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Decomposition of Al_2O_3 -Supported PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$ in the Regeneration of Methane Combustion Catalyst: A Model Catalyst Study

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Abstract: Exhaust gas aftertreatment systems play a key role in controlling transportation greenhouse gas emissions. Modern aftertreatment systems, often based on Pd metal supported on aluminum oxide, provide high catalytic activity but are vulnerable to sulfur poisoning due to formation of inactive sulfate species. This paper focuses on regeneration of Pd-based catalyst via the decomposition of alumina-supported aluminum and palladium sulfates existing both individually and in combination. Decomposition experiments were carried out under hydrogen (10% H_2/Ar), helium (He), low oxygen (0.1% O_2/He), and excess oxygen (10% O_2/He). The structure and composition of the model catalysts were examined before and after the decomposition reactions via powder X-ray diffraction and elemental sulfur analysis. The study revealed that individual alumina-supported aluminum sulfate decomposed at a higher temperature compared to individual alumina-supported palladium sulfate. The simultaneous presence of aluminum and palladium sulfates on the alumina support decreased their decomposition temperatures and led to a higher amount of metallic palladium than in the corresponding case of individual supported palladium sulfate. From a fundamental point of view, the lowest decomposition temperature was achieved in the presence of hydrogen gas, which is the optimal decomposition atmosphere among the studied conditions. In summary, aluminum sulfate has a two-fold role in the regeneration of a catalyst—it decreases the Pd sulfate decomposition temperature and hinders re-oxidation of less-active metallic palladium to active palladium oxide.

Keywords: sulfur deactivation; catalyst deactivation; aluminum sulfate; palladium sulfate; regeneration

1. Introduction

Exhaust gas aftertreatment systems (ATSs) have been used since the 1950s to remove at least a portion of the exhaust gases emitted from internal combustion engines of vehicles [1]. Nowadays, tight emission limits and durability requirements guide vehicle developers to implement regeneration procedures into the vehicle operation.

Exhaust gas ATS catalysts consist of a support material, active metal(s), and promoter(s). Alumina as a support material for exhaust gas ATS catalysts has been known to be the best alternative owing to its good thermal stability and high surface area [2,3]. Meanwhile, palladium is currently used as an active metal or as a promoter in almost all catalysts in vehicles exhaust gas ATSs, except in selective catalytic reduction (SCR) systems, which are commonly based on Fe- and Cu-promoted zeolites [4]. Diesel

oxidation catalysts (DOC) are palladium-promoted and platinum-rich in composition. A three-way catalyst (TWC) is palladium-rich and promoted with a small amount of rhodium, whereas methane oxidation catalysts (MOC) are palladium-rich and promoted with a small amount of platinum [1,5]. The reason for the popularity of palladium relies on its good thermal stability compared to platinum [6], but sometimes it is also mandatory due to activity such as in methane combustion catalysis [3,7].

One deactivation mechanism of exhaust gas ATS catalysts is sulfur poisoning. Even a low amount of sulfur deactivates the catalysts and, thus, increases vehicle-emitted exhaust gas emissions. Sulfur originates from fuels and lubricant oils. Standards in Europe have been regulated in such a way that sulfur level in fuels can be 10 ppm at the highest [8]. The sulfur content in natural gas and its biological counterpart, bio-gas, is even less than 1 ppm. However, in combustion, sulfur compounds form SO_2 , which further oxidizes to SO_x ($x = 3$ or 4) over a catalyst. The SO_x accumulates on the catalyst, forming stable and less active sulfates, such as aluminum sulfate [9,10] and palladium sulfate [3,11–14], during long-time operation.

Alumina sulfate formation in various conditions and catalyst systems have been previously studied owing to its role in many catalytic reactions and processes [15,16]. However, there has been no systematic research about the stability of Al_2O_3 -supported aluminum sulfate or its role in the decomposition of palladium sulfate. In addition, the literature concerning Al_2O_3 -supported palladium sulfate or sulfur-poisoned methane combustion catalyst is limited to regeneration studies under different gas atmospheres and varying temperatures [13,17–20]. No systematic and quantitative knowledge about the stability of the supported sulfates and catalyst structure after decomposition is available.

The study focuses on the stability and structure of individual and combined Al_2O_3 -supported aluminum and palladium sulfates. The stabilities of the samples will be measured under reductive conditions (H_2), in the absence of oxygen (He), low-oxygen atmosphere, and high-oxygen (lean) conditions. Sulfur content and structure of the catalysts are compared before and after decomposition reactions.

2. Results and Discussion

Regeneration of $\text{PdSO}_4/\text{Al}_2\text{O}_3$ methane combustion model catalyst was studied under both dry and wet synthetic exhaust gas. Figure 1 shows CH_4 conversion and SO_2 concentration during the regeneration procedure with and without water vapor in the exhaust gas stream. In both cases, a decrease in CH_4 conversion can be detected during the regeneration procedure, due to lack of O_2 in the reaction gas feed. However, SO_2 release and, thus, decomposition of sulfate can be detected only if water vapor is present in the exhaust gas stream. This is due to steam reforming and water–gas shift reactions [21,22], which provides H_2 for the sulfate to decompose. Without water vapor in the exhaust gas stream, CH_4 is the only reducing agent, and it is not as effective as H_2 . Decay in methane conversion after regeneration in the presence of water vapor is due to the loss of oxygen from the active PdO phase [23].

