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The Effect of Sulphur on the Activity of Pd/Al_2O_3, Pd/CeO_2 and Pd/ZrO_2 Diesel Exhaust Gas Catalysts

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Abstract Pd/Al_2O_3, Pd/CeO_2 and Pd/ZrO_2 diesel oxidation catalysts and their washcoat materials were studied after sulphur treatment. The catalytic activities were analysed in simplified diesel exhaust gas composition by FT-IR technique. ICP-OES or XRF, physisorption and CO chemisorption was used to catalyst characterisation. The result shows that the sulphur treatment clearly deactivates the studied catalysts.

Keywords Diesel · Palladium · Propene · SO_2 poisoning · Sulphur

1 Introduction

Emission regulations as well as Kyoto Protocol regarding CO_2 emissions are by far the most prominent drivers in automotive industry. New techniques and vehicles are required to comply with the legislation. Engines, which are operating in lean conditions (i.e. excess oxygen), have a potential to improve fuel efficiency and so to reduce CO_2 emissions. These kinds of engines give excellent fuel economy, but at low temperatures (>130 °C) and high temperatures (>300 °C) as well as in the presence of poisons, providing a high activity is a challenge [1]. In addition, conventional three-way catalysts (TWC) or diesel oxidation catalysts (DOCs) working on excess of oxygen, reducing NO_x emissions are still a challenge.

Diesel oxidation catalysts (DOCs) are a possible technique to reduce harmful emissions in normal operating conditions. Its catalytic performance is typically evaluated by aging studies [2]. Laboratory studied stimulating the long-term vehicle operations are often done to find correlations to vehicle or bench agings and similarities between the two types of agings [3]. Laboratory aging is a convenient and resource efficient approach to study catalyst deactivation phenomenon.

Starting in 2010, the sulphur content of diesel fuels in EU countries will be set at a maximum of 10 ppm [4]. However, in many countries diesel fuels with high sulphur content are still in use. In the future, bio-based diesel made from biomass is recently being paid more and more attention [5]. The problem in biofuels and low sulphur fuels is still coming from the harmful compounds, such as S, Zn, Ca, Ba, originating also from lubricant oils. These compounds can deactivate the catalyst material by acting as a poison [6]. Investigations have also been demonstrated that the lubricant oils have also an effect on diesel emissions, naturally depending on the sulphur content, metal content, volatility and density of the lube oil [7]. Particulate matter (PM) in diesel emissions also deactivates the catalyst. PM has been analysed to contain elemental carbon ($\approx$31%), sulphates and moisture ($\approx$14%), unburnt fuel ($\approx$7%) and

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lubricant oil (≈40%) as well as the remainings may be metals and other substances [8].

Deactivation of automotive exhaust gas catalysts by sulphur is a complex phenomenon. It can involve changes in the morphological, structural, and electronic properties of the catalyst [9]. Ceria-zirconia mixed oxides are a crucial component in a modern automotive emission-control catalyst; due to their redox properties, they provide the oxygen storage capacity (OSC) [10]. The effect of SO_2 on ceria and zirconia with or without noble metals has already been studied mainly over three-way catalysts [11, 12], and methane combustion processes [13–15] all in different sulphur contents and temperatures.

In the present work, Pd-containing diesel oxidising catalyst powders were treated with the sulphur treatment procedure. The goal of this work was to investigate the differences between fresh and sulphur-treated Pd-based Al_2O_3, CeO_2 and ZrO_2 samples to find out the effects of the treatment on the samples with or without a high noble metal content (4 wt%). Samples were characterised by ICP-OES or XRF, N_2 physisorption and CO-chemisorption. The effect of sulphur treatment in CO and C_3H_6 oxidation reactions is determined.

2 Experimental

2.1 Catalyst Samples and SO_2 Poisoning

Fresh and sulphur-treated Pd/Al_2O_3, Pd/CeO_2 and Pd/ZrO_2 catalyst were studied. Al_2O_3, CeO_2 and ZrO_2 washcoat precursor materials were also treated with sulphur and analysed to understand the effect of noble metal. The amount of Pd in the catalyst was 4 wt% for each catalyst studied. The fresh samples were provided by Ecocat Oy.

