Sulfation of Pt/MnCeAl catalyst for soot oxidation

Master's Thesis in Materials Chemistry and Nanotechnology

ANNA-MARIA DIMITRIEVA

Department of Material Science and Engineering,
Tsinghua University
Department of Chemistry and Chemical Engineering,
Chalmers University of Technology
Gothenburg, Sweden 2015
Master's Thesis 2015:06

Abstract

The aim of this project was to investigate the sulfur stability of Pt/MnCeAl catalysts for soot oxidation. The Pt/MnCeAl catalysts were prepared in different conditions; fresh, sulfated in wet conditions, sulfated in dry conditions and impregnated with sulfuric acid. Thermal ageing and sulfur poisoning treatments were performed to examine the stability of the catalysts. The catalysts were characterized and the activities were measured with different techniques. The catalyst in wet conditions (PMCA-HS) showed a better SO_2 conversion and the least severe sulfur poisoning. This may indicate that in wet conditions the catalyst adsorbed less sulfur than in dry conditions, although it converted more SO_2 to SO_3. However, no conclusions could be drawn regarding which type of sulfates that were formed, and whether they were bulk or dispersed surface sulfates. The catalyst in wet conditions showed the lowest T_{50}, which means it had the highest soot oxidation at a lower temperature. The conclusions that could be drawn from the experiments were that the PMCA-HS sample is a promising catalyst for soot oxidation, it exhibits a good thermal stability and resistance to sulfur dioxide, however more research needs to be done.

Keywords

Pt/MnO_x–CeO_2-Al_2O_3; PMCA; soot oxidation; sulfur poisoning; sulfur dioxide; NO oxidation: thermal ageing

Table of Contents

1. Introduction

1.1 Introduction and background

One of the most common everyday toxins encountered by people is diesel fuel and its exhaust. As the population grows around the world so does the reliance on mass transportation such as cars, trucks and buses, commercial vehicle, different types of machinery for construction, farming, mining etc. Many of them rely on diesel fuel. Diesel exhaust is 100 times more toxic than gasoline exhaust when compared on an equal horsepower basis. Continued exposure to diesel exhaust can lead to high acute and chronic respiratory disease morbidity. The mixture of diesel exhaust is complex; studies show it has various deleterious effects in humans and damages the environment [1]. China, and in particular the capital city Beijing, is having immense problems with air quality, smog occurs more frequently than ever. Among all the pollutants that cause smog, a substantial part comes from automotive exhaust [2]. The project is focused on diesel emissions control, to trap the soot particles, i.e. unburned carbon particles, from diesel engine by using a catalyst. If the catalyst turns out to be successful it could be used to reduce the particulates emission and improve the air quality, thus improve the living standard. With China being a large country with a huge population this would make a big impact on the people living there and most likely increase the health among the population. The particulates from diesel exhaust consist of toxic carbonaceous soot particles and other molecular compounds. In both the EU and the US this has lead to formulation of restrictive legislation which has lead to efforts reducing the soot emission from diesel [3]. An efficient way of elimination of soot particles is trapping in filter followed by oxidation. For un-catalyzed soot filter the oxidation of the diesel exhaust occurs at high temperatures, around 600°C, this is much higher temperature than the exhaust temperature from the diesel vehicles [4]. Therefore a catalyst is needed and among the investigated platinum shows a high level of catalytic activity, NO is oxidized to NO_2 in the exhaust gas. This has a significant effect in the oxidation of soot. One disadvantage with platinum is its high cost therefore an affordable alternative is needed [5].

1.2 Purpose

The project focuses on catalysis for soot oxidation and aims to find the best condition for sulfated Pt/MnCeAl catalysts for this purpose. It should preferably be a cheap method, and work properly at the thermal conditions.

1.3 Limitations

Since the project is time limited the focus will be on the suggested materials and not test different combinations of other materials. Also focus only on diesel exhausts and not on other types of exhausts from other fuels.

1.4 Clarification of the issue

The background for the project is that in diesel emissions there are particulates that have a harmful effect on humans. As mentioned, many of the carbonaceous soot particles and other small molecular compounds are toxic. An efficient way to eliminate soot particles is using a catalytic trap followed by oxidation. However, the oxidation occurs around 600ºC in a non-catalyzed soot filter, which is higher than the exhaust temperature of diesel vehicles. The use of a catalytic trap performing both filtration and catalytic combustion of soot is highly desired. In such catalytic applications platinum exhibits a high level of catalytic activity by oxidizing nitric oxide in the exhaust gas to nitric dioxide. The nitric dioxide has remarkable effect on the oxidation of soot but the cost of Pt is very high. By mixing manganese oxide and cerium oxide, MnO_x–CeO_2, high soot oxidation activities can be achieved in both excess oxygen, and nitric oxide with oxygen. This mixture of oxides has a reasonable price. It is also found that introducing aluminum oxide to the MnOx–CeO_2 mixture the thermal stability increases. However, it is known that cerium will react with sulfur dioxide over a wide range of temperatures when exposed even to small amounts of sulfur, hence the performance of cerium oxide will be significantly reduced. Therefore it is important to study in which condition the sulfur poisoned catalyst performs best [5].

This project is based on previous work at Tsinghua University. The previous work was focused on MnO_x–CeO_2 mixed oxides introduced to Pt/Al_2O_3 catalyst containing half the amount of platinum as compared to a Pt/Al_2O_3 reference. The introduction of MnO_x–CeO_2 mixed oxides was made to investigate if it is possible to achieve an improvement of the activity for soot oxidation by providing abundant NO_2 at low temperatures. The stability of the catalysts was examined by performing thermal ageing and sulfur poisoning treatments. The catalysts were also characterized by a series of structural and surface property measurements in order to explore possible modification mechanisms of the mixed oxides and different deactivation mechanisms. The results show that the modified catalyst exhibited a high thermal stability with an increase in T_{50} (the temperature at which 50% of the soot is oxidized) after calcination in air at 800 °C for 100 h, which is attributed to of the stabilization effect of alumina for MnO_x–CeO_2. High resistance to sulfur dioxide was also shown. The partially replacement of platinum with MnO_x–CeO_2 mixed oxides seems to be a promising way to lower the cost of soot oxidation catalysts [5]. In this project the Pt/MnO_x–CeO_2–Al_2O_3 catalyst will be further investigated in both wet and dry conditions. In the former study the sulfur resistance was evaluated in a dry airflow containing 100 ppm SO_2. The real diesel exhaust contains about 10% water. Hence, the sulfur resistance of the catalyst in wet condition should be evaluated.

