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Fundamentals of Sulfate Species in Methane Combustion Catalyst Operation and Regeneration—A Simulated Exhaust Gas Study

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Abstract: Emission regulations and legislation inside the European Union (EU) have a target to reduce tailpipe emissions in the transportation sector. Exhaust gas aftertreatment systems play a key role in low emission vehicles, particularly when natural gas or bio-methane is used as the fuel. The main question for methane operating vehicles is the durability of the palladium-rich aftertreatment system. To improve the durability of the catalysts, a regeneration method involving an efficient removal of sulfur species needs to be developed and implemented on the vehicle. This paper tackles the topic and its issues from a fundamental point of view. This study showed that $Al_2(SO_4)_3$ over Al_2O_3 support material inhibits re-oxidation of Pd to PdO, and thus hinders the formation of the low-temperature active phase, PdO_x. The presence of $Al_2(SO_4)_3$ increases light-off temperature, which may be due to a blocking of active sites. Overall, this study showed that research should also focus on support material development, not only active phase inspection. An active catalyst can always be developed, but the catalyst should have the ability to be regenerated.

Keywords: catalytic methane combustion; exhaust gas; catalyst durability; Liquefied natural gas; biogas; vehicle emission control

1. Introduction

Current and future emission regulations and legislation of fossil fuels inside the European Union aspire to decrease the tailpipe emissions of transportation. The exhaust gas aftertreatment system plays a key role in low emission vehicles, and one of the main issues is its durability. Exhaust gas aftertreatment systems of heavy-duty applications in Europe already have a durability requirement, that is, 700,000 km, or seven years maximum [1].

Natural gas and bio-methane will be the next generation alternative fuels in the transportation sector, generating low overall emissions. The fuels can be stored in liquid form, thus increasing their energy capacity, which generates interest in the sector. In addition, the gases emit less CO_2 per energy equivalent compared to regular diesel fuel, which decreases their carbon footprint. However, a small amount of un-burnt methane, the main constituent of natural and bio-gas, always slips from an engine to its exhaust gas. Due to the higher global warming potential of methane, compared to CO_2, its emissions must be converted with a catalyst.

The catalyst, at a reasonably low operation temperature, in an aftertreatment system of natural gas or bio-methane application, is palladium rich, and supported on Al_2O_3, if high methane conversion activity is needed [2–6]. However, palladium-rich lean-burn methane combustion catalysts are known to be sensitive to sulfur poisoning. Sulfur originates from lubricant oil and natural gas, and it oxidizes further during the burning process to SO_2, and on a catalyst, it further reacts with oxygen from SO_2 to SO_3. It accumulates in the presence of water vapor over a catalyst as $PdSO_4$ and $Al_2(SO_4)_3$ [7–9]. Attempts have been made to solve the disadvantage of sulfur poisoning on methane conversion activity by modifying washcoat materials [2,10–12], and by varying noble metal content and their combinations [13–15]. Fundamental studies of poisoned and aged methane oxidation catalysts have been conducted to understand the formation of the inactive form of the catalyst. In general, the formation of $PdSO_4$ has been concluded to be the reason for the deactivation of the catalyst [8,16–18]. Aluminum oxide has been known to be the best support for the palladium-rich methane combustion catalyst, because it hinders any poisoning of the catalyst by forming $Al_2(SO_4)_3$ [2,16,19]. The latest results show that in fact, $PdSO_4$ itself is not a poison, but it sensitizes the catalyst for water inhibition [20].

