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The activity of Pt/Al_2O_3 diesel oxidation catalyst after sulphur and calcium treatments

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ABSTRACT

A fresh powder-like Pt/Al_2O_3 diesel oxidation catalyst was treated with sulphur (S–), sulphur–water (SW–), calcium–water (Ca–), sulphur–calcium–water (SCa–), and water (W–). BET, TEM–EDS, XPS, ICP-OES, AAS analyses and catalytic activity tests were used to find the effect of sulphur, calcium and water on the Pt/Al_2O_3 catalyst and its performance. Based on the ICP-OES and EDS results, sulphur was found to accumulate on the surface, whenever it was used in the pretreatments. Calcium was found in a very small amount on the Ca- and SCa-treated Pt/Al_2O_3 catalysts according to AAS and EDS results. For all the cases, the specific surface area was decreased after pretreatment. As expected, for the S- and SW-treated Pt/Al_2O_3 catalysts the light-off temperatures for CO and propene were higher compared to the corresponding fresh catalyst. Ca-, SCa-, and W-treated Pt/Al_2O_3 catalysts had almost the same light-off temperatures of CO and C_3H_6 than the fresh catalyst, instead. Based on the TEM–EDS results, the particle size of Pt and alumina washcoat microstructure was found to be unchanged after all the pretreatments. The pronounced deactivation is explained with sulphates formation on the active sites and with a decrease in the specific surface area.

1. Introduction

New innovative solutions for emission reduction to fulfil the stringently regulated automotive exhaust gas emissions according to standards like Euro 5 (September 1, 2009) and further Euro 6 (September 1, 2014) as well as Kyoto Protocol regarding CO_2 emissions are required. Therefore, engine solutions in automobiles must be improved to conform to the requirements. One solution for diesel cars is the use of diesel oxidation catalysts (DOCs). Biofuels and fuels with low sulphur content ($<$10 ppm, beginning in 2010 in EU [1]) have also recently obtained increasing attention.

Unfortunately, impurities originating from fuels and typical chemical additives in the automotive lubricant oils such as phosphorus (P), calcium (Ca) and magnesium (Mg) can adversely affect the catalyst by contaminating the catalyst surface [2]. In addition, particulate matters (PM) in diesel emissions can also have a deactivating effect on the catalyst. PM has been analysed to contain elemental carbon ($\approx$31%), sulphates and moisture ($\approx$14%), unburnt fuel ($\approx$7%) and lubricant oil ($\approx$40%) as well as remainings which consist of metals and other substances [3].

Contaminants like phosphorus, zinc (Zn) and calcium are deposited on the catalyst surface, blocking the active sites. Zn and Ca remain in the external layer of the catalyst, whereas P is adsorbed on the washcoats and interacts with washcoat such as cerium oxide and alumina forming phosphates [4]. This effect leads to a decline in the catalyst activity over time. Deactivation of automotive exhaust gas catalysts by poisons or impurities can involve changes in the morphological, structural, and electronical properties of the catalyst [5].

To find out information concerning the poisoning of three-way catalysts (TWC), or DOCs, several papers have been published to examine the role of engine-oil derived catalyst poisons. For instance, phosphorus on the washcoat compound has lead to the formation of aluminium and cerium phosphates [6–8] causing the deactivation of the TWC-based catalyst. Sulphur has also known to have deactivating role in automotive exhaust gas purification. Already, a small amount of sulphur (1 ppm) has been observed to deactivate Pd-based TWC catalysts [9]. Also, both Pd- and Pt-based [10–12] DOC catalysts have been found to deactivate due to the presence of sulphur.

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Few studies are related to the combined effects of calcium and phosphorus [13,14]. Interestingly, the addition of calcium to a phosphorus-poisoned catalyst was found to reduce the poisoning effects of phosphorus by forming calcium phosphates [13,14] and it is even reported to have a regenerating effect [14,15]. Andersson et al. have analysed commercial diesel oxidation catalysts with SEM–EDS and found compositions of calcium, with phosphorus and sulphur, such as calcium sulphate ($CaSO_4$) and calcium phosphate ($Ca_3(PO_4)_2$) on the washcoat surface [12].