The gas phase sulphur poisoning was carried out for the catalyst and washcoat powders at 400 °C for 5 h. The sulphur poisoning was begun by heating the sample in an air and nitrogen flow with a heating rate of 10 °C/min. At 400 °C SO_2 was introduced into the gas flow for 5 h. Then, the reactor was cooled down to room temperature under air and nitrogen flow. The poisoning gas mixture contained 100 ppm SO_2 and 10 vol% air, balanced with N_2.

2.2 Catalyst Characterisation

The sulphur content of the Pd/Al_2O_3, Pd/CeO_2, Al_2O_3 and CeO_2 was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 5300DV). The Pd/ZrO_2 catalyst and ZrO_2 washcoat powders were not dissolved in any solution and therefore, these samples were analysed by X-ray fluorescence (Philips MagiX PW 2403 X-ray fluorescence). XRF-results' accuracy is semi-quantitative, and high Zr content on the sample disturbs the sulphur peak.

Before and after poisoning the specific surface area as well as the average pore sizes and volumes of the samples were determined with a Micrometrics ASAP 2020 analyser. Specific surface area (m^2/g) was calculated according to the BET theory. The average pore sizes and volumes were calculated using the BJH theory of nitrogen isotherm analysis. For the determination of the palladium metal dispersion, CO chemisorption measurements were carried out for the Pd-containing samples at room temperature by using Micrometrics ASAP 2020 analyser.

2.3 Catalytic Activity Measurements

Catalytic activity was measured by using laboratory scale light-off experiments for the fresh and sulphur-treated Pd/Al_2O_3, Pd/CeO_2 and Pd/ZrO_2 catalysts as well as Al_2O_3, CeO_2 and ZrO_2 washcoat materials. The activity was determined for a simplified diesel exhaust gas composition and this lean gas mixture contained 500 ppm CO, 300 ppm C_3H_6 and 12 vol% O_2, balanced with N_2. The measurements were carried out at atmospheric pressure in a tubular furnace with a quartz reactor. A powder sample (0.25 g) was mixed with quartz sand and placed in the reactor tube with a support of quartz wool. The gas flows were controlled by mass flow controllers (Brooks 5850TR) and the total flow during the experiment was 1 dm^3/min. The temperature of the catalyst was increased from room temperature up to 500 °C with a linear heating rate of 10 °C/min. The concentrations of feed and product gases were measured as a function of temperature every 5 s by Gasmet™ FT-IR gas analyser. Oxygen concentration was determined by using a paramagnetic oxygen analyser (ABB Advanced Optima).

3 Results and Discussion

The results showed that the sulphur treatment affected differently depending on the studied samples. Washcoat material was found to have an influence on the SO_2 oxidation reactions, and therefore deactivation.

3.1 Effect of SO_2 on the Catalytic Characterisation

According to the elemental analyses (ICP-OES or XRF), sulphur was detected to accumulate in the samples during the 5 h' sulphuring procedure at 400 °C as can be seen in Table 1. It was demonstrated that the sulphur content of the powdered samples was varying with different composition. The sulphur content of both the ceria containing samples was higher than that of the other studied samples.

Table 1 The sulphur contents (ICP-OES or XRF), CO chemisorption results, average pore sizes and total pore volumes (BJH) of the fresh and sulphur poisoned samples

Sample	S content (wt%)		Dispersion of Pd (%)		Pore size (nm)		Pore volume (cm^3/g)	
	ICP-OES	XRF	Fresh	Poisoned	Fresh	Poisoned	Fresh	Poisoned
Al_2O_3	0.4	–	–	–	9.9	9.7	0.53	0.51
CeO_2	2.3	–	–	–	9.8	10.1	0.33	0.28
ZrO_2	–	1.0[a]	–	–	3.4	3.7	0.18	0.14
Pd/Al_2O_3	1.7	–	12.8	<5	9.3	9.0	0.47	0.43
Pd/CeO_2	2.1	–	91[b]	10.4	10.1	10.3	0.31	0.26
Pd/ZrO_2	–	0.7[a]	15.5	<5	8.4	8.8	0.16	0.15