Deactivation of the exhaust gas aftertreatment system is still a challenge, and thus solutions are needed to meet the future durability requirements [21–23]. A possible solution to increase the life-time of the exhaust gas aftertreatment system could be a regeneration of the catalyst. However, the number of studies conducted in the field of regeneration so far is low, which has also been noted in a recent review article [24]. Based on the published research, sulfur removal in the presence of excess oxygen requires high temperature, at least 650 °C, and it has been concluded to be always incomplete [3,25]. The regeneration of the sulfur-poisoned catalyst by heating under vacuum [17] or treating with hydrogen gas, occurs at a remarkably lower temperature [26]. A small improvement in methane conversion activity has been achieved already after regeneration under hydrogen at 350 °C [25]. However, a better response to methane conversion activity has been achieved when the poisoned catalyst has been treated at 600 °C under the same gas atmosphere [27]. An alternative reductive method to regenerate a sulfur-poisoned catalyst, besides thermal or hydrogen treatments, has been presented by Arosio et al. [28]. They successfully used reductive methane pulses to partially regenerate the catalyst at 550 °C; such temperature could also be achieved in a real engine, but complete regeneration was achieved at 600 °C, which requires additional thermal energy, and may cause a fuel penalty. A reason for partial regeneration of the sulfur-poisoned catalyst has been proposed in a recent study [29], where $PdSO_4$ has been observed to decompose under a reductive atmosphere to Pd_4S. Hence, small quantities of sulfur will always remain in the regenerated catalyst. They concluded also that alternately reductive (rich) and oxidative (lean) pulses result in better sulfur removal in a regenerated catalyst compared to rich-only conditions.

This study focuses on the decomposition of sulfur-poisoned methane combustion catalyst with model catalysts. This paper answers the following research questions: How does the presence of $Al_2(SO_4)_3$ affect decomposition of $PdSO_4$? What is the state of palladium after the regeneration?

2. Results and Discussion

2.1. Methane Conversion Activity and Regeneration of Model Catalysts under Simulated Exhaust Gas

The activities of the model catalysts were evaluated in powder form with simulated exhaust gas in methane combustion. The effect of $Al_2(SO_4)_3$ (AS) on the performance of $PdSO_4$ (PS) in complete methane oxidation is presented in Figure 1, together with the sulfur-poisoned modern methane combustion catalyst as a reference [20]. The activity of the commercial reference catalyst is between the activities of the PS/Al_2O_3 and 0.25 AS+PS/Al_2O_3 catalysts. The similarity of CH_4 conversion curves of the commercial reference catalyst and model catalysts justifies the use of the model catalyst in further fundamental studies, when regeneration and texture of the catalysts will be examined. The shape analysis of the curves revealed that the methane oxidation reaction was temperature-controlled for the PS/Al_2O_3 model catalyst.

An addition of $Al_2(SO_4)_3$ into the catalyst led to a loss of active sites [30]. Hence, the temperature that is required to initiate methane conversion increased if $Al_2(SO_4)_3$ was added into the model catalyst.
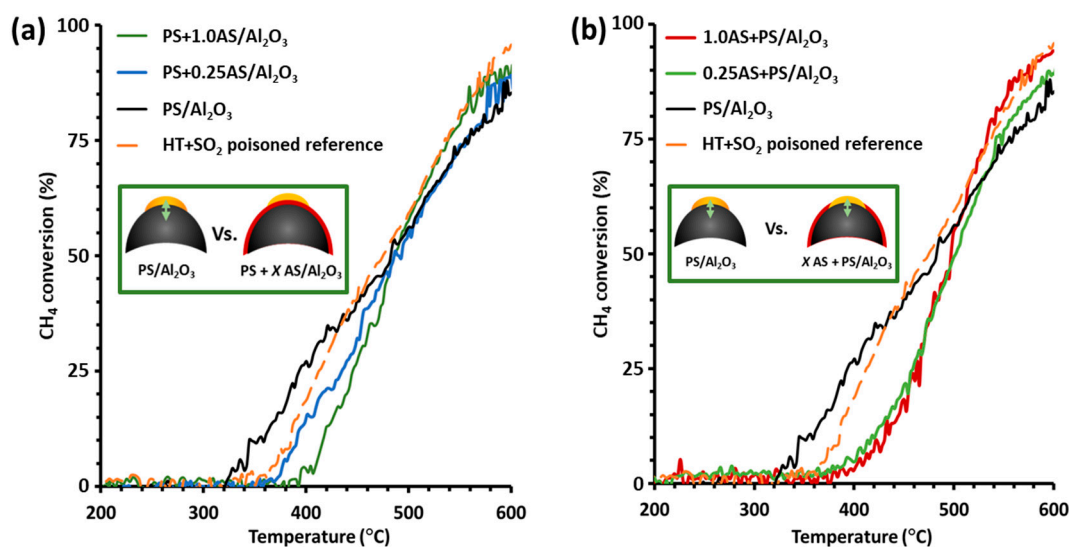
**Figure 1.** Methane conversion curves of (**a**) PS/Al_2O_3, PS + X AS/Al_2O_3, and (**b**) X AS + PS/Al_2O_3 (X = 0.25 or 1.0) model catalysts together with sulfur-poisoned commercial reference [20] before regeneration under simulated exhaust gas (indicated with an orange dashed line in the figures). See Scheme 1 for details about the catalysts.

