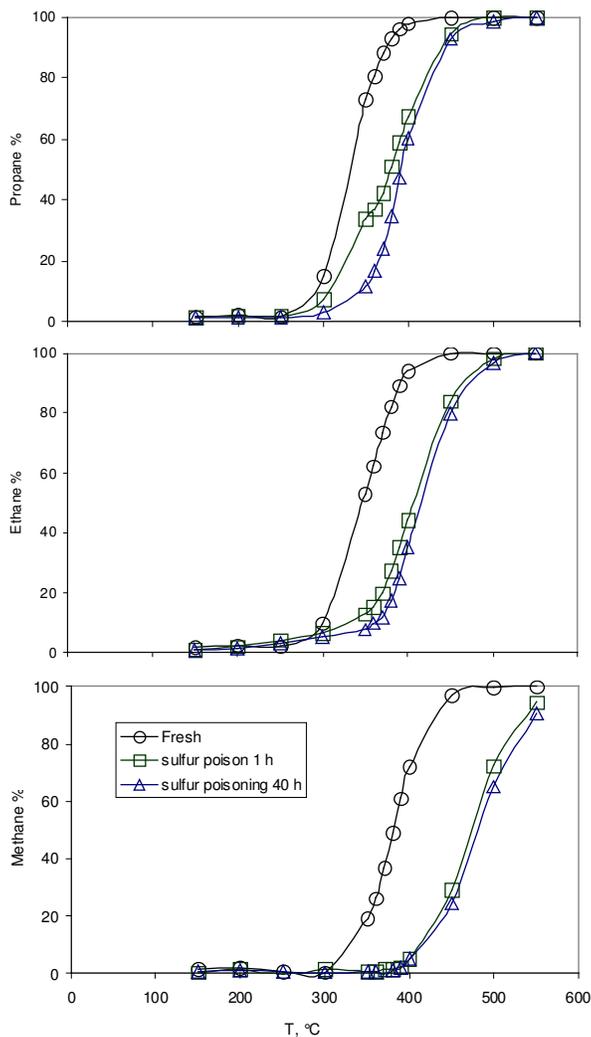


Figure 1. Light-off curves of methane, ethane and propane over Pd-based monolithic catalyst before and after aging. SV=100,000 h⁻¹. SO₂ aging conditions: 100 ppm SO₂, 400°C, the other components see Table 1.

The extent of light-off shift after SO₂ exposure depends on the type of hydrocarbon component. While T₅₀ of methane after SO₂ aging moves 100°C higher relative to

the fresh, light-off temperatures of ethane and propane shift 65°C and 50°C, respectively. This is consistent with Pd catalyst aging test results on a lean burn natural gas engine [4]. These authors report the deactivation of PdO by sulfur oxides is due to both a decrease in the chemisorption of hydrocarbons on PdO-SO_x and a decrease in the availability of oxygen from PdO-SO_x [5]. The PdO-SO_x sites are still active in propane oxidation, but not sufficient to activate methane molecules. Therefore, the light-off shift of propane is not so far as methane after SO₂ poisoning.

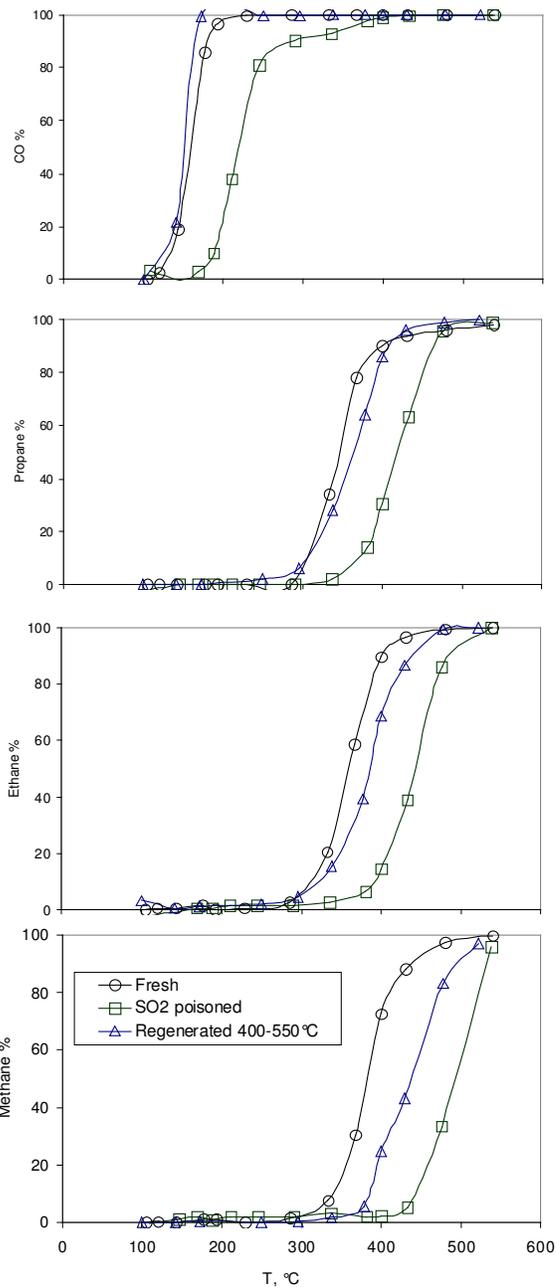


Figure 2. Light-off curves of CO, methane, ethane and propane over Pd-based catalyst when fresh, SO₂ aged or regenerated. SV=100,000 h⁻¹.

