



Deactivation of Pt/SiO₂-ZrO₂ diesel oxidation catalysts by sulphur, phosphorus and their combinations

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ABSTRACT

The impact of sulphur, phosphorus and water and their co-exposure on a monolith-type Pt/SiO₂-ZrO₂ diesel oxidation catalyst was investigated. The accelerated laboratory-scale sulphur treatments for Pt/SiO₂-ZrO₂ were done with and without water (S- and SW-treatments, respectively) at 400 °C. Similarly, the phosphorus treatment with water (PW-treatment) as well as the co-exposure of phosphorus, sulphur and water (PSW-treatment) were also done to find out the interactions between the impurities. The studied catalysts were characterized by using several techniques and the activity of the catalyst was tested in lean diesel exhaust gas conditions. Based on the XPS and the elemental analysis, more phosphorus was adsorbed on the Pt/SiO₂-ZrO₂ catalyst than sulphur. Sulphur, in the presence and absence of water, was found to have a negligible effect on the CO and C₃H₆ light-off temperatures (T₉₀) over the fresh Pt/SiO₂-ZrO₂, whereas the T₉₀ values of CO and C₃H₆ increased by 30–45 °C as a result of the PW-treatment and by 15–35 °C after the PSW-treatment. Based on the Transmission electron microscope (TEM) analyses, no morphological changes on the Pt/SiO₂-ZrO₂ surfaces were observed due to the phosphorus treatment. Therefore, the reason for the lower activity after the PW-treatment could be the formation of phosphates that are decreasing the specific surface area of the catalyst, blocking the accessibility of the reactants to the catalyst pores and active sites. However, it is worth noting that sulphur decreased the amount of adsorbed phosphorus and thus, inhibited the poisoning effect of phosphorus.

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1. Introduction

The diesel oxidation catalyst (DOC) is one of the most important parts of diesel exhaust gas after-treatment systems along with the diesel particulate filter (DPF) and the selective catalytic reduction (SCR) unit. The role of DOC is to oxidize harmful emissions such as carbon monoxide (CO), unburned hydrocarbons (UHCs) and soluble organic fraction (SOF) of particulates. In addition, the DOC has the

ability to oxidize nitrogen monoxide (NO) to nitrogen dioxide (NO₂) which improves the removal efficiency of NO_x in the following SCR unit. The European Union (EU) has set strict regulations towards the emissions from mobile sources, including light-duty vehicles [1]. To fulfil the EU emission standards, the high performance of the emission purification units are required in the exhaust gas treatment systems are needed. To achieve high activity over a long-term period, the DOC needs to be resistant towards chemical impurities e.g. sulphur and phosphorus present in the exhaust gas stream. Sulphur is generally present in the form of sulphur dioxide (SO₂) in the exhaust of coal and petroleum derivatives (gasoline, diesel) combustion, and fuel used in shipping [2,3]. Phosphorus compounds can be originated e.g. from biofuels and lubricant oils used [4,5]. Both sulphur and phosphorus have been widely reported to decrease the activity of platinum on aluminium oxide (Pt/Al₂O₃) catalysts [6–10] which are the most used and the most efficient materials in DOCs [4,7,8,11]. Thus, there is a need for novel diesel oxidation

Abbreviations: SW, sulphur + water; PW, phosphorus + water; PSW, phosphorus + sulphur + water.

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catalysts especially for marine and stationary applications that use biofuels and lubricant oils, which may contain impurities such as phosphorus and sulphur.

One option to substitute the commonly used Pt/Al₂O₃ catalysts is the Pt/SiO₂-ZrO₂ catalyst which has also shown high activity e.g. in CO oxidation [12]. Silicon dioxide (SiO₂) was found to have well controlled and known properties e.g. small particle size, high specific surface area and high porosity as a support material [13,14]. In addition, SiO₂ is reported to be inert to sulphur poisoning [15–17] which is due to the lack of basicity of the material [12]. The addition of zirconium dioxide (ZrO₂) on a SiO₂ support is reported to increase the Pt dispersion and hydrothermal stability of the catalyst [9,12]. Furthermore, the Pt/SiO₂-ZrO₂ catalysts are reported to have a higher activity in CO oxidation than the Pt/SiO₂ based catalysts [12]. These attractive features make the Pt/SiO₂-ZrO₂ catalyst a promising material for DOC applications. The effect of sulphur on the Pt/SiO₂-ZrO₂ catalyst has been investigated in a few studies [9,12]. According to Kim et al. [12], sulphur increases the CO light-off temperature over the Pt/SiO₂-ZrO₂ catalyst by ~40 °C, but still the Pt/SiO₂-ZrO₂ catalyst was found to be more resistant towards SO₂ compared to the Pt/Al₂O₃ and Pt/SiO₂ catalysts. In Park et al. [9], it has been presented that sulphur decreases slightly the activity of the Pt/SiO₂-ZrO₂ catalyst in the NO reduction. Based on our best knowledge, the effect of phosphorus on the SiO₂-ZrO₂ based catalysts has not yet been investigated earlier. Thus, the impact of both sulphur and phosphorus and their co-effect on the Pt/SiO₂-ZrO₂ catalysts are studied and reported in this study.