2. Method

To be able to fulfill the purpose of this project a literature study is necessary to gain knowledge within the field and knowledge about the different materials, as well as information about the different techniques that will be used. The literature study will mainly consist of searches on various online databases for scientific journals, articles and books.

For the experimental part the equipment used will be those available at the university, such as Fourier transform infrared spectroscopy (FTIR), temperature programmed oxidation (TPO), temperature programmed reduction (TPR), Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The material that will be used for the catalyst is platinum (Pt), manganese oxide (MnO_x), cerium oxide (CeO_2) and aluminum oxide ($Al_2O_{3.}$). The experimental part will also follow the previous work approach on the preparation of the catalysts with the required changes for this project.

3. Theory

In this section an introduction of catalysis and the different materials will be presented.

3.1 Catalysis

The definition of a catalyst is a substance that speeds up the chemical equilibrium between reactants and products. It does not change the reaction chemically or influencing the thermodynamic equilibrium of the process, it only improves the reaction time. During the reaction catalysts are usually not consumed, but the activity and/or selectivity can be decreased [6][7]. There are different types of catalysts, usually divided into heterogeneous and homogeneous. In this thesis the focus is on solid heterogeneous catalysts. Heterogeneous means that the catalyst is in a different phase than the reactants. Solid catalysts can be divided into three groups; supported metals, acid sites and/or basic sites. The preparation of metal supported catalyst is done through a metal (commonly a noble) being impregnated onto a porous material, often a metal oxide such as alumina or silica, with a suitable specific surface area or pore size distribution. Zeolites and alumina are examples of acid catalysts [7]. The heterogeneous catalyst has active sites, onto which one or several of the reactants are adsorbed. A wanted property of a catalyst is that the reactants adsorb strongly enough for a reaction to occur, but the product should be able to desorb [8].

The definition of selectivity is the rate at which the reactants convert into the desired products. The selectivity depends on different reaction parameters such as pressure, temperature of the catalyst and composition of the reactants. Activity on the other hand is the speed at which the equilibrium of the chemical reaction is reached. It can also be defined as the amount of reactants transformed into the desired product per unit of reactor volume or time [7]. The surface of the catalyst can have both acidic and basic sites that can interact. One of the sites can be dominant even if both are present. The definition of an acidic site is a site that can react with a base, and contrarily a basic site can react with an acid. Information about the strength of the sites can be obtained by temperature-programmed techniques, such as TPO and TPR (more about the techniques further down).

In catalysis the definition of poisoning is an impurity that reacts selectively with some active sites and by doing so stopping their activity. The main reasons for poisoning to occur are by a chemical reaction or by fouling (physical poisoning). In this thesis the poisoning will be due to a chemical reaction [7]. The catalytic cycle consist of 5 steps, first is the transportation of the reactants to the catalyst. The following steps are adsorption on the catalyst, product formation through reaction, desorption of product and transportation of product [8].

3.2 Platinum

Platinum is widely used as a catalyst; in catalytic converters (a converter that by catalyzing a redox reaction converts toxic pollutants in exhaust gas to less toxic pollutants [9]) platinum oxidizes carbon monoxide and hydrocarbons. The oxidation is most effective under oxygen-excess conditions. The advantages using platinum as a catalyst is that it has a high melting point, the interactions with poisons, such as sulfur compounds are limited to the metal surface and it is also efficiently recycled. Another advantage of platinum is that it usually does not become completely or irreversibly poisoned; the poisonous particles inhibit the catalyst. The disadvantage is the high cost [10].

3.3 Aluminum

Aluminum is the most abundant metal on earth, it mainly occurs in stable oxidizing environments even though it is reactive. Nitric acid and sulfuric acid can be stored in aluminum, the metal resists most acidic attacks. However, it dissolves in water environments and its oxide film is dissolved in alkaline solutions [11]. Alumina, Al_2O_3, is widely employed as a catalyst or support material The gamma alumina phase, γ-Al_2O_3, is highly porous and used in catalysis [12]. Alumina is inexpensive and is an alternative to lower the cost by lowering the amount of platinum needed when adding alumina. It is a common support for the vehicle exhaust purification [11]. γ-Al_2O_3 has a high surface area to volume ratio and is considered as the most promising advanced material for different applications, among others in catalysis [13].

3.4 Manganese

Manganese has a high melting point but is easily oxidized. Different oxidation states of MnO_x are powerful oxidizing agents; the most stable state for Mn is +2 [14]. Manganese is a recommended material as a oxidation catalyst for vehicle exhaust systems and for reducing nitric acid impurities [15]. MnO_x provide high specific surface area, the oxides are good material to use for carbon monoxide oxidation and decomposition of nitric oxide [16], [17].

3.5 Ceria

Ceria, also known as cerium dioxide, CeO_2, is a common material to use in catalytic converters in vehicle applications. The advantage of the oxide is it can provide oxygen without decomposition, in a combustion engine it can either release or take in oxygen in the exhaust stream. When combined with other catalysts, ceria is an effective material to reduce NO_x emissions and convert carbon monoxide to carbon dioxide. Another advantage is that it is inexpensive, combined with platinum it reduces the amount platinum needed for complete oxidation of NO_x. Ceria has a fluorite structure; in the ceria crystal the oxygen atoms are in the same plane. The structure allows rapid diffusion as a function of the number of oxygen vacancies. With an increase of vacancies the mobility of oxygen increases. This allows ceria to reduce or oxidize molecules. The catalytic activity of ceria is related to the number of oxygen vacancies. Reforming diesel fuel into carbon dioxide and hydrogen gas, ceria is a good alternative as a co-catalyst [18][19]. CeO_2 have a strong basicity and hence sulfur poisoning is an unavoidable problem, however at suitable conditions the sulfates can be removed in a regeneration process [20].