Figure 2 shows the catalytic performance of the catalyst sample that has been regenerated under reducing atmosphere for 3 h between 400-550°C. During

regeneration, the oxygen flow is replaced by nitrogen to maintain a constant flow rate and space velocity through the catalyst. The catalyst was regenerated first at 400°C for 2 h, and then the temperature is ramped at 10°C/min to 550°C for 1 h. The activity is recovered completely for CO oxidation, mostly for propane and ethane, but only half for methane oxidation. The recovery dependence on compounds indicates that some sulfur residue may exist in the catalyst and interact with Pd particles.

As shown in Table 2, a series of treatments have been undertaken to investigate the catalytic performance of various catalyst conditions. The catalyst samples were treated under various conditions step by step, followed by activity measurements at 400°C after each step: (a) Fresh catalyst; (b) During SO₂ poisoning at 400°C; (c) After 1h SO₂ poisoning; (d) Regenerating at 400°C for 1 h; (e) Regenerating at 400°C for another 1 h; (f) Regenerating at 550°C for 1 h. In order to check the reproducibility, the catalyst sample was replaced by a new one of the same batch after step (e), and the steps (a)~(e) were repeated. It was observed that the results of activity and SO₂ adsorption/desorption are reproducible. Some samples were characterized using TEM/EDS.

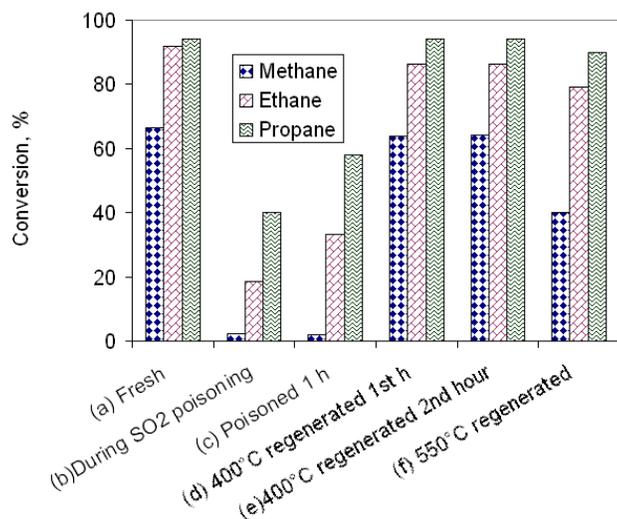


Figure 3. Oxidation activity of Pd/Al₂O₃ at 400°C with different catalyst conditions. The presented conversions after regeneration are collected immediately after regenerating.

Figure 3 shows the hydrocarbon conversions at 400°C for an overall comparison. It is noted that activity was recorded in the presence of 100 ppm SO₂ at steady state after 50 min poisoning for step (b). After regeneration at 400°C, the oxidation activity of the catalyst is almost fully recovered. However, the increase in regeneration temperature to 550°C does not help. No remarkable activity recovery is observed after removing the 100 ppm SO₂ from the gas steam, indicating an irreversible deactivation by SO₂ at 400°C under oxidizing atmosphere. It appears that the activity keeps constant at 400°C for at least 40 h after SO₂ poisoned even without sulphur in the stream.

After regeneration at 400°C or 550°C, some of the oxidation activity is recovered for a very short time. The activity decreases rapidly even in the absence of SO₂ in the stream, and is particularly pronounced for methane oxidation (Figure 4). The methane conversion decreases from 60% to 30% in less than one hour. For the same duration, the ethane conversion decreases from 88% to 72%, and only a negligible activity loss is observed for propane oxidation, from 93% to 87% in conversion. This activity loss is a typical symptom of SO₂ deactivation as discussed above and is indicating that sulfur transfers from the support to the Pd particles.

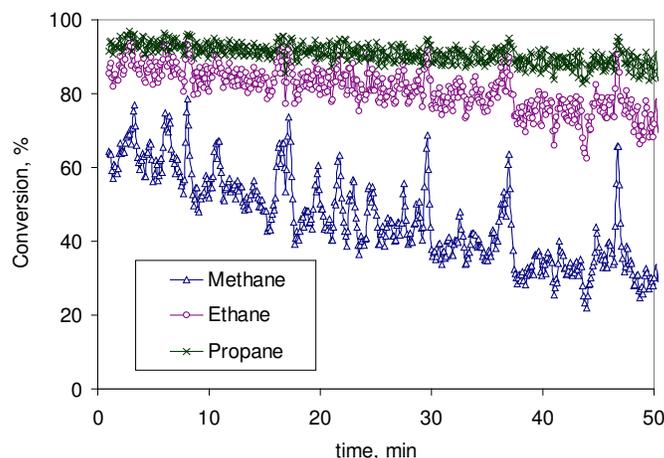


Figure 4. The hydrocarbon conversions decreased rapidly after regenerating at 400°C even though the gas stream contained no SO₂.