Figure 2 explains in greater detail the regeneration behavior of the methane combustion catalyst. It shows a detailed step-wise illustration of the reactions that may occur during the steady-state regeneration of the methane combustion catalyst, and it thus justifies the method that can be used in the fundamental study below. Point 1 to 2: Steady-state methane conversion under lean-burn conditions over an Al_2O_3 -supported PdSO_4 (PS) catalyst. Point 2 to 3: Oxygen from the exhaust gas is compensated with N_2 , initiating steam reforming and possibly water–gas shift reactions, which provides H_2 gas for low-temperature sulfate decomposition [21,22]. The activity of the catalyst against steam reforming and possibly water–gas shift reactions decays faster under steady-state rich conditions, which can be seen in Figure 2 as a decrease in CH_4 conversion. SO_2 also reaches its maximum at Point 3. A decrease in non-sulfur-poisoned methane conversion under rich conditions was observed earlier by other researchers [18,21,24] and it was concluded to be reversible if O_2 was introduced periodically after rich conditions were attained. Temperature-programmed reduction (TPR) is a feasible technique

to provide more detailed information about the decomposition of sulfates and the catalyst structure at this point. Due to the low rate of the steam reforming reaction, which can be observed as low CH_4 conversion, H_2 regeneration almost stops and the SO_2 concentration begins to decrease (Point 3 to 4). Temperature-programmed desorption (TPD) and oxidation (TPO) with low oxygen are relevant techniques to enhance the fundamental understanding of the catalyst decomposition and structure under these conditions. Lean operation conditions are restored at Point (4), which re-oxidizes and recovers the active form of the catalyst at Point 5, as discussed in our previous work [25].

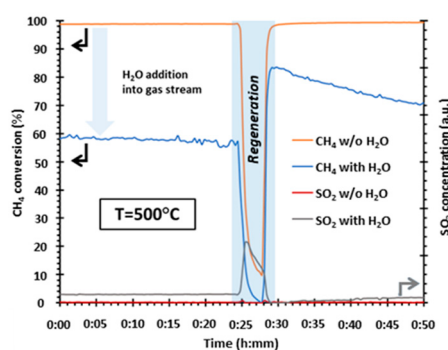


Figure 1. Effect of water vapor in the exhaust gas on regeneration of a model $\text{PdSO}_4/\text{Al}_2\text{O}_3$ methane combustion catalyst.

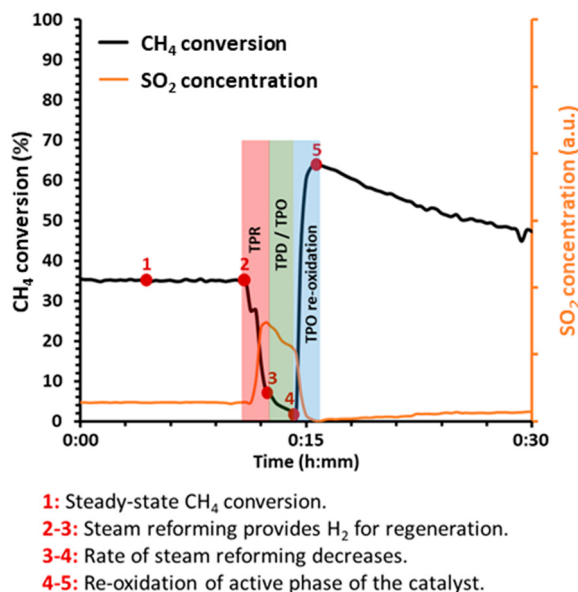


Figure 2. Detailed step-wise description of the lean-burn CH_4 combustion catalyst regeneration procedure. (TPR = Temperature Programmed Reduction, TPD = Temperature Programmed Desorption, and TPO = Temperature Programmed Oxidation).

2.1. Thermal Decomposition of Al_2O_3 -Supported PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$ under Hydrogen Gas

Temperature-programmed reduction (TPR), desorption (TPD), and oxidation (TPO) were used to clarify the decomposition of sulfur compounds. The TPR experiments were carried out under blended gas of 10% H_2 and Ar. The thermal decompositions of Al_2O_3 -supported PdSO_4 (PS) and $\text{Al}_2(\text{SO}_4)_3$ (AS) model catalysts individually and in combination under a hydrogen gas mixture are represented in Figure 3. Al_2O_3 -supported PdSO_4 decomposes at a lower temperature compared to individual supported $\text{Al}_2(\text{SO}_4)_3$. Hydrogen consumption started around 250 °C, but no sulfur release was observed with a quadrupole mass spectrometer detector before the temperature range of 400–500 °C. The result is well in line with previous observations [26]. The decomposition of sulfate combinations