It was decided to perform regeneration at 500 °C due to the threshold temperature observed by several researchers [25,29]. Simulated exhaust gas contains reducing agents such as CH_4, CO and NO, which can be expected to decrease the decomposition temperature of the sulfur species. The best regeneration was observed in the case of the PS/Al_2O_3 model catalyst, for which the methane conversion at 500 °C doubled to 60%, due to the regeneration (Figure 2). The co-existence of $PdSO_4$ and $Al_2(SO_4)_3$ was observed to have a disadvantageous effect on regeneration of the sulfated methane oxidation catalyst. After regeneration the catalysts PS + 1.0 AS/Al_2O_3 and 1.0 AS + PS/Al_2O_3 show higher methane conversion activities than the catalysts PS + 0.25 AS/Al_2O_3 and 0.25 AS + PS/Al_2O_3. A reason relies on the higher sulfur content of the samples, resulting in the catalysts bulk-kind-of-sulfates, which decomposes in regeneration at lower temperature [31]. In fact, the PS + 0.25 AS/Al_2O_3 model catalyst even showed a slight decrease in activity even though sulfur species were decomposed at least partially during the regeneration. The decrease in activity after regeneration may indicate that $PdSO_4$ does not decompose during the process, or the active phase does not form after the regeneration. However, SO_2 release can be detected in all the cases, and thus decomposition of inactive $PdSO_4$ to metallic Pd and Pd_4S can be noted to have occurred. Thus, a potential reason for the decrease in activity could be the lack of active phase re-formation (PdO_x) of the low-temperature methane combustion catalyst. Overall, the simulated exhaust gas regeneration results allow us to deduce the following hypothesis: "*After regeneration, $Al_2(SO_4)_3$ inhibits Pd re-oxidation to PdO, which leads to an activity decrease in low temperature methane oxidation, when lean operation conditions are returned.*"

2.2. Palladium State after Regeneration under Simulated Exhaust Gas

As shown in Figure 2, the presence of $Al_2(SO_4)_3$ in the model catalysts decreased methane conversion activity after regeneration under realistic operation conditions. Inspection of the crystalline palladium state after the regeneration treatment, was carried out by powder X-ray diffraction in order to support the hypothesis. The powder X-ray diffraction method may be used in this case, because regeneration affects the surface of less active $PdSO_4$. Thus, the regenerated active Pd/PdO may form on top of less active $PdSO_4$.