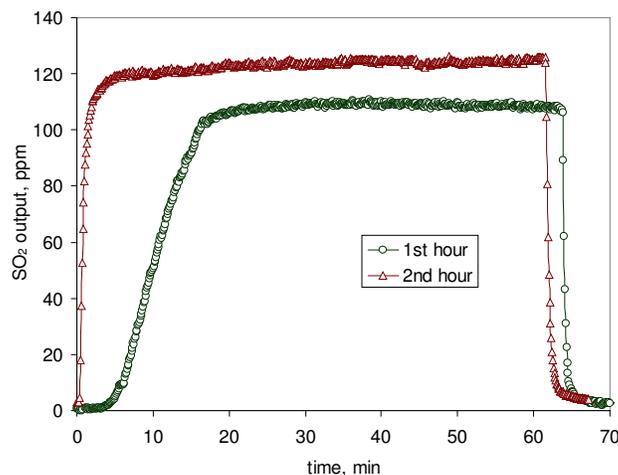


Figure 5. SO₂ adsorption during the first and second hour of poisoning. The catalyst was purged 30 min after the first hour of SO₂ poisoning. SV=100,000 h⁻¹. SO₂ aging conditions: 1st hour 105 ppm SO₂, 2nd hour 120 ppm; 400°C.

The SO₂ adsorption on the Pd catalyst is saturated within 10-30 min, as revealed in Figure 5. From Figure 1, the catalyst deactivation derived from 100 ppm SO₂ poisoning peaks in the first hour. One separate test was conducted to study the SO₂ adsorption during first and

second hour of SO₂ poisoning. The inlet SO₂ concentration during the first hour (105 ppm) is slightly different from the second hour (120 ppm). The catalyst was purged 30 min in the gas stream without SO₂ after the first hour of poisoning until the outlet SO₂ concentration reached zero. The Pd-based catalyst does not catalyze SO₂ oxidation to SO₃, at least after the catalyst is poisoned by SO₂. In the first hour of poisoning, the SO₂ concentration at exit increased from 0 to 105 ppm while the input SO₂ concentration remained constant at 105 ppm or so. It indicates that SO₂ adsorption was saturated during the first hour under the specified conditions. The SO₂ concentration at exit was determined during the second hour of poisoning. The SO₂ output reached 120 ppm in 5 min. The SO₂ accumulation is around zero during the second hour of poisoning. It is demonstrated that the SO₂ adsorption is saturated during the first hour of poisoning at 400 °C.

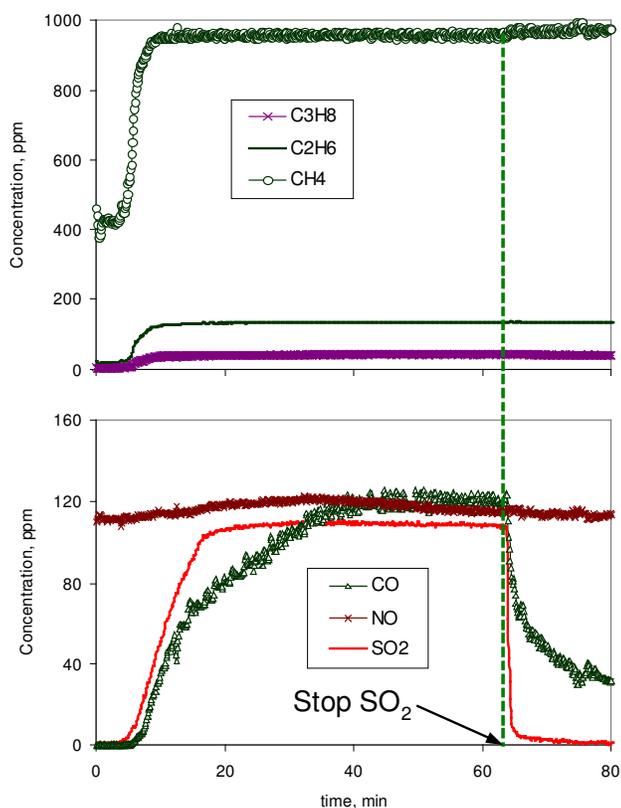


Figure 6. SO₂ adsorption and activity change (outlet concentration) during the first hour of poisoning. SO₂ aging conditions: 110 ppm SO₂, 400 °C.

The SO₂ accumulation in the catalyst is calculated based on the difference of input and output SO₂ concentrations in the gas stream. The molar ratio of accumulated SO₂ and palladium is about 2/1. It should be noted that the SO₂ exposure in this paper was conducted under engine emission conditions in the presence of H₂O, NO_x and 100 ppm SO₂. 100 ppm SO₂ was used in this work to accelerate the poisoning. The SO₂ concentration is not engine emission conditions, but it is a good simulation of long-term exposure to 1 ppm sulfur. The activity of poisoned catalyst is generally higher than the field aged

catalyst based on our experience, due to other contaminants and factors in the engine emissions [11]. After SO₂ poisoning, sulfate formation occurs only on the external surface of PdO_x particles, and the PdO_x particles contains some Pd metal even though the SO₂ exposure takes place in excess oxygen [12]. XPS analysis was conducted on unsupported PdO_x that had been exposed to SO₂ or SO₃ in air at 400 °C or 520 °C [5,12]. It was found that the maximum S/Pd atom ratio is 0.23 over unsupported PdO_x which is much smaller than the ratio of 2 observed here. It suggests that most of the adsorbed sulfur transported from PdO_x particles to the support.