However, the role of calcium as an individual catalyst poison is discussed in relatively few studies and the results reported are quite controversial. For instance, Kröger et al. have found in their studies that calcium has a deactivating effect on the commercial Rh/Al_2O_3/OSC exhaust gas catalyst [14]. Yue et al. have noticed that calcium has promotional effect on the Pd/Ce–Zr/Al_2O_3 catalyst during methane combustion [16], instead.

In the present work, the chemical deactivation of Pt-containing catalysts is studied. The individual and combined effects of sulphur, calcium and water have been examined. The purpose is to obtain new information on the behaviour of calcium on the Pt/Al_2O_3 diesel oxidation catalyst. Therefore, the catalyst powders poisoned with SO_2 (S−), $SO_2 + H_2O$ (SW−), $Ca + H_2O$ (Ca−), $SO_2 + Ca + H_2O$ (SCa−), and H_2O (W−) were studied by several characterization techniques in order to understand the poisoning-induced changes in the washcoat, the combined effects of S, Ca and water on the catalytic activity, as well as the influence of simultaneous poisoning.

2. Experimental

2.1. Catalyst samples

The catalysts investigated in this study were diesel oxidation catalysts (DOCs) provided by Ecocat Oy. In the studied catalyst material the nominal content of Pt supported on γ-Al_2O_3 was 4 wt%.

2.2. Sulphur and calcium pretreatments

Samples of the fresh Pt/Al_2O_3 catalyst were subjected to a number of different aging conditions in a laboratory scale flow reactor set-up. The samples were placed in a quartz-tube, with a surrounding electrical heating furnace, connected to mass flow controllers. Water was added to the reactor by injecting deionized water into the gas stream while it was passing the heated zone. The aging atmosphere comprises gaseous SO_2 (S−), $SO_2 + H_2O$ (SW−), $Ca + H_2O$ (Ca−), $SO_2 + Ca + H_2O$ (SCa−), or H_2O (W−). The poisoning gas mixtures contained 100 ppm of SO_2, 10 vol.% of H_2O, and 10 vol.% air, balanced with N_2. In the Ca- and SCa-treatments the aqueous salt solution of $Ca(NO_3)_2 \cdot 4H_2O$ was used as a source of calcium for the catalyst powders. The concentration of $Ca(NO_3)_2 \cdot 4H_2O$ inlet solution was 0.17 M.

The poisoning procedure was done by increasing the temperature of the catalyst from room temperature up to 400 °C with a linear heating rate of 10 °C/min in nitrogen and air flow. Then the catalyst was exposed for 5 h to the poisoning gas mixture. After the poisoning treatment, the catalyst was cooled down under nitrogen and air flow.

2.3. Characterization

2.3.1. Specific surface area

The specific surface areas of the catalysts samples were characterized as fresh and after the S-, SW-, Ca-, SCa-, and W-treatments. Before and after the treatments the specific surface area of the samples was determined by nitrogen adsorption at −196 °C with a Micrometrics ASAP 2020 analyser. Specific surface area [m^2/g] was determined according to the BET theory.

2.3.2. Sulphur and calcium analyses

The total sulphur and platinum contents [wt%] of the S-, SCa- and SW-treated Pt/Al_2O_3 catalysts were determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 5300DV). The total content of calcium [wt%] in the Ca- and SCa-treated Pt/Al_2O_3 catalysts was analysed by AAS (Perkin Elmer 4100 AAS) using air-acetylene flame. In both methods the samples were diluted by aqua regis (king water) before analyses.

2.3.3. Electron microscopy

The TEM measurements were carried out in analytical transmission electron microscope (TEM), JEM 2010 from Jeol (Tokyo, Japan), operated at 200 kV and equipped with Noran Vantage energy-dispersive spectrometer (EDS). TEM samples were prepared from catalyst powder by crushing it between glass slides. The crushed powder was dispersed onto a holey carbon-covered Cu grid with ethanol.