The aim of this work was to find out the effects of sulphur, phosphorus and water and their co-exposure on the Pt/SiO₂-ZrO₂ catalyst morphology and its performance. The treatment with gaseous SO₂ for the Pt/SiO₂-ZrO₂ catalyst was done at 400 °C in the absence and presence of water (denoted as S- and SW-treatments, respectively). The water and phosphorus treatments (W- and PW-treatments, respectively) as well as the co-exposure of phosphorus and sulphur (PSW-treatment) were also studied at the same conditions. Several characterization techniques such as XPS, DRIFTS, FESEM, TEM, XRD, BET/BJH and NO-TPD have been used to identify the morphological and chemical changes on the catalyst surface caused by the treatments. The activity of fresh, S-, W-, SW-, PW-, and PSW-treated catalysts was studied using a model diesel exhaust gas flow (CO + C₃H₆ + NO + H₂O + O₂ + N₂).

2. Experimental

2.1. Studied materials

The studied materials were two metallic monoliths provided by Dinex Ecocat Oy. The materials contained 0 or 0.5 wt-% of platinum as the active material on the silicon-zirconium oxide support (marked as SiO₂-ZrO₂ and Pt/SiO₂-ZrO₂, respectively). The support material was silicon-zirconium mixed oxide (80 wt-%) with SiO₂ as a binder (20 wt-%) that resulted in the SiO₂/ZrO₂ weight ratio of 30/70 in the final coating.

2.2. Treatments

The monolith-type samples containing the SiO₂-ZrO₂ support or the Pt/SiO₂-ZrO₂ catalyst were placed in a vertically positioned tubular quartz reactor. The diameter of the sample was 10 mm and length 37 mm. The total flow was kept constant (1 dm³/min) and the gas hourly space velocity (GHSV) was 21,000 h⁻¹. The reactor was heated to 400 °C (with the heating rate of 10 °C/min) under a gas mixture of 2 vol-% of O₂, and balance N₂. Then, the laboratory-scale accelerated treatments using water (H₂O), sulphur dioxide (SO₂) or aqueous ammonium phosphate ((NH₄)₂HPO₄) for 5 h at

400 °C and the mixtures of these were carried out. These treatments were done in the gas phase according to the following compositions:

1. S-treatment: 100 ppm SO₂, 10% air, and balance N₂
2. W-treatment: 10% H₂O, 10% air, and balance N₂
3. SW-treatment: 100 ppm SO₂, 10% H₂O, 10% air, and balance N₂
4. PW-treatment: aqueous solution of phosphorus containing 10% H₂O with c((NH₄)₂HPO₄) = 0.13 M, 10% air, and balance N₂
5. PSW-treatment: aqueous solution of phosphorus containing 10% H₂O with c((NH₄)₂HPO₄) = 0.13 M, 100 ppm SO₂, 10% air, and balance N₂

2.3. Characterizations

X-ray photoelectron spectroscopy (XPS) was used for characterizing the chemical states and concentrations of different elements on the catalyst and support. The spectrometer (Surface Science Laboratories SSX-100) was equipped with a monochromatic Al K_α X-ray beam and had a base pressure of 5 × 10⁻¹⁰ mbar. The samples were pressed as a powder form on the indium films prior to placing them into the measurement chamber. In order to prevent charging of the samples during measurements, an electron flood gun was used. The Shirley background subtraction was employed before fitting the Gauss-Lorentz functions to the experimental data. The binding energy values in the acquired spectra were calibrated by setting carbon 1s line at 284.6 eV. Carbon and indium were excluded from the compositional analysis.

The nature of compounds adsorbed on the catalyst surface were analysed using the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The experiments were carried out using the Bruker Vertex V80 vacuum FTIR spectrometer with a Harrick Praying Mantis™ DRIFT unit and an environmental cell. The sample was measured at 25 °C in atmospheric pressure using a mirror as a reference. The DRIFT spectra were recorded in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ with 32 spectra in each measurement.

The structure of the fresh and treated catalysts and supports was studied by a field emission scanning electron microscope (FESEM, Zeiss ULTRaplus) equipped with an energy dispersive X-ray spectrometer (EDS, INCA Energy 350 with INCAx-act silicon drift detector, Oxford Instruments). In addition, a transmission electron microscope (TEM, Jeol JEM-2020) equipped with an EDS (Noran Vantage with Si(Li) detector, Thermo Scientific) was used. The cross-sectional samples for FESEM studies were prepared with a conventional metallographic sample preparation technique including moulding of the monolith in resin, grinding and polishing and finally carbon coating to avoid sample charging. In the TEM studies, powdered samples or cross-sectional samples were used. The powdered TEM samples were mixed with ethanol and dispersed onto a copper grid with a holey carbon film. The cross-sectional TEM samples were prepared by placing the two small pieces of the monolith on a titanium grid by carbon glue and followed by thinning the grid with a dimple grinder (Model 656, Gatan Inc.) and a precision ion polishing system (PIPS, Model 691, Gatan Inc.).

The structure of scraped catalyst powders was also studied using an X-ray diffractometer (XRD, Empyrean, PANalytical with the PIXcel^{3D} detector using Cu K_α radiation). Crystallite sizes were determined from the XRD patterns with the aid of the HighScore plus software based on the Scherrer equation and phases were identified by using the database (PDF-4+ 2014) from International Centre for Diffraction Data (ICDD).

The determination of specific surface areas (S_{BET}), pore sizes and pore volumes of the fresh, S-, W-, SW-, PW-, and PSW-treated Pt/SiO₂-ZrO₂ catalysts were done by N₂ adsorption at -196 °C

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