3.6 Manganese-cerium-aluminum mixed oxides with impregnation of platinum

MnO_x-CeO_2 mixed oxides prepared by a sol-gel method is chosen as a part of the catalytic material, the combination of the oxides is proven to be better for soot oxidation when compared with the individual oxides separately [20]. When incorporating manganese cations into the ceria lattice the oxygen storage capacity is significantly improved, as well as the surface mobility [21]. The mixed oxides have a high NO_2 storage capacity and a high NO oxidation activity. When manganese and cerium interact, the oxidation state of manganese increases. This may be the reason for that the mixed oxides perform better than each of the oxides do. However, when calcination temperature increases from 500 ºC to 800 ºC the BET surface area (BET is a method that is based on adsorption of gas on a surface, the amount adsorbed at a specific pressure makes it possible to determine the surface area [22]) is decreased severely. Sintering of MnO_x and CeO_2 crystallites occurs during the increase of the temperature (thermally ageing). This affects the NO oxidation and soot oxidation activities negatively due to restricted accessibility and reduced reactivity of active sites. By mixing Al_2O_3 with the mixed oxides the sintering is hindered (at least up to the temperatures used on) but the beneficial effects of the mixing MnO_x and CeO_2 is sustained.

With platinum is impregnated onto the MnO_x–CeO_2/Al_2O_3 mixed oxides, the catalytic activity remain high after the thermal ageing and sulfur poisoning. This is due to platinum having a high tolerance towards sulfur poisoning, and Al_2O_3 creating a diffusion barrier that decreases the thermally ageing effect on MnO_x–CeO_2 [20].

3.7 Sulfur as a catalyst poison

The catalytic activity of most transition metals is significantly reduced when sulfur compounds are present. It has been shown that bonding between sulfur and a metal is an essential factor of deactivation of supported metal catalysts. But sulfur do not only adsorb onto metals, it can also adsorb onto the support [23]. The adsorption of sulfur affects the catalytic properties; the catalyst is completely poisoned when the surface is saturated with adsorbed sulfur. When the surface is partially covered by sulfur compounds the catalyst is inhibited, partially or totally, and prevents reactants accessing the active sites [24].

3.8 Diesel exhaust

Diesel exhaust is composed of several toxic chemicals; among others sulfur dioxide, carbon monoxide, nitrogen oxides, unburned carbon particles (soot), hydrocarbons etc. Half of the particles in air pollution are estimated to come from exhaust from diesel engines [1]. An alternative for the removal of diesel particulate from vehicle exhaust gases is a catalytic trap, which is used in this project [25].

3.9 Catalytic trap

As mentioned before the particulates emitted by diesel engines are a severe problem, a promising approach to lowering the emissions is a catalytic trap. A catalytic trap is a particulate filter that can be used by itself or in conjunction with a catalyst. The filter is made of porous material that also is temperature resistant. To minimize the fuel consumption and decrease the pressure drop the filtration area should be as high as possible. When the emissions contain low amount of particles the catalytic trap works efficiently. However, used over time or with more particles in the emission, the filter tends to become clogged. This increase the exhaust backpressure and the efficiency of the engine is reduced, which leads to additional fuel consumption. By regenerating the filter the soot can be eliminated, but it cannot be done effectively by burning off the soot since the temperature is not high enough during normal driving conditions. Regeneration is most effective when the filter is combined with a catalyst that enhances the soot combustion [26].

4. Equipment

4.1 Rotary Evaporator

Rotary evaporation is a method of distillation; it is used to remove volatile solvents from a non-volatile/less volatile product. A source of heat is used at the bottom while rotating the sample to increase the effective surface area. In addition the pressure is reduced to lower the boiling point [27].

4.2 FT-IR

FT-IR is an infrared spectroscopy method and is an abbreviation for Fourier transform infrared spectroscopy. In infrared spectroscopy a sample is analyzed by IR radiation, some of the radiation will be absorbed by the sample and some transmitted. A spectrum is received which characterizes the molecular absorption and transmission of the specific sample. The spectrum is a molecular fingerprint, the absorption peaks corresponds to the frequencies of vibrations between the bonds of the atoms making up the material. Since different materials are a unique combination of atoms, different spectrums will be received for different compounds. With FT-IR it is possible to identify unknown materials, the consistency and quality of a sample and also the amount of the containing components. The size of the peaks in the spectrum indicates the amount of the different compounds in the material.

FT-IR uses an optical device that is called interferometer; it measures the frequencies simultaneously and produces a signal with all the information about the infrared frequencies. The measurement of the signal is very fast, only a few seconds. The analyzer needs a frequency spectrum in order to identify the sample. The frequency spectrum is a plot of the intensity at each separate frequency. With computational help the mathematical technique Fourier transformation is interpreting the frequencies and spectral information is received. Before the analysis starts a background spectrum is measured, usually it is done with no sample but in our experiments KBr is used. The background measurement is then compared to those with a sample; the spectrum from the background is then removed from the sample's spectrum. Thus, the received spectrums from the samples are from only the sample (without KBr) [28]. In this project ex-situ FT-IR is performed. The difference between in-situ and ex-situ is that in-situ is performed directly in the electrochemical environment and ex-situ is performed without any reaction, therefore, the sample is kept unchanged [29].

4.3 SEM

Scanning electron microscopy, SEM, is a spectroscopy method that provides information about the density of electrons as a function of their energy in a sample. With SEM, information about the topography, morphology (information about the shape and size of the particles in the sample), composition (information about the elements and compounds in the sample, and the amount of the different elements) and crystallographic information is received. The sample is being scanned with a focused beam of primary electrons; there is an interaction between the sample and the electrons. This produces different signals that can be detected (the signals are from secondary electrons, backscattered electrons, x-rays, cathodoluminescence, and sample current) and these signals contain information about the topography and composition of the sample. The electron beam is in general scanned in a zigzag pattern, and the position of the beam combined with the detected signal produces an image. The images received are high resolution, better than 1 nanometer. In a SEM the column usually operates in vacuum. Usually secondary electrons emitted by atoms that are excited by the electron beam are detected. The scanning of the sample and detection of secondary electrons creates an image of the topography of the surface [30]. In this project SEM was used, however, the results were not clear. More about the SEM results in the discussion part further down.