2.3.4. Chemical states of surface compounds

The concentrations and chemical states of the samples were analysed using X-ray photoelectron spectroscopy (XPS, SSX-100). Small amount of a catalyst was pressed into a piece of indium. This provided a convenient method to transfer the sample into the system and take care of charge compensation during the measurement.

2.4. Catalytic activity measurements

Catalytic activity was measured by using laboratory scale light-off experiments. The dry lean gas mixture contained 500 ppm CO, 300 ppm C_3H_6, and 12 vol.% air, balanced with N_2. The total gas flow was 1 dm^3/min. 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 in order to prevent the agglomeration of the sample, and further, to prevent the diffusional effects in the catalyst bed. The sample with quartz sand was placed in the reactor tube with a support of quartz wool. The gas flows were controlled by mass flow controllers. 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^{TM} FT-IR gas analyser. Oxygen concentration was determined by using a paramagnetic oxygen analyser (ABB Advanced Optima) [10].

3. Results

3.1. The effect of pretreatment on catalyst surface area

As can be seen in Fig. 1 all the pretreatments have an effect on the specific surface area of the catalyst. When compared to the fresh catalyst, the sulphur-treated Pt/Al_2O_3 catalyst lost around 15% of its specific surface area. For the other pretreatments studied, the decrease in surface area compared to a fresh catalyst was around 7%, 8%, 11%, and 12% for the W-, SW-, Ca-, and SCa-treated Pt/Al_2O_3 catalysts, respectively. Therefore, the loss in specific surface area by sulphur is reduced when water or calcium is present on the pretreatment gas flow.

3.2. The total content of platinum, sulphur and calcium in Pt/Al_2O_3

According to the ICP-OES results, sulphur had contaminated the Pt/Al_2O_3 catalyst during the 5 h pretreatment at 400 °C. The sulphur content of the S-, SW-, and SCa-treated Pt/Al_2O_3 catalysts

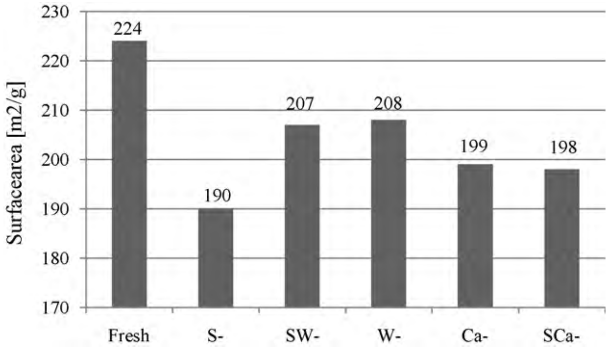

Fig. 1. The specific surface area for the fresh, SO_2 (S–), $SO_2 + H_2O$ (SW–), H_2O (W–), Ca + H_2O (Ca–), and SO_2 + Ca + H_2O (SCa–) treated Pt/Al_2O_3 catalysts.

Table 1
The total content of Pt and sulphur [wt%] by ICP-OES for the SO_2 (S–), SO_2+H_2O (SW–), and SO_2+Ca+H_2O (SCa–) treated Pt/Al_2O_3 catalysts. The total content of calcium [wt%] by AAS for the Ca+H_2O (Ca–), and SO_2+Ca+H_2O (SCa–) treated Pt/Al_2O_3 catalysts.

Compound/pretreatment	Ca– [wt%]	S– [wt%]	SW– [wt%]	SCa– [wt%]
Pt	–	3.4	3.5	3.9
S	–	1.6	1.4	1.4
Ca	<0.1	–	–	<0.1

is given in Table 1. The pretreatment procedure did not have any effect on the amount of platinum.

Based on the AAS results a very small amount of calcium had contaminated the Ca- and SCa-treated Pt/Al_2O_3 catalysts. The calcium content of both the Ca- and SCa-treated catalysts is given in Table 1.