The powder X-ray diffractograms of the catalyst in Figure 3 show that the peak of crystalline metallic Pd is pronounced if the catalyst contained $Al_2(SO_4)_3$. Closer inspection of the peak data, shown in Table 1, reveals that the presence of $Al_2(SO_4)_3$ results in a high amount of metallic Pd. The results support the conclusions that $PdSO_4$ decomposed during the regeneration process, and the lower activity after regeneration could be due to less active metallic Pd phase formation. Thus, we rely on the fact that $Al_2(SO_4)_3$ may hinder the re-oxidization of metallic Pd after regeneration, thus inhibiting the formation of active PdO_x.
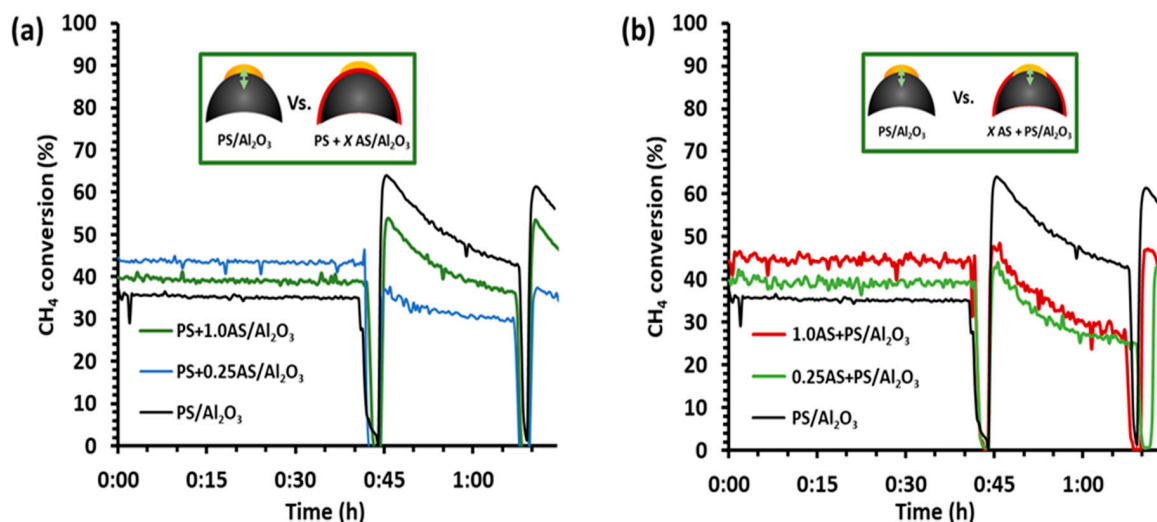
Figure 2. Methane conversion during steady-state operation and regeneration at 500 °C under simulated exhaust gas for (**a**) PS/Al_2O_3, PS + X AS/Al_2O_3 and (**b**) X AS + PS/Al_2O_3 (X = 0.25 or 1.0) model catalysts. See Scheme 1 for details about the catalysts.
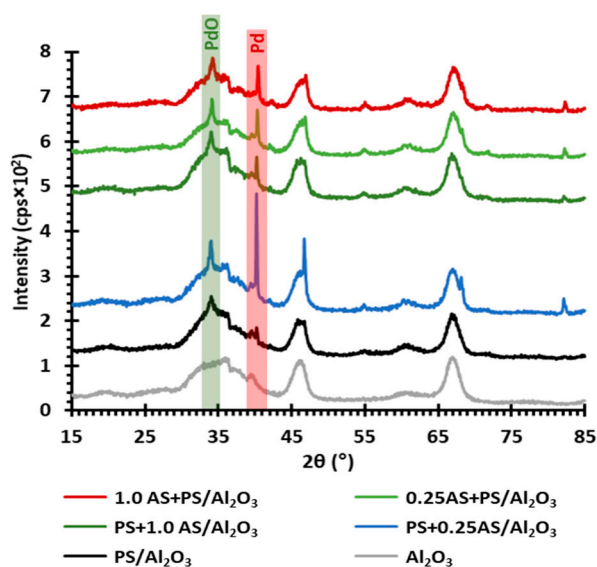
Figure 3. Powder X-ray diffraction patterns of PS/Al_2O_3, PS + X AS/Al_2O_3 (X = 0.25 or 1.0) and X AS + PS/Al_2O_3 (X = 0.25 or 1.0) model catalysts after regeneration at 500 °C under simulated exhaust gas. See Scheme 1 for details about the catalysts.

Table 1. Pd and PdO peak areas and crystallite sizes of model catalysts after regeneration under simulated exhaust gas.

Catalyst [1]	PdO(101) Peak Area [2]	PdO(101) Crystallite Size (nm) [2]	Pd(111) Peak Area [2]	Pd(111) Crystallite Size (nm) [2]	PdO(101):Pd(111) [3]
PS/Al$_2$O$_3$	55.3	4.7	17.3	13.1	3.20
PS + 0.25 AS/Al$_2$O$_3$	41.0	15.6	52.1	111.0	0.79
PS + 1.0 AS/Al$_2$O$_3$	51.5	11.2	20.0	50.9	2.58
0.25 AS + PS/Al$_2$O$_3$	27.0	23.6	24.7	60.8	1.09
1.0 AS + PS/Al$_2$O$_3$	31.1	13.9	20.6	56.8	1.51

[1] See Scheme 1 for details about the catalysts. [2] Peak areas and crystallite size were measured for the catalysts after regeneration under simulated exhaust gas. [3] PdO(101):Pd(111) ratio was calculated based on corresponding peak areas of X-ray diffraction patterns. Alumina signals were used as internal references.