4.4 TGA

Thermogravimetric analysis, TGA, is used for material characterization. The sample is subjected to a controlled temperature program in controlled atmosphere; the mass of the sample is monitored as a function of temperature or time. In TGA sample pans are used that are supported by a precision balance, they reside in the furnace during the experiment. First the masses of the pans are measured without any samples, and then the experiment can be started. During the experiment the mass of the sample is monitored. To control the environment of the sample an inert or reactive gas is used, it flows over the sample and exits through an exhaust. With TGA it is possible to quantify loss of water, loss of solvent, decomposition, oxidation and so on [31].

4.5 DSC

Differential scanning calorimetry, DSC, is a thermo analytical technique. The technique measure the amount of heat required to increase the temperature of different samples and their references as a function of temperature. Usually the temperature increases linearly as a function of time to make the comparison of the samples and references more convenient [32].

4.6 TPR

Temperature programmed reduction, TPR, is a method that is used for characterization of the reduction of a catalyst. TPR yields quantitative information of the oxide's surface reducibility and the reducible surface's heterogeneity. TPR is used to characterize metal oxides, mixed metal oxides and mixed metals on support. In TPR a reducing gas mixture (usually hydrogen diluted with nitrogen) flows over the sample as the temperature linearly increases. Using a thermal conductivity detector, TCD, the changes in the thermal conductivity of the gas stream is measured. TCD is measuring the difference in thermal conductivity between the carrier gas and the mixture of the carrier gas with reactant gas. Therefore the sensitivity is the largest when the thermal conductivities of the two gases are very different. By using a level calibration the TCD signal is converted to concentration of active gas. The area under the concentration is integrated with time or temperature; this gives the gas consumed [33]. H_2-TPR is when hydrogen is used as active gas, a reduction occur at a specific temperature and the consumption of hydrogen is recorded by the detector [34].

4.7 TPO

TPR and TPO are similar; TPO is an abbreviation for temperature programmed oxidation. TPO is used for characterization of the oxidation of a catalyst, instead of the reduction as in TPR. TPO is a method that determines the oxidation reactivity; a gas mixture is used to perform the technique. Usually hydrogen or oxygen is used diluted in helium. As for TPR the temperature is linearly increased, TCD measures the changes in the thermal conductivity of the gas stream. In NO-TPO the amount of NO oxidized is recorded, in SO_2-TPO the oxidation of SO_2 is recorded and in soot-TPO information about the amount of soot oxidation that has occurred is provided [7].

For soot oxidation the different catalytic activities are evaluated with TPO and T_{50} is calculated with the soot-TPO. T_{50} is the temperature when 50% of the soot is oxidized, and it is an indicator at which temperature most of the soot is oxidized and a lower temperature is preferred since less energy is required [5].

Oxidation of NO to NO_2 is an important step in the NO-TPO measurements since NO_2 is crucial for soot oxidation [35]. The activation energy for soot oxidation to occur is lower for NO_2 than O_2. The energy required for NO_2 to oxidize soot is 60 kJ/mole and for O_2 it is 177 kJ/mole, the energy difference makes it an important step [36].

5. Experimental part

The experimental part and the different ratios of the materials are based on the previous project.

5.1 Overview of the approach of the experimental part

Catalytic materials: Pt/MnO_x-CeO_2-Al_2O_3

Catalyst synthesis:
(1) Prepare MnO_x-CeO_2-Al_2O_3 (MCA) with citric acid-assisted sol-gel method;
(2) To impregnate Pt(NO_3) onto MCA through wet impregnation to obtain Pt/MnO_x-CeO_2-Al_2O_3 (PMCA with 0.5 wt.% Pt);

Catalyst sulfation:
To treat the as-received catalyst in a wet (100 ppm SO_2+10% H_2O+air) or a dry (100 ppm SO_2 +air) flow around 300 °C for a period of 10 and 50 h.

Catalyst characterization:
(1) **Activity tests**: To measure the NO and soot oxidation activities of the as-received, sulfated catalysts in a fixed-bed reactor with the effluent gases monitored by an infrared spectrometer.
(2) **Sulfates detection**: To detect the surface sulfates on the sulfated catalysts with Infrared (IR) spectroscopy, and to quantify the amount of surface/bulk sulfates with TGA.
(3) **Structural properties**: To detect the CeO_2 grain size and Pt particle size with SEM (or CO titration).

5.2 Catalyst

5.2.1 Catalyst preparation

The first step is preparation of the manganese-ceria-aluminum catalyst, the MCA-catalyst. The MnO_x–CeO_2–Al_2O_3 mixed oxides (MCA) should have a molar ratio of 15:85 of Mn/Ce, and a 1:2 weight ratio of (Mn_2O_3 + CeO_2):Al_2O_3. The following amount is measured of the different substances:

$Ce(NO_3)_3 \circ 6\ H_2O$	8.68 gram
$MnAc_2 \circ 4\ H_20$ (manganese acetate tetrahydrate)	0.86 gram
γ-Al_2O_3	8 gram
Citric acid	19.75 gram

Polyethylene glycol	1.98 gram

The substances for the preparation of MCA-catalyst are synthesized by a citric acid-assisted sol-gel method. Cerium nitrate and manganese acetate are dissolved in deionized water (circa 200 ml) according to the molar ratio and mixed with γ- Al_2O_3 powder. Citric acid is added drop wise as a chelating agent with a 2:1 ratio of the acid to the metal ions (i.e. Al^{3+}, Ce^{3+} and Mn^{2+}), and polyethylene glycol is added with 1/10 of the citric acid weight. The solution is then mixed with a magnetic stirrer for 1 hour starting at 20°C and heated up to 80°C until a porous gel is formed. The gel turns yellow which is a result from water evaporating and decomposition of NO_3 to NO_2. Thereafter the gel is dried in an oven (OHG-9033BS-III, Shanghai CIMO Medical Instrument Manufacturing Co. LTD) at 110°C overnight, followed by decomposition in a furnace (Nabertherm GmbH, model LH 30/13) at 300°C for 1 hour and calcination for 5 hours at 500°C. During the calcination the nitrate and acetate will oxidize. The temperature in the furnace rises with 10°C per minute and starts at room temperature. The MCA support is now obtained.