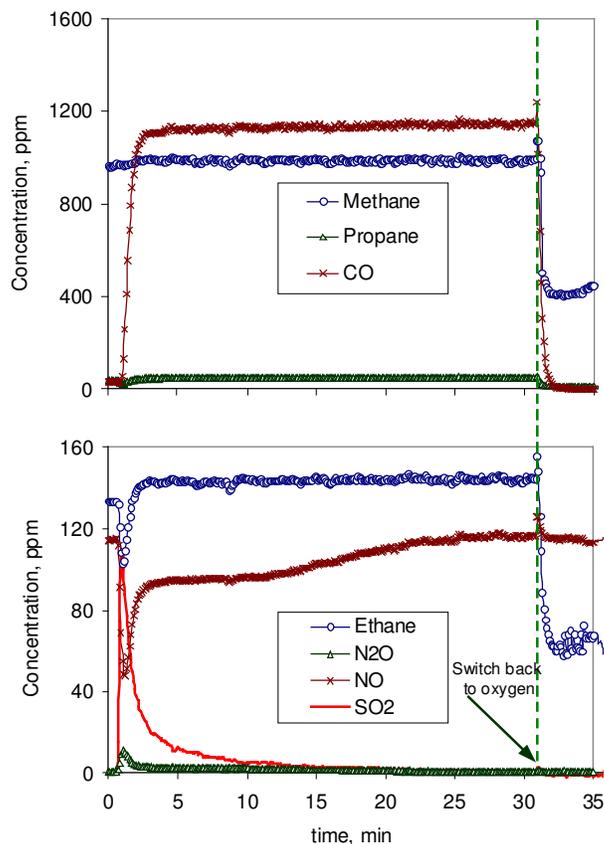


Figure 7. Transient-state study (outlet concentration) during the regeneration of sulphur-aged Pd/Al₂O₃ catalyst. Oxygen was replaced by N₂ with the same flow rate during the regeneration at 400 °C. The gas was switched back to oxidizing atmosphere at 30.5 min as shown in the figure.

The concentrations of the other gas components were monitored during the SO₂ exposure using the gas analyzer, as shown in Figure 6. The concentrations of methane, ethane and propane increased dramatically during the initial 10 minutes of SO₂ exposure, and stabilized quickly in 10 minutes. After stopping SO₂ introduction, hydrocarbon concentrations were little changed. The results show that the hydrocarbon oxidation activity remains constant once sulfur adsorption is saturated, regardless of the SO₂ concentrations afterwards in the gas stream. However, the CO concentration increased from 0 to 120 ppm during the initial 40 min, and decreased to 35 ppm in 20

min after stopping SO₂ introduction. The SO₂ molecules may compete for PdO_x or PdSO₄ sites. It is worthy to compare the SO₂ adsorption and activity of hydrocarbon oxidation. The outlet reactor concentrations of all the three hydrocarbons reached their maximum points during the first 10 min, while SO₂ concentration was only 50 ppm at the same time. It took an extra 10 min for the SO₂ to reach its maximum concentration, 110 ppm. The difference implies that SO₂ molecules adsorb and convert selectively on the PdO_x particles, and spillover to the surrounding Al₂O₃ surface.

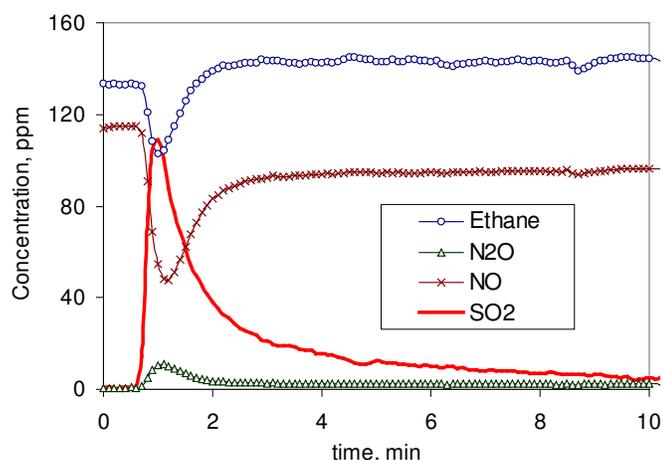


Figure 8. Transient-state study (outlet concentration) during the regeneration of sulphur-aged Pd/Al₂O₃ catalyst. Oxygen was replaced by N₂ with the same flow rate during the regeneration at 400 °C.

The SO₂ release from the catalyst was observed while the gas stream was switched to reducing atmosphere, presented by Figure 7. The transient SO₂ release occurs in the first few minutes of oxygen removal, a zoomed in view of this region is shown in Figure 8. It should be noted that no H₂S release was detected during the regeneration. The SO₂ release during reducing atmosphere is further evidence that the sulfur exists in the form of sulfates on the surface of the catalyst. The release is 15% of the accumulated SO₂ during poisoning. As mentioned above, the maximum S/Pd ratio in PdO_x particles is 0.23. The SO₂ release is equivalent with the S/Pd ratio of 0.3, indicating that only the sulfates on the PdO_x particles and vicinity were reduced at 400 °C in the reducing atmosphere. It is also interesting to notice the changes of other components during the transient state. All of the hydrocarbons and NO exhibit inverse peaks, probably due to the reactions between them. During the transition from oxidizing to reducing atmosphere, there was a stoichiometric point at which NO may react with hydrocarbons. Another evidence for the NO reduction is the release of N₂O during the transition. N₂O is generally recognized as a product of NO reduction.