The observation can be further supported and confirmed with TPO re-oxidation measurements. Re-oxidation of metallic Pd to active PdO can be observed as a downward peak in Figure 4 in a temperature range of between 470 °C and 700 °C. The presence of Pd$_4$S should bear in mind as detected in the latest experiments if the catalyst is heated under hydrogen gas [29,31]. Because steam reforming and water gas shift reactions form hydrogen during regeneration in simulated exhaust gas, Pd$_4$S structure is possible to form during the regeneration period. The most feasible re-oxidation product of Pd$_4$S may be PdSO$_4$, PdO and metallic Pd. Due to the stoichiometry of Pd$_4$S structure, in respect of Pd atoms, re-oxidation may form one PdSO$_4$, and three Pd units may form PdO or remain in the metallic Pd state. Quantitative oxygen uptake was determined by integrating the peaks and the values represented in Table 2. Individual PdSO$_4$ supported on Al$_2$O$_3$ (PS/Al$_2$O$_3$) had the highest oxygen uptake, being 19.2 µmol g$_{cat}^{-1}$, corresponding to an O:Pd mole ratio of 0.43. This means that regenerated metallic Pd oxidizes only partially into an active PdO form. Oxygen uptakes of model catalysts including Al$_2$(SO$_4$)$_3$ were lower than that of PS/Al$_2$O$_3$, between 9.0 and 15.7 µmol g$_{cat}^{-1}$, corresponding to O:Pd mole ratios of 0.22–0.36, revealing the fact that Al$_2$(SO$_4$)$_3$ hinders oxidation of metallic Pd back to an active PdO form. The addition of Al$_2$(SO$_4$)$_3$ increases the re-oxidation temperature of metallic Pd, and thus the formation of Al$_2$(SO$_4$)$_3$ might be undesirable in the CH$_4$ catalyst, even though conclusions in literature have been contradictory [2,6]. The results confirm the above hypothesis that Al$_2$(SO$_4$)$_3$ hinders the re-oxidation of metallic Pd to active PdO. Inhibition of the re-oxidation was the strongest for the PS + 0.25 AS/Al$_2$O$_3$ model catalyst, which explained the observed decrease in activity after the regeneration.
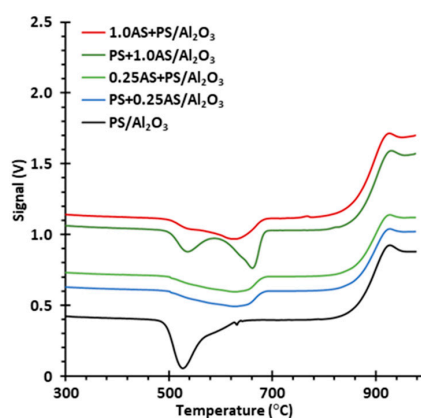

Figure 4. Re-oxidation of metallic Pd to an active PdO form after thermal decomposition. Re-oxidation was studied by decreasing the temperature after thermal decomposition of model catalysts under a gas blend of 10% O$_2$ in He. See Scheme 1 for details about the catalysts.

Table 2. Quantitative O_2 uptake of the catalysts during cooling down.

Catalyst [1]	Oxygen Uptake (μmol g_{cat}^{-1})	O:Pd Mole Ratio	Regenerated CH_4 Conversion (%) [2]
PS/Al$_2$O$_3$	19.2	0.43	63.7
PS + 0.25 AS/Al$_2$O$_3$	11.1	0.25	37.6
PS + 1.0 AS/Al$_2$O$_3$	15.7	0.36	53.4
0.25 AS + PS/Al$_2$O$_3$	9.0	0.22	42.7
1.0 AS + PS/Al$_2$O$_3$	11.4	0.22	47.0

[1] See Scheme 1 for details about the catalysts. [2] CH_4 conversion is the maximum that has been achieved after the regeneration procedure (Figure 2).