The support is then impregnated with a platinum solution, Pt(NO3)2 (17.01 weight-% platinum) is used as the precursor. The support should be impregnated with 0.5 weight-% platinum. 20 grams of support is used, to receive an impregnation of 0.5 weight-% 0.5879 gram of Pt(NO3)2 is needed. The measurement is done in a mass analyzer. The MCA is added to a evaporation flask, diluted with distilled water and then slow addition of the Pt(NO3)2. The evaporation flask is attached to a rotary evaporator (Greatwall Scientific Industrial and Trade Co, model WB-2000), at a temperature of 80°C and for 1 hour until the water is evaporated. The as-received catalyst is treated at 500°C for 2 hours in the furnace. Now PMCA-F is received, the platinum impregnated manganese-ceria-aluminum-fresh catalyst.

A sample of PMCA-F is saved; the rest is pressed to a tablet. Then the tablet is mortared and the particles sieved through a grid with 50 holes/square inches. This is then sieved with another grid with 100 holes/square inches. The particles that go through the 100 holes/square inches are too small. The particles between 50-100 holes/square inches are used for the sulfur poisoning. The sulfur poisoning is done with SO_2-TPO in a self-established reactor by the department. The sample is treated with 100 ppm SO_2, 20% oxygen and 80% N_2 at 350°C for 3 hours and 25 minutes. The total gas flow is 1 liter/minute. The starting temperature of the furnace is at room temperature and it is heated up to 350°C. When the furnace reaches 350°C the data is starting to be measured and the SO_2-gas is connected. The measuring goes on until 80 ppm of SO_2 is reached. A program called ACCU ECOM EN2-F is used to see how much SO_2 is being pumped at the catalyst. The powder is then collected and named PMCA-DS; which means sulfated PMCA in dry conditions.

The previous procedure is repeated but in wet conditions. The sample is treated as above but with 10% water, the water is added when the temperature has reached 350℃. The rest of the conditions are the same. The powder is then collected and named PMCA-HS; which means sulfated PMCA in wet conditions. The data from the sulfur poisoning is transferred to a computational program called OMNIC where time is plotted against concentration of SO_2. PMCA-DS and PMCA-HS are compared to each other.

Another catalyst is also prepared; the usage of the catalyst will be as a comparison. It is designed to be similar to the PMCA-DS; it will contain approximately the same amount sulfur as PMCA-DS. PMCA-F is mixed with sulfuric acid, 1 gram sample is mixed with 0.81 gram H_2SO_4 (10 weight-%). The sample is mixed drop-wise with H_2SO_4. The mixture is inserted in an oven (Nabertherm L9/11/SKM) at room temperature and the temperature is increased with 10℃/minute until 350℃ is reached. PMCA-I (PMCA-impregnated) is received.

5.2.2 Catalyst characterization and activity measurement

Soot-TPO, soot-temperature programmed oxidation, is performed on PMCA-DS, PMCA-HS and PMCA-I. Starting with mixing PMCA-DS with soot (pure carbon with a surface area of 100 m^2/gram) and silica. 0.1 gram PMCA-DS and 0.01 gram soot is measured in a mass analyzer. The powders are mixed together before 0.3 gram silica is added. The powders are mixed again and added to a silica tube that is attached to an infrared spectrum analyzer, Thermo Nicolet IS10. The sample will be analyzed starting at room temperature and up to a maximum of 760℃. The analyze takes approximately 73 minutes since the temperature in the furnace is heated with 10℃/minute. The tube is inside the furnace, and connected to a temperature stick and a gas stream. The temperature stick measures the temperature. The inlet gas stream consists of 1 000 ppm NO and 10% O_2/N_2. The total flow of the gas stream is 0.5 liter/minute. The catalytic activities for soot oxidation are evaluated in temperature programmed oxidation (TPO) reactor, the tests are conducted in a fixed-bed reactor and the gases are monitored by an infrared spectrometer (Thermo Nicolet IS10). T_{50} is the temperature at which 50% of the soot is oxidized. Lower temperature is preferred since less energy is required for the oxidation to occur.

The next step is to analyze PMCA-F, PMCA-DS, PMCA-HS and PMC-I with FT-IR. NICOLET 6700 FT-IR is used to record the IR-spectra and the reactor is equipped with a MCT detector. Liquid nitrogen is added to lower the operating temperature since the detector won't work correctly at room temperature. The first analysis is done on pure KBr. Thereafter the second test was PMCA-DS mixed with KBr and so forth. All of the samples are mixed with a ratio of 1:3 where the samples of the different catalysts were 1 and KBr 3. KBr is a white powder that does not usually show any absorption spectrum in infrared region. KBr is used to avoid the sample from absorbing light [37].

TGA, Thermogravimetric analysis, is carried out with the reactor TGA/DSC1 STAR System, Mettler Toledo. The reactor operates with N_2-gas and the temperature is increasing with 10 ℃/minute until 1 000 ℃ is reached. The gauge pressure is at 0.1 atm (10.1 kPa) and the gas flow rate is 20 ml/minute. PMCA-F, PMCA-HS, PMCA-DS and PMCA-I is analyzed. The samples are put into small beakers, for reference an empty is also analyzed. The mass of the empty beaker is measured and subtracted from the other samples.

H_2-TPR is performed on the samples, Chemisorption Analyzer, Micrometrics AutoChem II 2920 is used. The technique provides information of the different types of oxygen in the sample. The hydrogen consumption is caused by oxygen in the catalyst. Starting with PMCA-F, 0.05 gram of the sample is added to a U-shaped silica tube with silica cotton on the bottom. Liquid nitrogen is connected to the reactor. The tube is inside a furnace that is first cooled down with the liquid nitrogen. By doing so the heating and cooling down of the sample is more controlled. The furnace is heated up to 400℃, when the temperature is reached helium is pumped in with a gas flow of 50 ml/minute. The sample is cooled down to room temperature and the gas is replaced with H_2. The gas flow is 50 ml/minute and the furnace is heated up to 800 ℃ with a heating rate of 10 ℃ /minute. The consumption of H_2 during the experiment is monitored as TCD signals. This procedure was then repeated with PMCA-DS, PMCA-HS and PMCA-I.