3.3. Microstructural analyses

In the elemental analyses (EDS) both sulphur and calcium were detected. The contents of sulphur were from 0.2 wt% to 0.9 wt% in different areas of the Pt/Al_2O_3 catalyst. The amount of calcium was from 0.2 wt% to 0.4 wt% in the Ca-treated catalyst. In the SCa-treated catalyst the analyses of calcium showed values below 0.2 wt% and thus the reliable measurement of the content was not possible with the EDS. Regardless of the treatment the microstructural analyses revealed no changes in the alumina washcoat or in the size of platinum particles. TEM-images of the fresh and SCa-treated Pt/Al_2O_3 catalyst powders are presented in Fig. 2.

3.4. Surface analysis

The binding energy scale was calibrated so that the C1 line was at 284.5 eV. The binding energy of platinum was between 315.7 eV and 316.3 eV in all the samples pointing towards platinum oxide. Sulphur was found between 168.1 eV and 168.9 eV which suggests that there are sulphates species on the surface. Calcium appeared at 347.0 eV which is typical for calcium carbonate. The relative percentages of Pt, Al, C, O, Ca, and S detected at the surface layer are given in Table 2. In the quantitative analysis, relative sensitivity factors for the system were used after Shirley background subtraction. The carbon signal was not included in the quantitative analysis.

Table 2
The relative percentages of Pt, Ca, S, Al, and O on the fresh, SO_2 (S–), SO_2+H_2O (SW–), H_2O (W–), Ca+H_2O (Ca–), and SO_2+Ca+H_2O (SCa–) treated Pt/Al_2O_3 catalysts' surface layers, measured by XPS.

Compound/ pretreatment	Fresh [%]	S– [%]	SW– [%]	W– [%]	Ca– [%]	SCa– [%]
Pt	4.8	3.2	3.1	3.1	3.7	2.7
Ca	–	–	–	–	0.3	0.2
S	–	1.6	1.0	–	–	1.2
Al	36.2	29.2	32.9	31.9	23	25.9
O	59	66	63	65	73	70

3.5. The effect of pretreatments on catalytic activity

The model gas composition containing CO, C_3H_6, and O_2 was chosen to illustrate the simplified diesel exhaust gas composition. Catalytic performance of automotive exhaust catalysts is typically described by some parameters such as light-off temperature (T^{50} value). This is defined as the temperature value that involves conversion of 50% for a given reactant [17]. As can be seen in Fig. 3, differences between the pretreatment methods for the Pt/Al_2O_3 catalyst were relatively small. Based on light-off temperatures for CO and C_3H_6 the effect of pretreatment can be classified as follows: SCa $\sim$ Ca $\sim$ W $<$ fresh $<$ SW $<$ S.

In all cases, C_3H_6 oxidation occurred after CO oxidation as observed in Fig. 4. The reason for this phenomenon is that just after the CO molecules are removed from the metallic surfaces the presence of CO significantly suppresses the oxidation of C_3H_6 [18,19]. The extent of suppression depends on the concentration of CO in the gas feed, since CO was adsorbed strongly on Pt and inhibited its oxidative activity [20].

The relatively high CO conversion for the S-treated Pt/Al_2O_3 catalyst below the light-off temperature can be explained by a strong CO adsorption. Based on activity results the S-treated Pt/Al_2O_3 was deactivating more than the other studied catalysts.

4. Discussion

According to the results presented above, both sulphur and calcium accumulated during the pretreatments on the Pt/Al_2O_3 catalyst. However, according to the TEM-analyses, the washcoat microstructure and particle size were unchanged. Therefore, it is