To summarize the results, the relation between regenerated CH_4 conversion is illustrated in Figure 5, together with three indicators: O:Pd mole ratio (Table 2), oxygen uptake of the catalyst (Table 2) and PdO(101):Pd(111) ratio (Table 1). The trends of all three indicators show that addition of Al$_2$(SO$_4$)$_3$ into the PdSO$_4$-containing catalyst hinders the formation of the active phase, such as PdO after regeneration, and thus activity in CH_4 conversion decreases, compared to the case of the individual PdSO$_4$ model catalyst. Thus we conclude that the formation of Al$_2$(SO$_4$)$_3$ is not beneficial for the low temperature methane combustion catalyst, because it causes a decrease in the methane conversion activity of the catalyst after regeneration. Unforeseen correlation of methane combustion activity of the model catalysts, together with the PdO(101):Pd(111) ratio could be explained, at least partially, by the formation of a regenerated, active Pd/PdO structure on top of less active PdSO$_4$. Regeneration studies were done at 500 °C, which may be low to re-oxidize regenerated metallic Pd to PdO$_x$. However, higher regeneration temperature may enhance re-oxidation, but it exposes the catalyst to sintering, and thus may decrease its methane conversion activity.
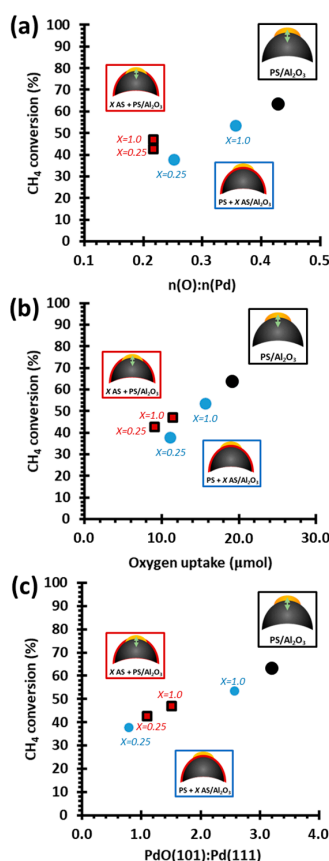
Figure 5. Regenerated CH_4 conversion under simulated exhaust gas as a function of (**a**) O:Pd mole ratio, (**b**) oxygen uptake of the catalyst and (**c**) PdO(101):Pd(111) ratio. See Scheme 1 for details about the catalysts.

3. Materials and Methods

3.1. Catalysts

The modern commercially available methane combustion catalyst contains 0.97 wt.% of sulfur after sulfur poisoning treatment [20]. A modern sulfur-poisoned methane combustion catalyst was used as a reference in activity experiments for model catalysts to justify their similar performance and behavior after sulfur poisoning treatment. The catalyst was provided by the Dinex Finland Oy. To model and mimic the catalyst composition, a series of catalysts were prepared (Table 3 and Scheme 1) by using $PdSO_4$ (Sigma Aldrich, Saint Louis, MO, USA, CAS: 13566-03-5), $Al_2(SO_4)_3 \times 18H_2O$ (Merck, Darmstad, Germany, CAS: 7784-31-8), and Al_2O_3 (Sasol) as starting materials. Bulk $PdSO_4$ and $Al_2(SO_4)_3$ compounds were used in model catalyst preparation to quantitatively control the amount of sulfur and structure of sulfate. If the sulfating were done in the gas phase with SO_2 gas, the formed sulfates species and amounts could be hard to control. Impregnation of $PdSO_4$ and $Al_2(SO_4)_3$ was carried out in cold water by mixing at least for 2 h. After impregnation, the solid was dried at room temperature, and to finalize the catalyst it was heated at 90 °C under air. Detailed preparation procedures are described in our previous work [31]. Amounts of added $PdSO_4$ correspond to 1 wt.% of sulfur and 4 wt.% of palladium loading, whereas X indicates the amount of sulfur in $Al_2(SO_4)_3$-containing catalysts, and it is 0.25 or 1.0 wt.% of sulfur. Sulfates are abbreviated as follows to clarify the names of the catalysts: PS refers to $PdSO_4$, and AS refers to $Al_2(SO_4)_3$.

Table 3. Model catalyst compositions.