Thereafter NO-TPO is performed; the tests are carried out in a fixed-bed reactor. The effluent gases are monitored by an infrared spectrometer (Thermo Nicolet IS10). The procedure is the same as soot-TPO with the exception of no soot is mixed with the sample. 0.1 gram sample is mixed with 0.3 gram silica. The gas flow consists of 1000 ppm NO, 50 ml/minute N_2 and 50 ml/minute O_2. Start with PMCA-F, then PMCA-DS, PMCA-HS and lastly PMCA-I. The temperature starts at room temperature and increases with 10℃/minute up until a maximum of 730 ℃.

6. Results

Soot-TPO: In order to investigate the activity for soot oxidation over the fresh and sulfated samples soot-TPO experiments were performed. The results are shown in Figure 1.

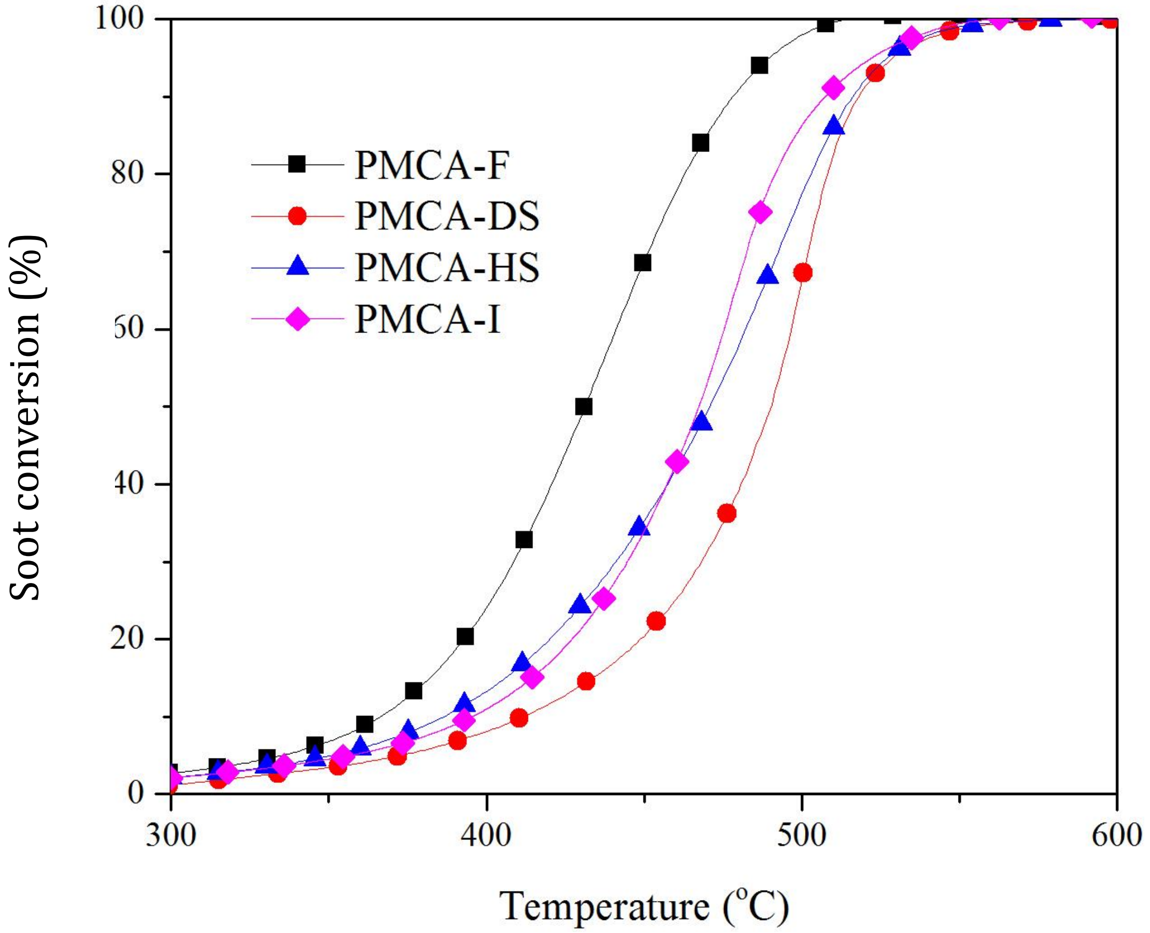

Figure 1. Soot-TPO performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I.

The activity for soot oxidation is highest for the PMCA-F sample as expected and approximately the same for the PMCA-I and PMCA-HS samples. This implies that PMCA-HS has better activity than PMCA-DS. However, the soot oxidation activity is better for PMCA-I than PMCA-DS even though the amount of sulfur is similar.

In Table 1 (below) the measurement of the soot conversions over the different catalysts in the soot-TPO are shown. T_{50} is, as mentioned before, the temperature at which 50% of the soot was oxidized.

Table 1. T_{50} (℃) in an atmosphere of NO + O_2 gas.

	Fresh	**DS** (dry conditions)	**HS** (wet conditions)	**I (**impregnate)
PtMnCeAl	432	490	471	468

From the table it can be seen that the fresh catalyst has the highest activity followed by I and HS, then by DS. I and HS are similar, only 3℃ difference which may be due to experimental error and do not count as a real distinction.

TGA and DSC: The TGA curves provide information about the degree of sulfation of the samples and the results are shown in Figure 2a. The DSC-experiments provide information about the heat required to increase the temperature of the samples and the results are shown in Figure 2b.