began, however, at about a temperature of 100 °C lower than that for the individual one, and the amount of $\text{Al}_2(\text{SO}_4)_3$ in the catalyst affected this directly—the higher the $\text{Al}_2(\text{SO}_4)_3$ content, the lower the decomposition temperature. This may indicate that the presence of $\text{Al}_2(\text{SO}_4)_3$ de-stabilizes PdSO_4 . One explanation could be the exothermic decomposition reaction of sulfates that promotes itself when the reaction proceeds. Moreover, the high overall sulfate content of the catalyst may decrease the support material effect and thus make the sulfates more like a bulk sulfate, which decomposes at a lower temperature than do support-material-stabilized sulfates. The elemental analysis results of the samples, tabulated in Table 1, showed that the sulfur content of each TPR-treated catalyst was 0.30 wt.% if PdSO_4 was included in the catalyst. The residual sulfur content corresponds to the stoichiometric sulfur amount in the Pd_4S structure. Powder X-ray diffraction (PXRD) measurements were recorded to confirm the Pd_4S structure (Figure 4). Based on the PXRD results, if $\text{Al}_2(\text{SO}_4)_3$ is present in the catalyst, more crystalline Pd_4S is formed during TPR treatment. The result gives an indication that Pd_4S may be one factor that is affecting catalyst regeneration.

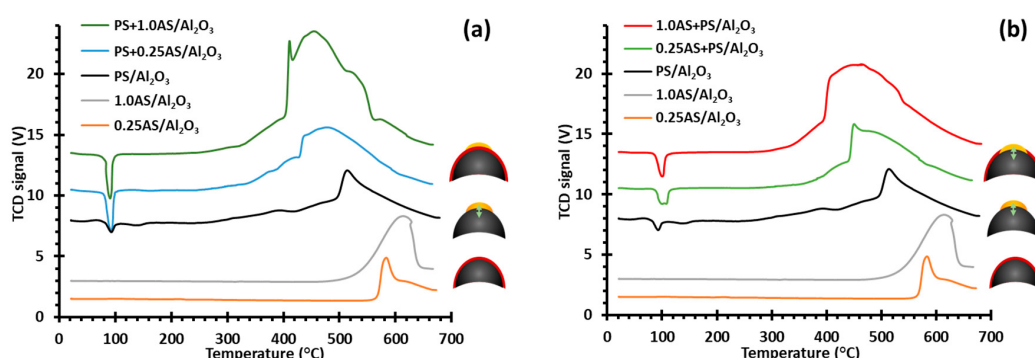


Figure 3. Thermal decomposition under hydrogen gas of (a) alumina-supported combined sulfates PdSO_4 (PS) + 0.25 $\text{Al}_2(\text{SO}_4)_3$ (AS)/ Al_2O_3 and PS + 1.0 AS/ Al_2O_3 , and (b) alumina-supported combined sulfates 0.25 AS + PS/ Al_2O_3 and 1.0 AS + PS/ Al_2O_3 together with individual alumina-supported sulfates PS/ Al_2O_3 , 0.25 AS/ Al_2O_3 and 1.0 AS/ Al_2O_3 . Experiments were carried out under 10% H_2 in an argon gas atmosphere.

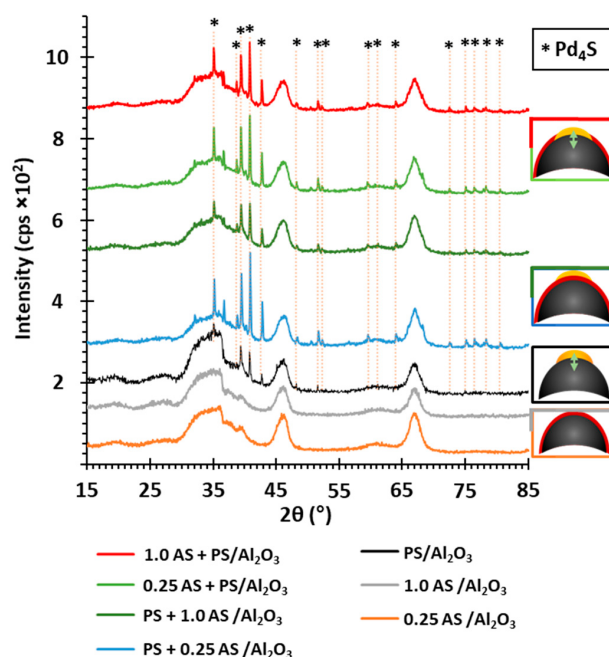


Figure 4. Powder X-ray diffraction results of alumina-supported sulfates together with characteristic peaks of Pd_4S (*) after temperature-programmed reduction treatment under hydrogen gas.

Table 1. Designation of the catalysts, sulfur contents, and PdO and Pd peak areas and crystallite sizes.