[a] Semi-quantitative analysis, S peak is disturbed by Zr on the sample

[b] The CO dispersion value for the fresh Pd/CeO_2 catalyst is probably too high, because CO can be adsorbed on ceria

3.1.1 Sulphur Accumulation on Al_2O_3 and Pd/Al_2O_3

According to our results, the accumulation of sulphur was increased in the presence of Pd for the Al_2O_3 sample. Mowery and McCormick [16] have demonstrated in their in situ IR study that $PdSO_4$ and aluminium sulphate ($Al_2(SO_4)_2$), were formed when SO_2 was exposed to PdO supported on alumina. Lampert et al. [17] have found in their lean burn natural gas vehicle studies that SO_x is adsorbed also on alumina as a carrier to Pd. Based on our sulphur content results for the Pd/Al_2O_3 and Al_2O_3, it seems that in the presence of palladium the formation of sulphate species was enhanced. However, in our studies more research work is required to confirm the adsorbed surface species.

3.1.2 Sulphur Accumulation on CeO_2 and Pd/CeO_2

In the case of Pd/CeO_2, the sulphur content was a bit lower comparing to pure CeO_2. According to Rodriguez et al. [18] the O centres in CeO_2 are very efficient for oxidising and trapping SO_2. Luo and Gorte [12] have reported in their FT-IR study that bulk sulphates were formed under oxidising conditions on Pd/CeO_2 when it was exposed to 20 ppm of SO_2 at 400 °C. Waqif et al. [19] have done ceria sulphation studies by IR. They found that SO_2 oxidation gives two types of sulphates: surface and bulklike species. Karjalainen et al. [20] have done thermodynamic calculations about the ceria sulphation. They have noticed that under 500 °C $Ce(SO_4)_2$ species are very stable.

As well-known, ceria has an ability to act as an oxygen storage compound. Therefore, the reason for deactivation effect of sulphur on ceria, is the presence of sulphates which are formed by the redox reaction between SO_2 and CeO_2 [11, and references sited therein]:

$$6CeO_2 + 3SO_2 \leftrightarrow Ce_2(SO_4)_3 + 2Ce_2O_3 \quad (1)$$

The reason for a bit lower sulphur content on the Pd/CeO_2 catalyst compared to the pure CeO_2 sample might be that palladium inhibits in some extent the formation of the bulklike sulphate species.

3.1.3 Sulphur Accumulation on ZrO_2 and Pd/ZrO_2

The sulphur content of the ZrO_2-based samples was lower than that of the Al_2O_3- and CeO_2-based samples. However, the ZrO_2 samples were behaving the same way as was in the case of CeO_2: the sulphur content was higher on the washcoat than on Pd containing catalyst. Luo and Gorte [12] found only surface sulphates under oxidising conditions on the Pd/ZrO_2 catalyst, when it was exposed to SO_2. A number of research works has been done where sulphated-zirconia (SZ) was prepared by impregnation of ZrO_2 with a solution of sulphur. However, the gas phase sulphation for fresh ZrO_2 washcoat material without anu noble metal was not reported.

3.1.4 Pore Size and Volume

In Table 1, the average pore size distribution for the fresh and sulphur treated samples are presented. For the fresh Pd/CeO_2 and Pd/ZrO_2 catalysts the average pore size was slightly increased after the sulphur treatment. Only exception was the Pd/Al_2O_3 catalyst for which the pore size was decreased slightly after the sulphur treatment. The average pore sizes were also increased to CeO_2 and ZrO_2 washcoats after sulphur treatment. The average pore size was decreased after sulphur treatment for the Al_2O_3 washcoat. When comparing the fresh washcoats and Pd containing samples to each other, it was observed that the pore sizes were increased when Pd was added to the fresh CeO_2 or fresh ZrO_2 washcoat. The most significant difference in pore sizes was between the fresh Pd/ZrO_2 catalyst and the fresh ZrO_2 washcoat. Also this time the addition of Pd to fresh Al_2O_3 caused the pore size decrease.