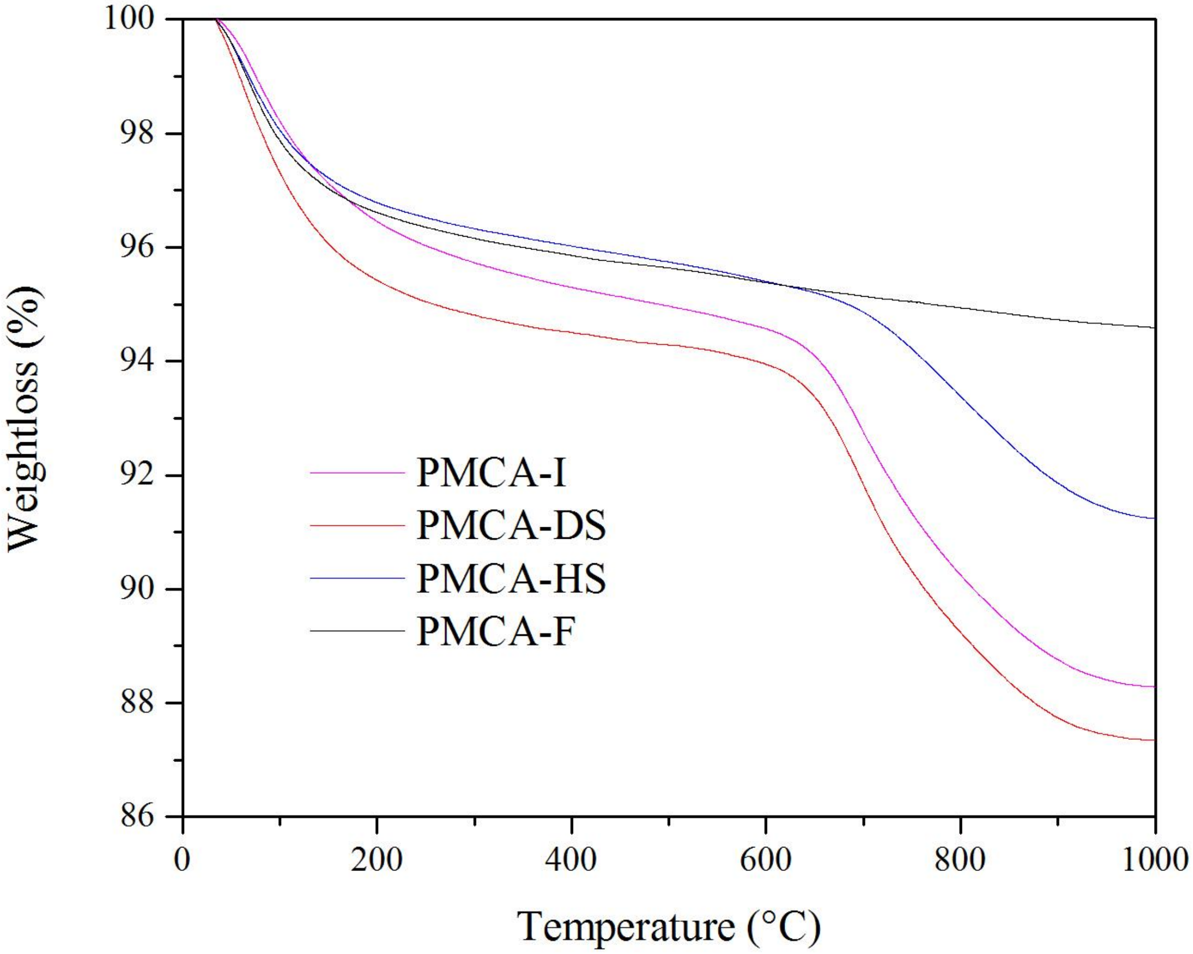

Figure 2a. TGA performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I.

The small weight loss for the fresh sample could be accounted for by the water evaporation that occurred below 250℃. The decomposition of the sulfates for PMCA-DS and PMCA-I occur from approximately 650 ℃ to 900 ℃. The high decomposition temperatures are due to the high stability of the sulfates that are formed on the ceria samples. The weight loss due to sulfate decomposition are 6.6%, 4,2% and 6.3% for PMCA-DS, PMCA-HS and PMCA-I respectively. This indicates that PMCA-HS has the least severe sulfur poisoning and PMCA-DS the most severe. It can also be seen that the weight loss for the PMCA-HS sample due to water evaporation is lower than the PMCA-DS sample [5].

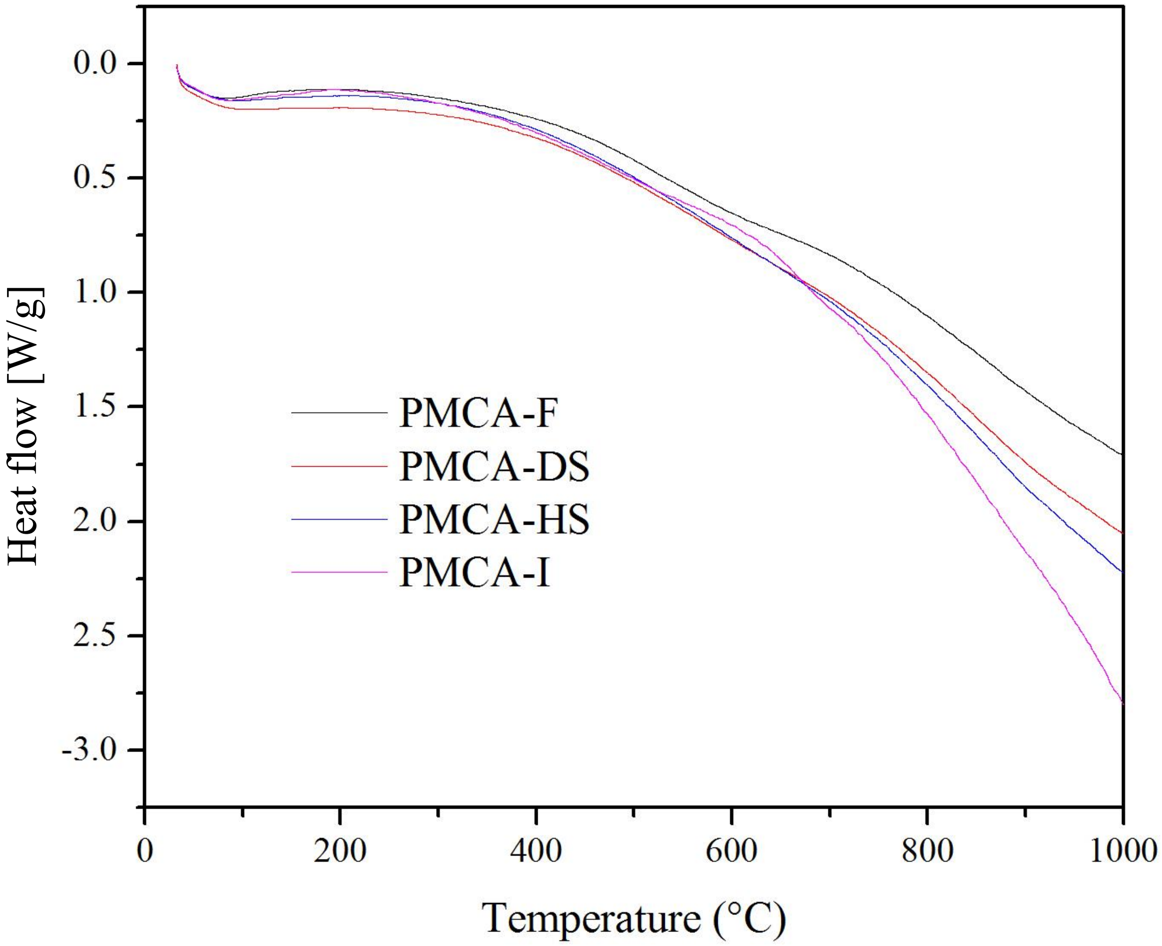

Figure 2b. DSC performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I.