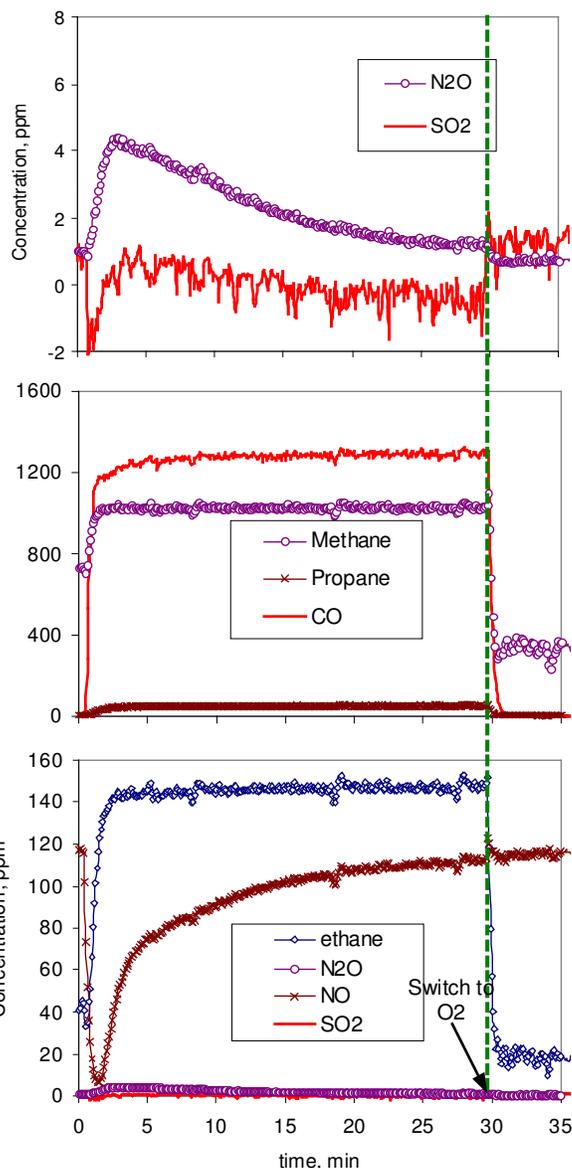


Figure 9. Transient-state study (outlet concentration) during the 2nd time regeneration of sulphur-aged Pd/Al₂O₃ catalyst. Oxygen was replaced by N₂ with the same flow rate during the regeneration at 400 °C.

Figure 9 presents the concentration changes during the second regeneration at 400 °C in the reducing atmosphere. As shown in Figure 4, the catalytic activity deteriorates quickly after regeneration. It is suspected that SO₄²⁻ species transfer from the support to PdO_x particles and lead to a fast deactivation. After one hour of purging in the oxidizing atmosphere, oxygen was replaced again by nitrogen. The concentrations of hydrocarbons, CO and NO_x went through the similar changes to the first regeneration at 400 °C. From the top part of the Figure 9, only a trace of SO₂ was detected at the outlet. It reveals that a small amount of sulfur migrates from the support Al₂O₃ to the sulfur-free PdO_x particles. It is consistent with the previous studies [13]. TPD and activity studies by Gelin et al suggest that, while not being completely removed from the catalyst, sulfate species can migrate back and forth between PdO and

alumina sites, depending on the temperature, therefore preventing the complete regeneration of the catalyst. The activity was almost fully recovered at the beginning, indicating the remarkable impact of traces of sulfates at the surface of the PdO_x particles. However, the regenerated catalyst suffered from a quick deactivation with respect to methane activation, as shown in Figure 4.

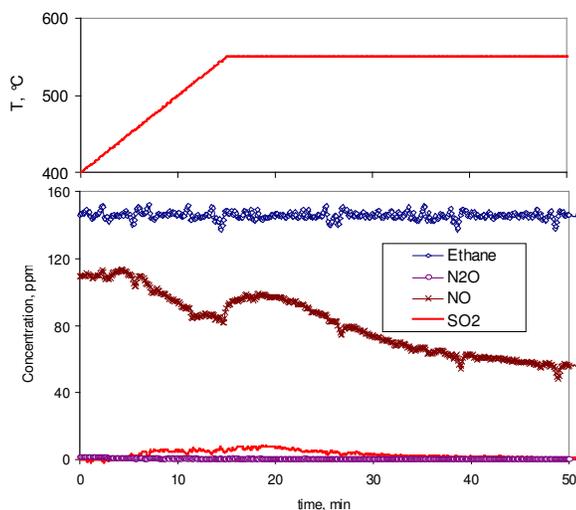


Figure 10. Transient-state study (outlet concentration) during the temperature-programmed regeneration of sulphur-aged Pd/Al₂O₃ catalyst. The catalyst had been regenerated at 400°C for 2 hours prior to temperature increasing. The temperature increased from 400°C to 550°C at ramping rate of 10°C/min.