Catalyst	Treatment	Sulfur Content (wt.-%) ¹	Relative Sulfur Content (%) ²	PdO Peak Area	PdO Crystallite Size (nm)	Pd Peak Area	Pd Crystallite Size (nm)
PS/Al ₂ O ₃ ³	Prepared	0.88	100	-	-	-	-
	10% O ₂ /He	0.41	47	148.1	12.1	71.5	12.3
	0.1% O ₂ /He	0.11	13	121.3	5.7	118.8	14.4
	He TPD	0.06	7	-	-	143.0	20.7
	TPR	0.30	34	-	-	-	-
0.25 AS/Al ₂ O ₃ ⁴	Prepared	0.29	100	-	-	-	-
	10% O ₂ /He	0.23	79	-	-	-	-
	0.1% O ₂ /He	0.11	38	-	-	-	-
	He TPD	0.08	28	-	-	-	-
	TPR	0.05	16	-	-	-	-
1.0 AS/Al ₂ O ₃ ⁴	Prepared	0.97	100	-	-	-	-
	10% O ₂ /He	0.48	49	-	-	-	-
	0.1% O ₂ /He	0.30	31	-	-	-	-
	He TPD	0.23	24	-	-	-	-
	TPR	0.07	7	-	-	-	-
PS + 0.25 AS/Al ₂ O ₃ ^{3,4}	Prepared	1.39	100	-	-	-	-
	10% O ₂ /He	0.24	17	40.7	34.8	75.2	96.0
	0.1% O ₂ /He	0.05	4	18.3	20.1	114.7	110.4
	He TPD	0.03	2	-	-	121.6	122.8
	TPR	0.30	22	-	-	-	-
PS + 1.0 AS/Al ₂ O ₃ ^{3,4}	Prepared	2.10	100	-	-	-	-
	10% O ₂ /He	0.35	17	56.7	20.5	25.8	74.7
	0.1% O ₂ /He	0.09	4	24.5	17.7	64.7	66.5
	He TPD	0.07	3	-	-	63.2	48.0
	TPR	0.30	14	-	-	-	-
0.25 AS + PS/Al ₂ O ₃ ^{3,4}	Prepared	1.03	100	-	-	-	-
	10% O ₂ /He	0.30	29	45.1	33.1	56.1	94.0
	0.1% O ₂ /He	0.10	10	16.0	23.4	85.6	101.2
	He TPD	0.07	6	-	-	90.9	111.5
	TPR	0.30	29	-	-	-	-
1.0 AS + PS/Al ₂ O ₃ ^{3,4}	Prepared	1.71	100	-	-	-	-
	10% O ₂ /He	0.40	23	53.2	23.0	49.5	73.5
	0.1% O ₂ /He	0.12	7	7.7	38.8	71.5	85.7
	He TPD	0.07	4	-	-	67.6	109.8
	TPR	0.30	18	-	-	-	-

¹ Sulfur content of the sample before treatment (prepared) or after treatment (10% O₂/He, 0.1% O₂/He, He TPD, TPR). ² Relative sulfur contents were calculated (sulfur content of a treated sample/sulfur content of a prepared sample) *100%. ³ Palladium loading of the catalyst is 4% in a metallic state. ⁴ 0.25 and 1.0 refer to the percentage sulfur content of Al₂(SO₄)₃/Al₂O₃.

2.2. Thermal Decomposition of Al₂O₃-Supported PdSO₄ and Al₂(SO₄)₃

The thermal decomposition results for the PS/Al₂O₃ model catalyst in the absence of oxygen (He TPD), under low oxygen concentration (0.1% O₂/He), and in excess oxygen (10% O₂/He) are shown in Figure 5a. Two separate decomposition steps were observed in each case, as concluded in our previous study [27]. However, the first step of the PdSO₄ decomposition reaction was observed to decay as a function of the oxygen concentration. The analysis relies on the mass signals of O₂ and SO₂ recorded during the thermal decomposition. It has also been suggested that in the absence of oxygen, sulfate species could decompose via a one-step mechanism [26]. The decomposition of Al₂O₃-supported PdSO₄ was initiated at 600 °C in He gas, whereas the corresponding temperature under 10% O₂/He was 800 °C. The oxygen concentration also affected the quantitative sulfur content—the lower oxygen concentration corresponded to better sulfur removal (Table 1) due to the longer time period at temperatures required for the decomposition. FTIR spectra of the PS/Al₂O₃ model catalyst recorded after different treatments (Figure 5b) supported the result as the relative intensity of the asymmetric stretching vibration of sulfate decays as the oxygen concentration of the gas mixture decreases.

The formation of Al₂(SO₄)₃ over an Al₂O₃-supported methane oxidation catalyst has been reported [9,10], and it is thus crucial to know its decomposition temperature relative to that of PdSO₄

and, further, its role in the decomposition of PdSO_4 . The decomposition experiments for the bulk $\text{Al}_2(\text{SO}_4)_3$ and $\text{AS}/\text{Al}_2\text{O}_3$ model catalysts were carried out as in the case of the $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst under three different gas atmospheres. The unsupported bulk $\text{Al}_2(\text{SO}_4)_3$ decomposed completely between 600 °C and 800 °C [28]. The thermal decomposition of Al_2O_3 -supported $\text{Al}_2(\text{SO}_4)_3$ under different gas atmospheres is shown in Figure 6a,b. The decomposition of Al_2O_3 -supported $\text{Al}_2(\text{SO}_4)_3$ took place at a higher temperature than did that of bulk $\text{Al}_2(\text{SO}_4)_3$ or Al_2O_3 -supported PdSO_4 . Overall, the trends in the decomposition temperatures of the bulk and supported $\text{Al}_2(\text{SO}_4)_3$ showed strong support interaction. The decrease in the oxygen concentration of the feed gas resulted in higher removal of sulfur during the decomposition of supported $\text{Al}_2(\text{SO}_4)_3$ based on FTIR data (Figure 6c,d) and quantitative sulfur analysis (Table 1). However, the removal of sulfur was evidently less than that in the case of the $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst. It can be concluded that individual and Al_2O_3 -supported $\text{Al}_2(\text{SO}_4)_3$ is more stable than PdSO_4 , and the decomposition order of the supported sulfates is the same as that observed already in TPR, despite the gas atmosphere, even though the decomposition temperature under a hydrogen gas mixture is lower. Moreover, it is worth noting that the decomposition route of $\text{AS}/\text{Al}_2\text{O}_3$ was different from that of $\text{PS}/\text{Al}_2\text{O}_3$, as no O_2 peak was observed before simultaneous release of O_2 and SO_2 .