Catalyst	Total Sulfur Content of the Catalyst (wt.%)
PS/Al_2O_3 [1]	0.88
PS + 0.25 AS/Al_2O_3 [1,2]	1.39
PS + 1.0 AS/Al_2O_3 [1,2]	2.10
0.25 AS + PS/Al_2O_3 [1,2]	1.03
1.0 AS + PS/Al_2O_3 [1,2]	1.71

[1] Amount of PS ($PdSO_4$) corresponds to 4 wt.% active metal loading of Pd and 1.0 wt.% loading of sulfur. [2] Amount of AS ($Al_2(SO_4)_3$) corresponds to 0.25 or 1.0 wt.% loadings of sulfur.
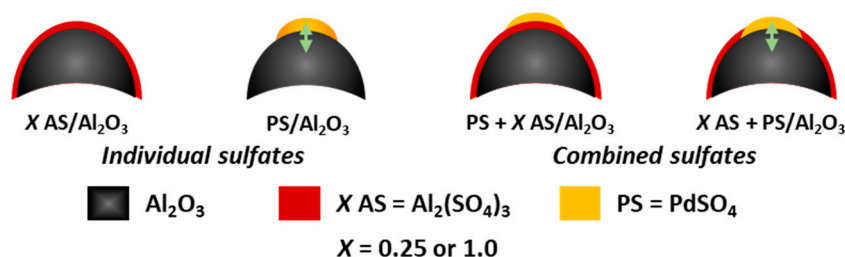
Scheme 1. Illustration of model catalyst ideas and composition [31].

3.2. Characterization Techniques

Methane conversion activities were measured for five $PdSO_4$-containing model catalysts. Regeneration experiments were carried out under steady-state conditions with a laboratory reactor at 500 °C in the presence of simulated exhaust gas. Gasmet™ DX-4000 Multigas FTIR (Gasmet technologies, Helsinki, Finland) was used as a detector in both light-off and regeneration experiments. An amount of 0.2 g model catalyst powder was used in the experiments. The exhaust gas composition used in the experiments was 2000 ppm of CO, 2000 ppm of CH_4, 500 ppm of C_3H_8, 500 ppm of NO, 10 ppm of SO_2, 6% of CO_2, 10% of O_2 and a balancing amount of N_2. The total gas flow rate of 1180 cm^3 min^{-1} corresponded to a space velocity of 354,000 cm^3 $gcat^{-1}$ h^{-1} through the model catalyst powder. Regenerations were carried out by replacing oxygen from the exhaust gas with N_2 in order to maintain a constant gas flow rate. Otherwise, the composition of the gas mixture remained the same.

Powder X-ray diffractograms of catalyst samples were recorded with a Bruker-AXD D8 Advance diffractometer (Bruker, Karlsruhe, Germany) using Cu Kα radiation. The diffraction pattern at a range of 2θ from 15° to 85° was recorded with a scanning speed of 0.11° min^{-1}, and a step size of 0.04°. Bragg–Brentano geometry was utilized in the experiments. TOPAS software was utilized in estimating palladium and palladium oxide crystallite sizes of the model catalysts and peak areas [32].

Re-oxidation model catalysts were studied with a Quantachrome Autosorb iQ device using a temperature programmed oxidation (TPO) hysteresis technique. A sample of 100 mg was heated from room temperature to 1000 °C with a heating rate of 10 °C min^{-1} under continuous flow of 10% O_2/He gas. The gas flow rate was 20 mL min^{-1}. To obtain re-oxidation, the sample was cooled down to 250 °C under the same gas atmosphere. No pretreatment was done prior to the measurement and cold trap was used in the measurement.

Elemental analyses were carried out with an Elementar varioMICRO cube device (Elementar, Langenselbold, Germany). Sulfanilamide was used both for calibrating the device, and also as a reference compound for sulfur in the measurements. The mass of the samples varied between 10 mg and 30 mg.

4. Conclusions

The role of $Al_2(SO_4)_3$ on the regeneration of the low-temperature methane combustion catalyst was studied in the presence of simulated exhaust gas. This study showed that the presence of $Al_2(SO_4)_3$ over Al_2O_3 support material inhibits the re-oxidation of metallic Pd back to its active form of PdO_x. Hence, the low temperature activity of the regenerated catalyst decreases, and does not necessarily increase after regeneration. The outcome was supported with powder X-ray measurements and finally confirmed with the TPO re-oxidation method. These aspects should be taken into account when developing a regeneration method for an aftertreatment system of natural gas or bio-methane fueled engines. From the catalyst development point of view, this study shows that we should also focus on support materials, not only on the active phase, because a good catalyst can always be developed, but the catalyst should have the ability to be regenerated.

Conflicts of Interest: The authors declare no conflict of interest.

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