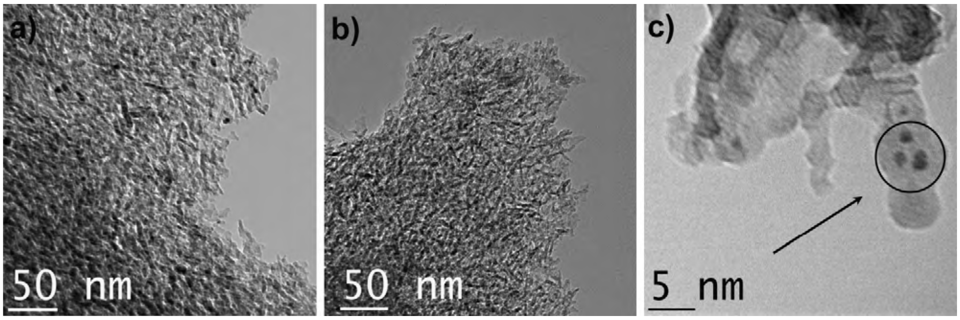

Fig. 2. (a) The microstructure of the fresh Pt/Al_2O_3 catalyst and (b) the SCa-treated Pt/Al_2O_3 catalyst as well as (c) Pt-particles presented with arrow and circle in the SCa-treated Pt/Al_2O_3 catalyst.

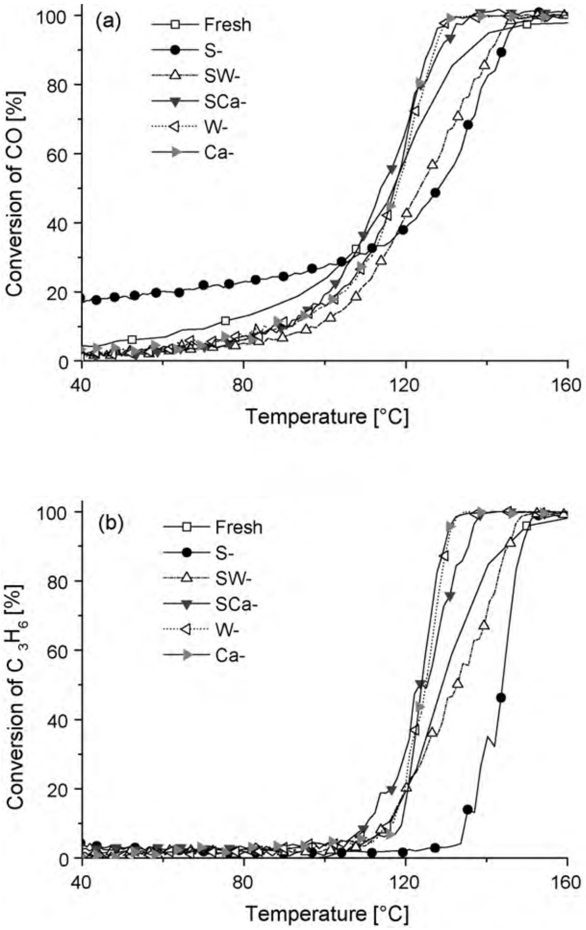

Fig. 3. The conversion curves of (a) CO and (b) C_3H_6 in the reaction of CO + C_3H_6 + O_2 for the fresh, SO_2 (S–), SO_2 + H_2O (SW–), SO_2 + Ca + H_2O (SCa–), H_2O (W–), and Ca + H_2O (Ca–) treated Pt/Al_2O_3 catalysts. Gas mixture contained 500 ppm CO, 300 ppm C_3H_6, and 12 vol.% air, balanced with N_2.

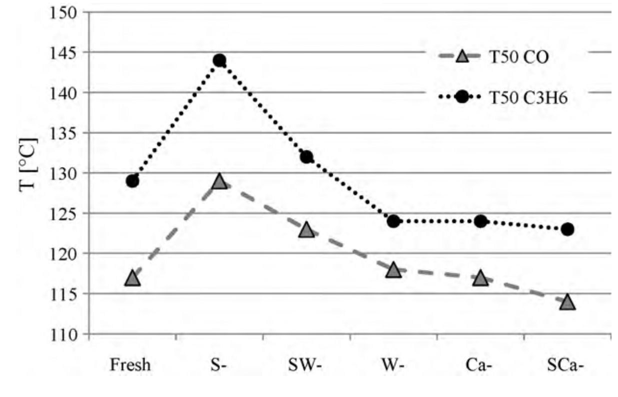

Fig. 4. The light-off temperature (T^{50} value) of the CO and C_3H_6 in the reaction of CO + C_3H_6 + O_2 for the fresh, SO_2 (S–), SO_2 + H_2O (SW–), SO_2 + Ca + H_2O (SCa–), H_2O (W–), and Ca + H_2O (Ca–) treated Pt/Al_2O_3 catalysts. Gas mixture contained 500 ppm CO, 300 ppm C_3H_6, and 12 vol.% air, balanced with N_2.