The total pore volume was higher for the washcoat samples compared to the Pd-containing samples (see

Table 1). This means that the addition of Pd to the fresh washcoat caused the pore volume to decrease. The sulphur treatment decreased the pore volume for the Pd-containing samples. The same effect was observed for the washcoat samples, too.

3.1.5 Surface Area Decrease After SO_2 Treatment

The physisorption studies showed that the sulphuring treatment had in some cases an effect on the specific surface area of the catalyst samples. The specific surface areas for fresh and sulphur treated samples are presented in Fig. 1. According to the results, in every case, samples without Pd had a bit higher specific surface area than samples with Pd. This effect was found both before and after sulphur treatment. The surface area of the fresh Pd/Al_2O_3 and Pd/CeO_2 catalysts did not differ considerably from the surface area measured for the samples without Pd. Instead, for the Pd/ZrO_2 and ZrO_2 samples, the surface area difference was significant. The most pronounced decrease after the sulphuring treatment was detected in ZrO_2 washcoat as presented in Fig. 1b. The sulphur treatment affected only slightly the specific surface areas for the other studied samples.

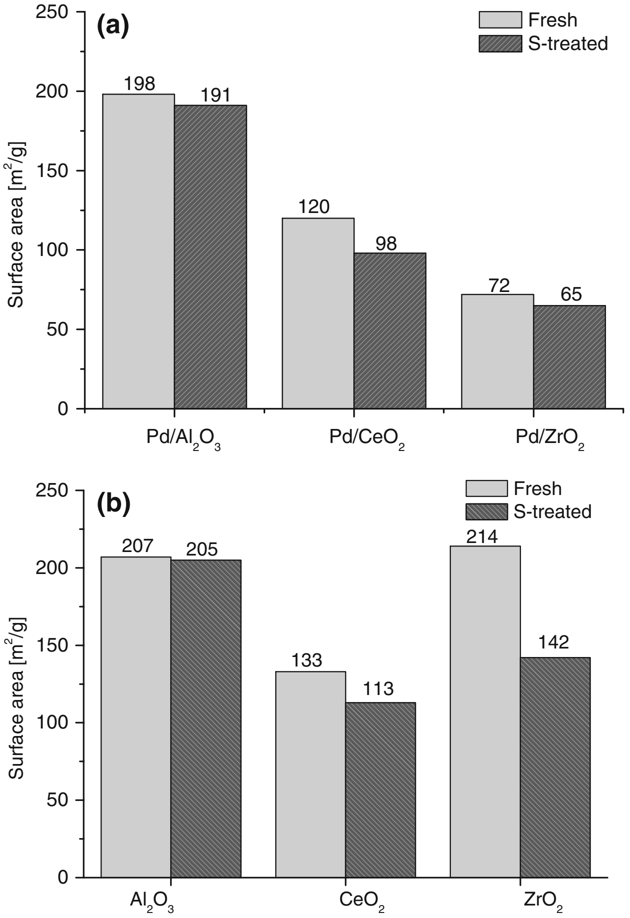

Fig. 1 The specific surface area of the fresh and sulphur-treated samples with (**a**) Pd and (**b**) without the noble metal

Lassi et al. [3] have demonstrated that the pore size and volume changes after poisoning could give some explanation to the results of the BET analyses [3]. Apparently, during the preparation of Pd-containing catalysts, the noble metal is impregnated and dispersed on washcoat. The noble metal blocks pores and cavities, and thus the pore size decreases. The dramatic difference in BET results for the fresh Pd/ZrO_2 and ZrO_2 samples is due to Pd impregnation procedure which includes calcinations at elevated temperature.

3.1.6 Pd Dispersion

Upon the sulphation of samples, the dispersion of Pd was observed to decrease (Table 1). Ciuparu et al. [21] argued that when metal oxides, such as CeO_2 and $Ce_xZr_{x-1}O_2$ are in close contact with the active metal, CO can also be adsorbed on ceria, which results in excessively high dispersion values. In our case, this effect has apparently taken place.