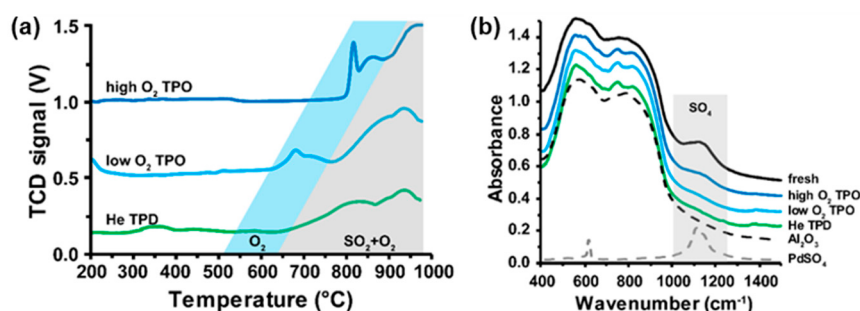


Figure 5. (a) Thermal decomposition curves of the $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst and (b) FTIR spectra of the $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst before and after decomposition, accompanied by reference spectra of bulk PdSO_4 and Al_2O_3 .

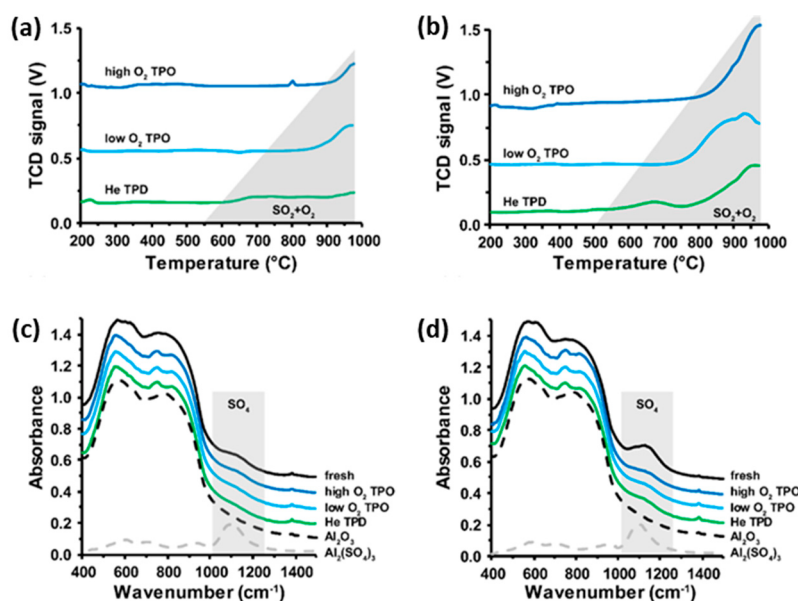


Figure 6. Thermal decomposition curves of (a) 0.25 $\text{AS}/\text{Al}_2\text{O}_3$ and (b) 1.0 $\text{AS}/\text{Al}_2\text{O}_3$ model catalysts together with FTIR spectra of (c) 0.25 $\text{AS}/\text{Al}_2\text{O}_3$ and (d) 1.0 $\text{AS}/\text{Al}_2\text{O}_3$ model catalysts before and after decomposition, accompanied by reference spectra of bulk $\text{Al}_2(\text{SO}_4)_3$ and Al_2O_3 .

2.3. Thermal Decomposition of Al_2O_3 -Supported PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$ Combinations

The co-existence of PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$ species on sulfur-poisoned lean-burn methane oxidation catalyst is conceivable [2,9,10,12]. Thus, the effect of $\text{Al}_2(\text{SO}_4)_3$ on the decomposition of PdSO_4 was examined under three dry gas atmospheres (Figures 7 and 8). The stability of sulfate species decreased as a function of the decreasing oxygen concentration in the feed gas in the same way as described above for the PS/ Al_2O_3 and AS/ Al_2O_3 model catalysts. The decomposition began at a temperature 100 °C lower than that for PS/ Al_2O_3 , showing that $\text{Al}_2(\text{SO}_4)_3$ de-stabilized the PdSO_4 phase, promoting its decomposition. The relative sulfur release of the PS + X AS/ Al_2O_3 model catalysts ($X = 0.25$ or 1.0) was greater than that together for the PS/ Al_2O_3 and X AS/ Al_2O_3 ($X = 0.25$ or 1.0) model catalysts (Table 1). This also indicated the favorable effect of PdSO_4 on the decomposition of $\text{Al}_2(\text{SO}_4)_3$.