The regenerating temperature was ramped to 550°C to check if more SO₂ would be released from the catalyst sample (Figure 10). As mentioned above, the SO₂ aged sample had been regenerated 2 h at 400°C. Prior to ramping the temperature, the gas stream was changed to reducing atmosphere and the catalyst purged for 30 min. The temperature increased from 400°C to 550°C at a rate of 10°C/min. The temperature is limited at 550°C because Pd may sinter at higher temperatures and in the reducing atmosphere [14,15]. SO₂ molecules were detected at the outlet with a very broad peak. As mentioned above, sulfates on the PdO_x particles had been reduced at 400°C, or before the temperature increase from 400°C to 550°C. This part of released SO₂ was likely originated from the alumina rather than PdO_x sites. The slow SO₂ release indicated that sulfate species at the alumina sites needed to migrate to PdO_x sites in order to be reduced. The reducing rate is likely limited by the strong resistance of mass transfer from the Al₂O₃ surface to PdO_x particles. The amount of SO₂ release here is about 10% of the total adsorption during SO₂ poisoning. In addition to the SO₂ release of the previous regenerations at 400°C, the total SO₂ release is around 25% of the accumulated sulfur in the catalyst.

Energy Dispersive X-Ray Spectrometry (EDS) reveals the existence of the sulfur after the regenerations in Figure 11. A strong sulfur peak can be observed after regenerations at 400°C, and the sulfur peak is still

present even after regeneration at 550°C. There is no sulfur peak in the EDS spectra of the fresh sample. TPR results showed that regeneration of SO₂ aged Pd/Al₂O₃ started at 350°C and completed at 800°C [7]. The regeneration temperature may not be high enough in our research to remove all the sulfur in the catalyst. The TEM images are shown in the Figure 12. The palladium particles are around 10 nm for fresh and regenerated catalysts. Therefore, PdO_x species did not sinter significantly with the treatments in this work.

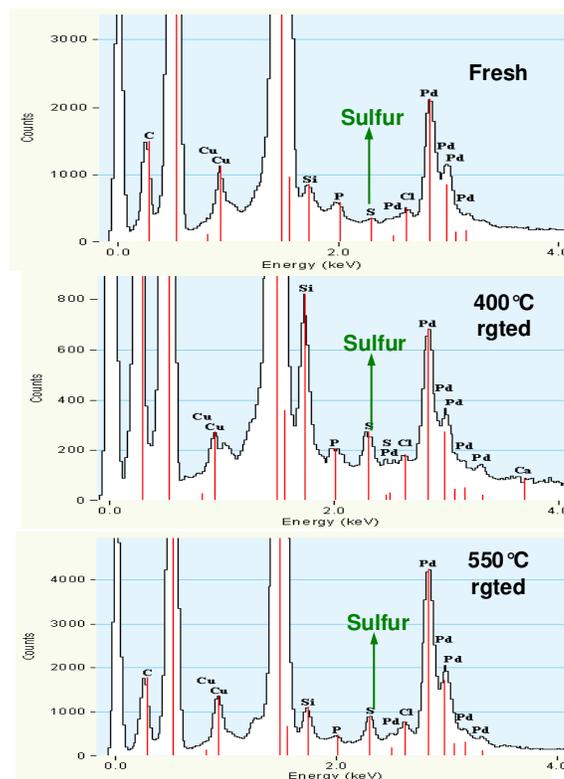


Figure 11. Energy Dispersive X-Ray Spectrometry (EDS) spectra reveals the existence of sulfur even after regeneration.

The mechanisms of poisoning, regeneration and deactivation are illustrated in Figure 13 based on the experimental results. SO₂ oxidation is catalyzed by PdO_x, forming sulfate species selectively on the surface of PdO_x particles. The sulfates are believed to transport to alumina sites. Once the neighboring alumina sites are occupied, the adsorption and conversion of SO₂ is very slow or even stopped. Under simulated engine emission conditions, 400°C and 100,000 h⁻¹, it takes about 20 min to reach saturation in the presence of 100 ppm SO₂. Even removing SO₂ in the stream, the sulfates would not decompose at 400°C. Sulfates may move and re-distribute around the catalyst surface, but the rate depends on temperature and it is likely very slow at 400°C. When the gas stream changes to rich-burn conditions, the sulfates on PdO_x particles (PdSO₄) are immediately reduced to SO₂ that will be released from the catalyst. The sulfate reduction likely happens only on PdO_x sites at reaction temperatures below 550°C [16]. The sulfates at the vicinity migrate onto PdO_x particles and get reduced, but the migration is probably very slow

and depends on the temperature. The PdO_x particles are reduced to Pd metal at 400 °C by CO or hydrocarbons. When the gas stream becomes lean, Pd is oxidized to PdO_x , and traces of sulfates move onto clean PdO_x particles. Hydrocarbon oxidation is very sensitive to sulfates, particularly for methane, probably due to the modification of electronic properties by sulfate groups. Even after reduction at 550 °C, significant amount of sulfates still exist in the catalyst.