Gandhi and Shelef [22] have found that the dispersion of metal particles on the support is an important factor in the oxidation of SO_2. Thus, this could in some extent explain the differences between sulphur contents on the Pd-containing catalysts. For all studied catalysts, the Pd dispersion value was decreased dramatically during the sulphur treatment (see Table 1).

3.2 The Effect of SO_2 on Catalytic Activities

Activity measurements were done to study the effects of sulphur treatment on the functional characteristics of the Pd-containing samples. The CO + C_3H_6 + O_2 model gas composition was chosen to illustrate the simplified diesel exhaust gas composition. Propene and carbon monoxide light-off temperatures (T^{50}) of the fresh and sulphur poisoned catalysts were compared with each other (see Table 2). T^{50} is defined as the temperature of 50% conversion of C_3H_6 or CO. In addition, the difference (ΔT) between the light-off temperatures of CO and C_3H_6 for the fresh and poisoned samples is shown in Table 2.

3.2.1 The Effect of SO_2 on the Activity of Washcoat Materials

From the light-off temperatures presented in Table 2, it can be observed that the activities in CO and C_3H_6 were significantly higher in the case of Pd-containing samples than the activities for the washcoat materials. The most substantial effect was detected in the case of pure ZrO_2, where

Table 2 Light-off temperatures[a] (T^{50} values (°C)) and differences between light-off temperature (ΔT) of CO and C_3H_6 over fresh and sulphur poisoned samples

Sample	CO T^{50} (°C)			C_3H_6 T^{50} (°C)		
	Fresh	Poisoned	ΔT[b]	Fresh	Poisoned	ΔT[b]
Al_2O_3	273	n.d.[c]	–	361	408	47
CeO_2	315	327	12	302	300	−2
ZrO_2	n.d.	363	–	437	273	−164
Pd/Al_2O_3	133	150	17	151	169	18
Pd/CeO_2	86	157	71	154	182	28
Pd/ZrO_2	60	162	102	118	176	58

The feed gas mixture contained 500 ppm CO, 300 ppm C_3H_6 and 12 vol% O_2, balanced with N_2

[a] Defined as the temperature of 50% conversion of CO and C_3H_6

[b] ΔT = Poisoned T^{50}−fresh T^{50}

[c] n.d. means not detected, due to the T^{50} value being not reached

CO and C_3H_6 light-off temperatures were decreased after sulphur treatment. Brown et al. [15] have observed in their study, that sulphation enhances the ZrO_2 ability in methane combustion. They argued that the result is to due to the “superacidic” behaviour of the sulphated-zirconia.

3.2.2 *The Effect of SO_2 on the Activity of Catalysts*

In Fig. 2, the light-off curves for the Pd-containing catalysts are presented. According to the results, the fresh catalysts were more active to oxidise CO and C_3H_6 than the sulphur-treated catalysts. Even at ambient temperature, CO oxidation was measured to be quite high, especially for the fresh catalysts. This might be due to the CO adsorption on the catalyst washcoat. Based on the light-off temperatures in Table 2, the sulphur treatment affected most on the capability of Pd/ZrO_2 to oxidise CO and C_3H_6 more than over the other studied catalysts.

Catalytic activity of fresh Pd/ZrO_2 in the oxidation reactions can be explained by the presence of anionic vacancies (O^{2-} vacancies) nearby Zr^{3+} cations. Zr^{3+} ions are present as defects in ZrO_2 support which contain mainly Zr^{4+} ions [23]. The presence of palladium must have an influence on the stabilization (total or partial) of zirconia tetragonal phase which leads to a higher number of anionic vacancies [23], and thus higher oxidation activity.