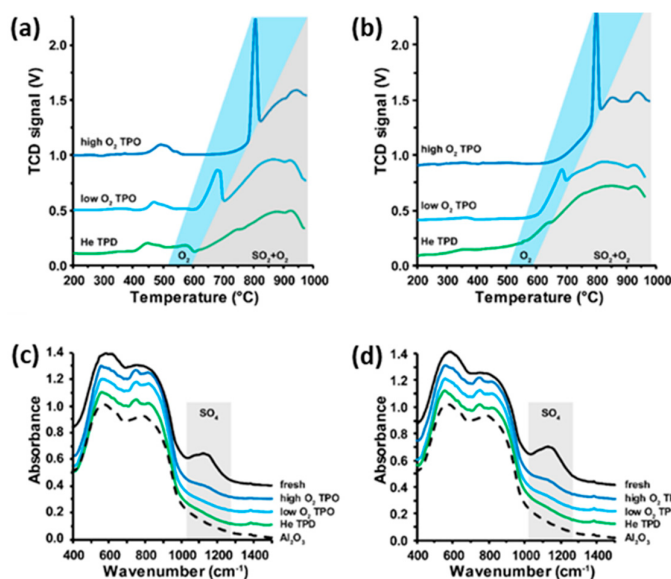


Figure 7. Thermal decomposition curves of (a) PS + 0.25 AS/ Al_2O_3 and (b) PS + 1.0 AS/ Al_2O_3 model catalysts and (c) FTIR spectra of PS + 0.25 AS/ Al_2O_3 and (d) PS + 1.0 AS/ Al_2O_3 model catalysts before and after decomposition, accompanied by a reference spectrum of Al_2O_3 .

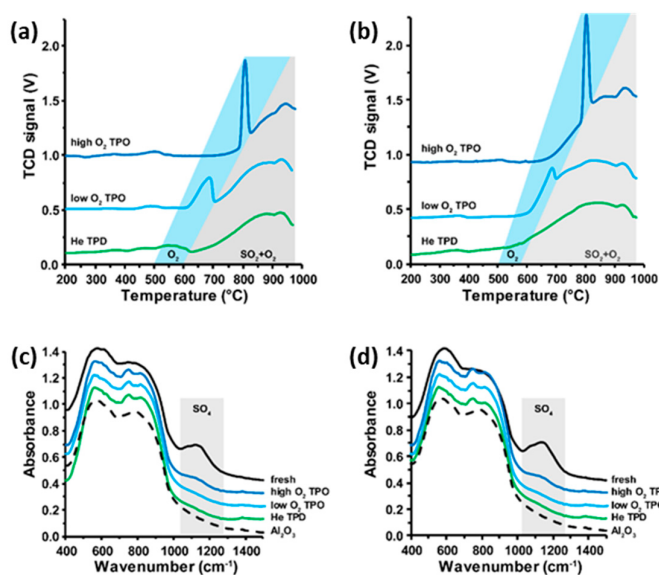


Figure 8. Thermal decomposition curves of (a) 0.25 AS + PS/ Al_2O_3 and (b) 1.0 AS + PS/ Al_2O_3 model catalysts and (c) FTIR spectra of 0.25 AS + PS/ Al_2O_3 and (d) 1.0 AS + PS/ Al_2O_3 model catalysts before and after decomposition, accompanied by a reference spectrum of Al_2O_3 .

2.4. State of Palladium after Thermal Decomposition of Al_2O_3 -Supported PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$

The powder X-ray results presented in Figure 9 reveal that a decrease in oxygen concentration in the feed gas resulted in a higher content of metallic palladium in the regenerated $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst. The qualitative PdO and Pd peak areas and crystallite sizes are tabulated in Table 1. The decomposition of the $\text{PS}/\text{Al}_2\text{O}_3$ model catalyst under helium gas resulted in the formation of only metallic Pd. Earlier, Hoyos et al. [13] concluded that decomposition under an inert gas atmosphere led to PdO, although the presence of an active phase was not directly observed. Qualitatively powder X-ray diffraction results showed that if $\text{Al}_2(\text{SO}_4)_3$ was present in the catalyst, a high content of metallic Pd was observed. This indicates that $\text{Al}_2(\text{SO}_4)_3$ stabilized the metallic Pd phase and/or lead to sintering of metallic Pd particles, possibly prevented re-oxidation of metallic Pd to the active PdO form. Overall, the formation of metallic Pd is undesirable, because it is known to be inactive in low-temperature methane oxidation under lean-burn conditions and it is also known to be vulnerable to sintering [29–31]. Overall, a high oxygen concentration in the feed gas resulted in a prominent amount of PdO in the model catalyst after the thermal decomposition of the sulfate species, whereas a low oxygen concentration in regeneration led to a high metallic Pd content.