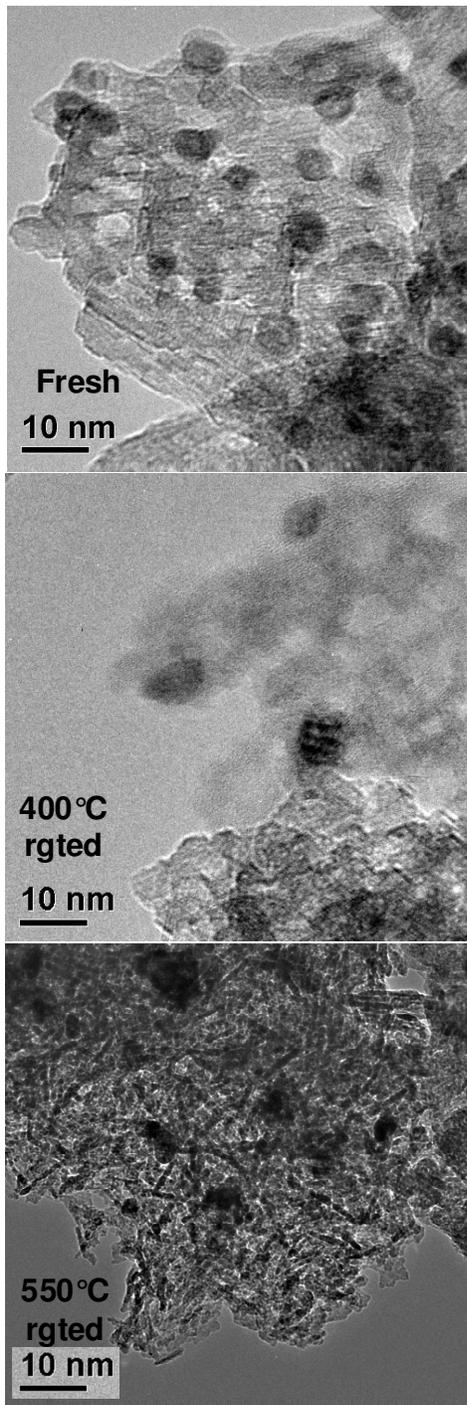


Figure 12. TEM images of catalyst when fresh and regenerated at different temperatures.

The oxidation state of palladium and its effect on oxidation reactions has been extensively studied, and reviewed [17]. It is generally accepted that PdO is the

active site for hydrocarbon oxidation, and metallic Pd is much less active. In oxidizing atmosphere, PdO is stable up to 600-650 °C based on temperature programmed study [18] and thermodynamic calculations [17]. PdO decomposes to less active Pd at temperatures more than 850 °C. After being exposed to high temperatures a re-oxidation takes place when the catalyst is cooled to 650 °C, causing re-dispersion of PdO on alumina as well as the formation of PdO_x/Pd particles [18]. Temperature programmed oxidation shows that oxidation of Pd⁰ (supported on Al_2O_3) occurs between 300-450 °C [19]. After rich regeneration, at least a part of Pd⁰ converts to PdO at 400-550 °C in the presence of 10% O_2 and NO_2 .

There are some publications on the mechanism for the deactivation of PdO catalysts by sulfur-containing compounds [12]. For the SO_2 poisoning, we agree to the suggestions by Lampert et al and Gelin et al [5, 13].

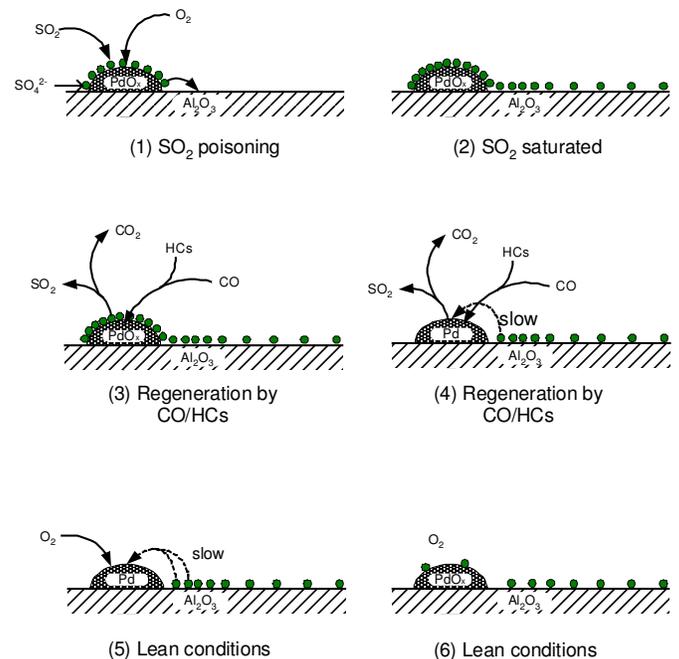


Figure 13. Scheme of SO_2 poisoning, regeneration, and sulfate re-distribution mechanism for Pd/ Al_2O_3 catalyst.

Regeneration of S-poisoned palladium catalysts with reducing atmosphere was studied in the literature [3,6-8, 15]. Lampert et al proposed an operating strategy of NGV engines based on alternative long periods (14 min) of lean conditions followed by short periods (0.5 min) of rich combustion conditions [3]. The temperature is at about 650 °C in order to achieve a partial regeneration. Arosio et al found that the SO_2 -aged Pd/ Al_2O_3 could not be regenerated by CH_4 at temperatures up to 500 °C [7]. Based on this work, the sulfates on PdO_x particles can be reduced at 400 °C by CO and hydrocarbons, which are typical components under rich combustion conditions of NG engines. Unfortunately the advantage of the sulphur-free PdOx is short lived due to migration of sulphur from the alumina support on to the PdOx particle.