The reason why fresh Pd-containing catalysts were active in CO oxidation even at low temperatures (see Fig. 1a), can be due to a synergistic effect between Pd and the washcoat [24]. The presence of metallic Pd^0 sites is required for adsorption as well as for the initiation of the CO oxidation reaction [25]. Cerium oxides are well-known oxygen storage materials, which enhance oxygen activation/dissociation by generating anion vacancies and, thereby, the catalytic properties of Pd by favoring the formation of metallic sites [26]. During SO_2 poisoning, the Pd^0 active sites on Pd/Al_2O_3 and Pd/ZrO_2 catalysts are deactivated by adsorbed sulphur on the surface.

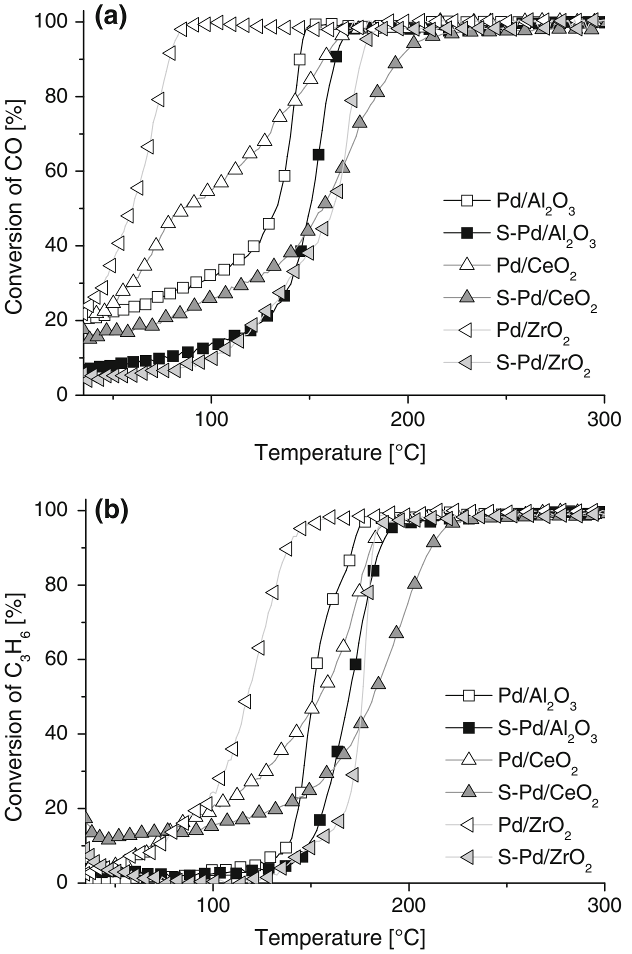

Fig. 2 Light-off curves of (**a**) CO and (**b**) C_3H_6 as a function of temperature for the fresh and sulphur-treated Pd/Al_2O_3, Pd/CeO_2 and Pd/ZrO_2 catalysts. The gas flow contained 500 ppm CO, 300 ppm C_3H_6 and 12 vol% O_2, total flow 1,000 cm^3/min balanced with N_2

The BET, ICP/XRF, physisorption and CO chemisorption results clearly give an explanation on the CO and C_3H_6 oxidation activity decrease for the sulphur-treated studied catalysts. For the Pd/ZrO_2 catalyst, the activity decrease might be due to the fact that sulphur is probably adsorbed only on the surface, which covers almost all the noble metal and/or zirconia anionic vacancy sites.

4 Conclusion

The effect of sulphur on the catalytic materials deactivation has to be studied for developing more tolerant catalysts. In this study the laboratory scale deactivation method is tested for the diesel oxidation catalysts. Results presented indicate clearly that sulphur has a strong effect on the palladium containing samples. The sulphur treatment was observed to decrease the catalytic activity to oxidise CO and C_3H_6 on the Pd/Al_2O_3, Pd/ZrO_2 and Pd/CeO_2 diesel oxidation catalysts. This deactivation effect is due to strong adsorption of sulphur as sulphates on the surface, which covers the active sites for the oxidation reactions. The sulphur treatment of the samples caused increase in the average pore size and pore volume decreased in the case of Pd/CeO_2 and Pd/ZrO_2. Thus, sulphur treatment has also an effect on the structure of catalyst.

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