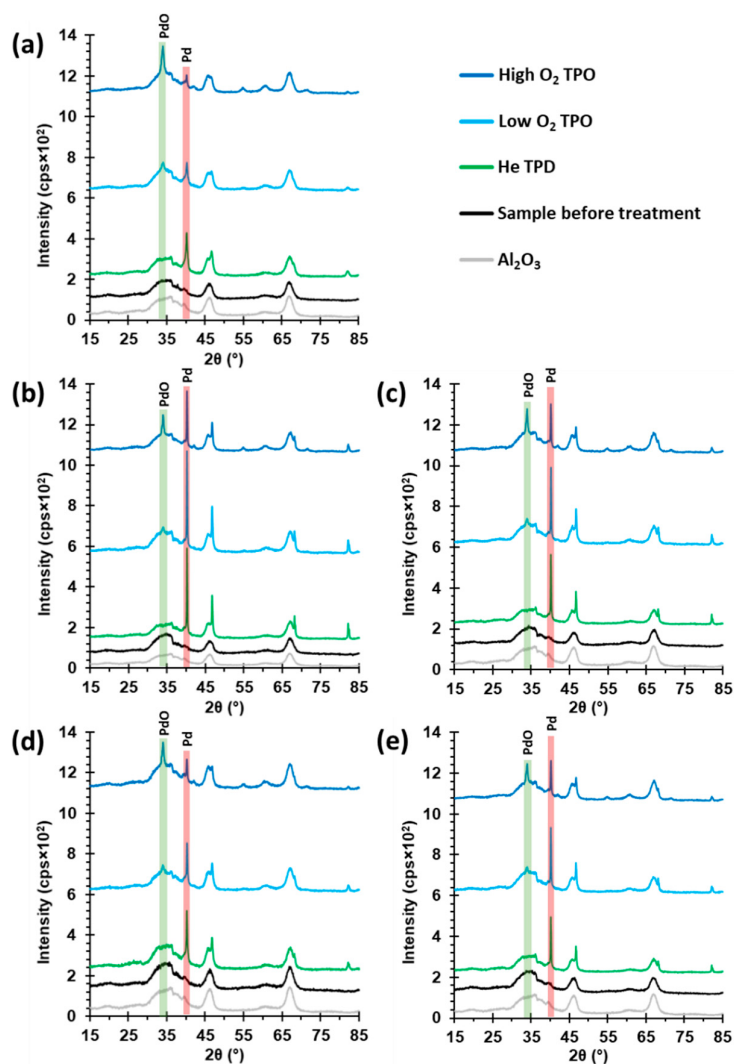


Figure 9. Powder X-ray diffraction patterns of (a) $\text{PS}/\text{Al}_2\text{O}_3$, (b) $\text{PS} + 0.25 \text{ AS}/\text{Al}_2\text{O}_3$, (c) $0.25 \text{ AS} + \text{PS}/\text{Al}_2\text{O}_3$, (d) $\text{PS} + 1.0 \text{ AS}/\text{Al}_2\text{O}_3$, and (e) $1.0 \text{ AS} + \text{PS}/\text{Al}_2\text{O}_3$ model catalysts after decomposition under varied oxygen concentrations. The characteristic main peaks of active PdO and inactive metallic Pd are highlighted in the figure.

3. Materials and Methods

3.1. Catalysts

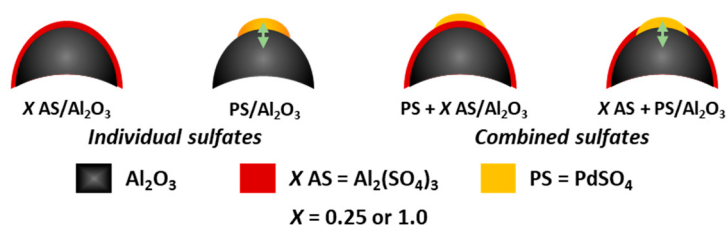
Modern commercially available methane combustion catalyst after sulfur poisoning treatment contains 0.97 wt. % of sulfur [27]. A modern sulfur-poisoned methane combustion catalyst was used as a reference in activity experiments for model catalysts to justify their similar performance and behavior after sulfur poisoning treatment. To model and mimic the catalyst composition, a series of catalysts were prepared by using PdSO_4 (Sigma Aldrich, Saint Louis, MO, USA, CAS: 13566-03-5), $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ (Merck, Darmstadt, Germany, CAS: 7784-31-8), and Al_2O_3 (Sasol, Hamburg, Germany) as starting materials. Bulk PdSO_4 and $\text{Al}_2(\text{SO}_4)_3$ compounds were used in model catalyst preparation to control quantitatively the sulfur amount and sulfate structure. If the sulfating were to be done in the gas phase with SO_2 gas, the formed sulfate species and amounts could be hard to control. The preparation of model catalyst powders was carried out at room temperature, and detailed preparation procedures are described below for each of the model catalysts. The 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 $\text{Al}_2(\text{SO}_4)_3$ -containing catalysts, and it is 0.25 or 1 wt.% of sulfur. The catalyst was provided by the Dinex Ecocat Oy. Sulfates are abbreviated as follows to clarify the names of the catalysts: PS refers to PdSO_4 and AS refers to $\text{Al}_2(\text{SO}_4)_3$.

PS/ Al_2O_3 : PdSO_4 precursor was mixed into water at room temperature. Al_2O_3 powder was added into the mixture of PdSO_4 and water to disperse PdSO_4 over Al_2O_3 . The mixture was stirred at room temperature with ultrasonic treatment. The catalyst powder of the $\text{PdSO}_4/\text{Al}_2\text{O}_3$ model catalyst was obtained by evaporating the water at room temperature and finishing the drying in an oven at 90 °C.