CONCLUSIONS

Sulfur poisoning and regeneration of Pd/Al₂O₃ were performed under simulated lean and rich conditions. The SO₂ adsorption gets saturated quickly (30 min) in the presence of 100 ppm SO₂, and the oxidation activity deactivates and stabilizes even faster. The support Al₂O₃ accommodates more than 80% adsorbed sulfur.

Under rich conditions, sulfates on PdO_x particles [PdSO₄] are quickly reduced and released from the catalyst as SO₂. Sulfates on alumina [Al₂(SO₄)₃] cannot be removed in a reasonable time at temperatures below 550°C. Under lean conditions, the sulfates on alumina migrate to PdO_x particles and cause rapid deactivation even without sulfur in the gas stream.

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REFERENCES

[1] A.M. Samsam Bakhtiari, "The price of natural gas", OPEC Review 25 (4) (2001) 357–368.

[2] Patrick Gelin, Michel Primet, "Complete oxidation of methane at low temperature over noble metal based catalysts: a review", Applied Catalysis B: Environmental 39 (2002) 1–37

[3] J.K. Lambert, M.S. Kazi, R.J. Farrauto, "Methane Emission Abatement from Lean Burn Natural Gas Vehicle Exhaust: Sulfur's Impact on Catalyst Performance", SAE Paper No. 961971.

[4] Robert L. McCormick, Anthony W. Newlin, Deborah Mowery, Michael S. Graboski, and T. R. Ohno, "Rapid Deactivation of Lean-Burn Natural Gas Engine Exhaust Oxidation Catalysts", SAE Paper No. 961976.

[5] Jordan K. Lampert, M. Shahjahan Kazi, Robert J. Farrauto, "Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles", Applied Catalysis B: Environmental 14 (1997) 211-223.

[6] Luis Javier Hoyos, Helene Praliaud and Michel Primet, "Catalytic combustion of methane over palladium supported on alumina and silica in presence of hydrogen sulfide", Applied Catalysis A: General, 98 (1993) 125-138.

[7] F. Arosio, S. Colussi, G. Groppi, A. Trovarelli, "Regeneration of S-poisoned Pd/Al₂O₃ catalysts for the combustion of methane", Catalysis Today 117 (2006) 569–576

[8] Thierry Leprince, Joe Aleixo, Shazam Williams, Mojghan Naseri, "Regeneration of palladium based

catalyst for methane abatement", CIMAC Congress 2004, Paper No. 210.

[9] Shazam Williams, Mojghan Naseri, Joe Aleixo, Kristoffer Sandelin, "Field experience and laboratory analysis of oxidation catalyst on dual fuel engines", ASME Conference, Paper No. ICES2006-1362.

[10] Deborah L. Mowery, Michael S. Graboski, Tim R. Ohno, Robert L. McCormick, "Deactivation of PdO–Al₂O₃ oxidation catalyst in lean-burn natural gas engine exhaust: aged catalyst characterization and studies of poisoning by H₂O and SO₂", Applied Catalysis B: Environmental 21 (1999) 157–169.

[11] Ronald M. Heck, Robert J. Farrauto, Suresh T. Gulati, Catalytic Air Pollution Control, 2nd Edition, New York, John Wiley & Sons, 2002.

[12] Deborah L. Mowery, Robert L. McCormick, "Deactivation of alumina supported and unsupported PdO methane oxidation catalyst: the effect of water on sulfate poisoning", Applied Catalysis B: Environmental 34 (2001) 287–297.

[13] Patrick Gelin, Laetitia Urfels, Michel Primet, Emmanuel Tena, "Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn natural gas fuelled vehicles emissions: influence of water and sulphur containing compounds", Catalysis Today 83 (2003) 45–57.

[14] Weiqing Zou and Richard D. Gonzalez, "Thermal stability of silica supported palladium catalysts prepared by the sol-gel method", Applied Catalysis A: General, 126 (1995) 351-364.

[15] J.M. Jones, A. Dupont, R. Brydson, D.J. Fullerton, N.S. Nasri, A.B. Ross, A.V.K. Westwood, "Sulphur poisoning and regeneration of precious metal catalysed methane combustion", Catalysis Today, 81 (2003) 589-601.

[16] Y. Pelovski, V. Petkova, "Mechanism and kinetics of inorganic sulphates decomposition", Journal of Thermal Analysis, 49 (1997)1227-1241.

[17] Ahmad Kalantar Neyestanaki, Fredrik Klingstedt, Tapio Salmi, Dmitry Yu. Murzin, "Deactivation of postcombustion catalysts, a review", Fuel, 83 (2004) 395–408.

[18] R.J. Farrauto, M.C. Hobson, T. Kennelly and E.M. Waterman, "Catalytic chemistry of supported palladium for combustion of methane", Applied Catalysis A: General, 81(1992) 227-237.

[19] G. Lapisardi, L. Urfels, P. Gelin, M. Primet, A. Kaddouri, E. Garbowski, S. Toppi, E. Tena, "Superior catalytic behaviour of Pt-doped Pd catalysts in the complete oxidation of methane at low temperature", Catalysis Today, 117 (2006) 564–568.