interesting to notice that for the W-, Ca- and SCa-treated Pt/Al_2O_3 catalysts the loss in specific surface area did not decrease the catalytic activity. For the S- and SW-treated Pt/Al_2O_3 catalysts, the activity to oxidise CO and propene was decreased, instead.

Thus, as is already well-know the reason why sulphur deactivates the catalyst is the formation of $Al_2(SO_4)_3$ on the Pt/Al_2O_3 catalyst [17,21,22]. Sulphates were also observed in our XPS studies. According to Galisteo et al. $Al_2(SO_4)_3$ modifies the acidic properties of the support and the electronic properties of the platinum particles. Galisteo et al. reported also that new Brønsted acid sites are formed and, moreover, the capacity of the Pt particles to chemisorb CO and O_2, the latter as strongly chemisorbed O species, is seriously deteriorated [17]. In addition, Yao et al. have proposed that on γ-Al_2O_3 the surface sulphates are formed in the presence of Pt at around 200 °C and this decreases the associative chemisorptions of propene on platinum in Pt/γ-Al_2O_3 catalysts [23]. Skoglundh et al. have made a conclusion based on their results that the main reaction pathway for propene oxidation over a Pt/Al_2O_3 catalyst proceeds via platinum. They proposed that the inhibiting effect of SO_2 below the light-off temperature (around 200 °C) on the Pt/Al_2O_3 catalyst is due to the blocking effect of the active Pt sites [24].

As can be seen in our activity results, the water-treatment improves to some extent the effect of sulphur deactivation. Kwon et al. have found that CO and C_3H_6 oxidation over a commercial TWC occurs at lower temperatures when water is present in the reaction gas mixture. The reason for this phenomenon is the reaction between CO and OH from water forming carbonate groups on the catalyst surface [25]. Thus, based on the above observations and our own results the reason why water treated catalysts (W–, SW–, Ca– and SCa–) inhibit the effect of sulphur deactivation is probably due to OH-groups originating from water which inhibits the formation of surface sulphates. However, further studies are needed to prove this assumption.

As can be observed from the results presented, the effect of accumulated calcium was relatively small. Based on the thermodynamic calculations, the formation of $CaSO_4$ is more favourable even at room temperature than the formation of $Al_2(SO_4)_3$. In fact, Andersson et al. have deduced in their SEM–EDS results that the formation of $CaSO_4$ is possible when sulphur and calcium have contaminated the DOC washcoat supported by a cordierite monolith [12]. In our case, sulphur and calcium were found to disperse in SEM experiments evenly on the powder-like SCa-treated Pt/Al_2O_3 catalyst. Thus, there was no clear sign for sulphur and calcium overlap. However, it is still possible that calcium probably inhibits the formation of surface sulphates during the SCa-treatment.

5. Conclusion

It is clear that the sulphur poisoning treatments cause deactivation of the S–Pt/Al_2O_3 catalyst by the formation of sulphates and by decreasing the specific surface area, not by sintering and Pt particle size increase. Thus, the number of active sites for the CO and C_3H_6 oxidation is lower for sulphur-treated catalyst compared to the other treated catalysts. The effect of water needs further studies to explain why it to some extent improved the activity of sulphated Pt/Al_2O_3 catalyst. The amount of calcium found on the calcium- and sulphur–calcium-treated catalyst samples was relatively small. Still, calcium seems to have a some effect on the activity of the SCa-treated Pt/Al_2O_3 catalyst.

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