X AS/ Al_2O_3 (X = 0.25 or 1.0): $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ precursor was dissolved into water at room temperature. Al_2O_3 powder was added into the $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ solution to disperse $\text{Al}_2(\text{SO}_4)_3$ over Al_2O_3 . The mixture was stirred for 2 h at room temperature. Model catalyst powders with different $\text{Al}_2(\text{SO}_4)_3$ contents were obtained by evaporating the water at room temperature and finishing the drying in an oven at 90 °C for 1 h.

PS + X AS/ Al_2O_3 (X = 0.25 or 1.0): PdSO_4 and X $\text{Al}_2(\text{SO}_4)_3/\text{Al}_2\text{O}_3$ (X = 0.25 or 1.0) powder precursors were mixed into water. The mixture was stirred for 2 h at room temperature with ultrasonic treatment. The catalyst powders of $\text{PdSO}_4 + \text{X Al}_2(\text{SO}_4)_3/\text{Al}_2\text{O}_3$ (X = 0.25 or 1) were obtained by evaporating water at room temperature and finishing the drying in an oven at 90 °C for 1 h.

X AS + PS/ Al_2O_3 (X = 0.25 or 1.0): $\text{Al}_2(\text{SO}_4)_3$ and $\text{PdSO}_4/\text{Al}_2\text{O}_3$ powder precursors were mixed into a water solution. The mixture was stirred for 2 h at room temperature with ultrasonic treatment. The catalyst powders with different $\text{Al}_2(\text{SO}_4)_3$ loadings were obtained by evaporating water at room temperature and finishing the drying in an oven at 90 °C for 1 h. The catalyst composition was the same as above, but the addition order was different, which leads to different natures of PdSO_4 on the Al_2O_3 support material as illustrated in Scheme 1.



Scheme 1. Illustration of model catalyst composition.

3.2. Characterization Techniques

Regenerations of the model methane combustion catalyst were obtained under dry and wet synthetic exhaust gas. Synthetic exhaust gas consisted of 2000 ppm of CH_4 , 2000 ppm of CO , 500

ppm of NO, 6% of CO₂, 10% of H₂O if wet, and 10% of O₂ balanced with N₂. Water vapor in dry gas regeneration was compensated with additional N₂ to maintain a total gas flow rate of 1.18 L min^{−1}. The amount of catalyst in the measurements was 0.2 g. A Gasmet™ DX-4000 Multigas FTIR spectrometer (Gasmet technologies, Helsinki, Finland) was used for gas analysis during regeneration.

Temperature-programmed reduction (TPR) experiments were done under a blend gas of 10% H₂ in Ar with a Quantachrome Autosorb iQ device (Quantachrome Corporation, Boynton Beach, FL, USA). A sample (100 mg) was heated under the measurement gas and the TCD signal was recorded from room temperature up to 700 °C with a heating rate of 10 °C min^{−1}. A cold trap was used in the measurements. A quadrupole mass spectrometer (MS) was utilized to examine the gaseous products on a qualitative level during the measurements.

An Elementar varioMICRO cube (Elementar, Langenselbold, Germany) device was used in sulfur analyses. Sulfanilamide was used as a reference and for the calibration. The catalyst sample amount varied from 10 mg to 30 mg in the measurements.

The stability of the sulfur compounds was studied via 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 helium, 0.1% O₂/He, or 10% O₂/He gases. The gas flow rate was 20 mL min^{−1}. The sample was cooled down to 250 °C under the same gas atmosphere as that used during heating. No pretreatment was done prior to the measurement and a cold trap was used in the measurement. A thermal conductive detector (TCD) and quadrupole mass spectrometer (MS) were used to analyze the gaseous products.

Temperature-programmed desorption measurements with helium (He TPD) gas were conducted with similar parameters as the TPO measurements, but instead of oxygen blend gas, only helium was used.

The IR spectra of the solid catalyst samples were recorded using a Bruker Vertex 70 spectrometer (Bruker, Karlsruhe, Germany) using the pressed pellet technique. Catalyst samples were finely ground and diluted in KBr. The number of scans was 32 and the resolution was 2 cm^{−1}.

A Bruker-AXD D8 Advance diffractometer (Bruker, Karlsruhe, Germany) was used in the powder X-ray diffraction measurements of catalyst samples. Cu Kα radiation was used in the measurements. 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 (Bruker, Karlsruhe, Germany) was applied to estimate crystallite sizes and peak areas of metallic Pd and PdO [32].

4. Conclusions

The Al₂O₃-supported PdSO₄/Al₂(SO₄)₃ model catalysts were studied under various gas atmospheres in order to study their decomposition routes as well as their texture before and after each treatment. The lowest sulfate decomposition temperature was achieved in treatment under a hydrogen gas atmosphere in all the cases, being the optimal conditions among the studied cases. Aluminum sulfate decomposed almost completely under hydrogen gas, whereas in the case of palladium sulfate, the decomposition was always incomplete, leading to Pd₄S formation. The TPD always resulted in decomposition of PdSO₄ to metallic palladium. Combining both aluminum and palladium sulfates into the same catalyst led to a decrease in the decomposition temperature and a high portion of metallic palladium under all the gas atmospheres.

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