From figure 2b it is shown that PMCA-F absorbed the least amount of heat during the heating ramp, and PMCA-I the most. PMCA-HS and PMCA-DS are similar, though

PMCA-DS absorbs slightly less heat.

Ex-situ IR: In order to be able to distinguish different types of sulfates on the surface and in the bulk of the samples, IR experiments were performed.

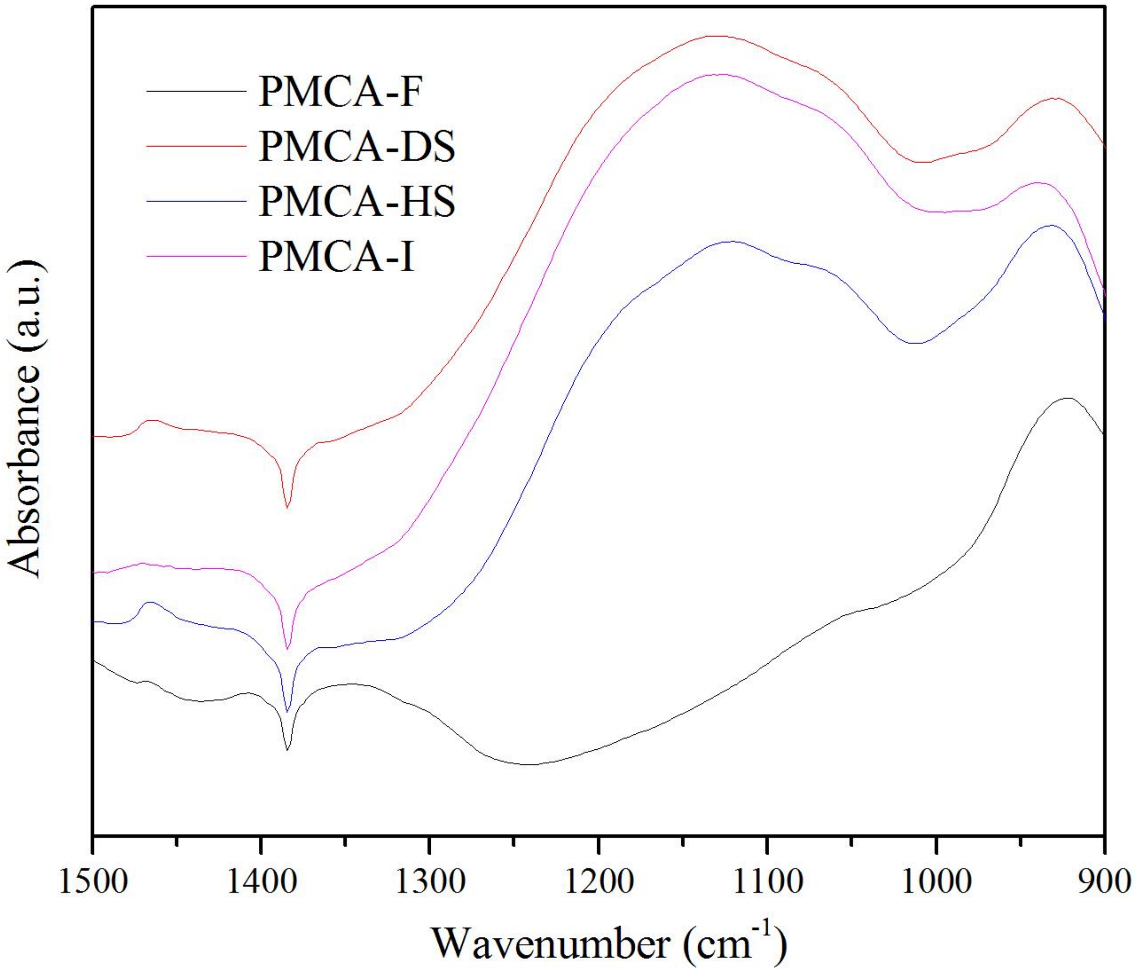

Figure 3. FT-IR performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I.

Figure 3 shows the results of the IR-experiments. There was no absorbance in the 1300-1000 cm^{-1} range for the PMCA-F sample which is likely related to that this sample was not sulfated (this is the range different forms of sulfates are shown). The PMCA-F sample exhibits a band at 1350 cm^{-1}; this can be associated with C-H and C-O bands of the organic and hydroxyl groups that were incorporated for the as-received powders [5]. These species disappear after sulfation. For the rest of the samples, PMCA-I, PMCA-DS and PMCA-HS, it is difficult to distinguish the bands of sulfates. All three of them show three broad adsorption bands at around 1250 cm^{-1}, 1180 cm^{-1} and 1070 cm^{-1}, which can be associated with different types of sulfate species. The bands at the higher wavenumbers can be assigned to bulk and the lower numbers to surface sulfate species on the ceria-based oxide support. The sulfate species are more likely to be present on the ceria-based oxide support as SO_2 is more prone to react with oxidic Mn and Ce sites than with the γ-Al_2O_3 support [38]–[40]. There is no significant difference between the curves; hence it may indicate that the types of sulfates (surface and bulk) are similar for the different samples.

SO_2-TPO: SO_2-TPO experiments were performed to receive information about the amount of SO_2 that was oxidized to SO_3. However, it does not provide information about the amount of SO_3 that is adsorbed onto the surface. For that purpose TGA is required. In Figure 4 the SO_2-TPO results are shown.

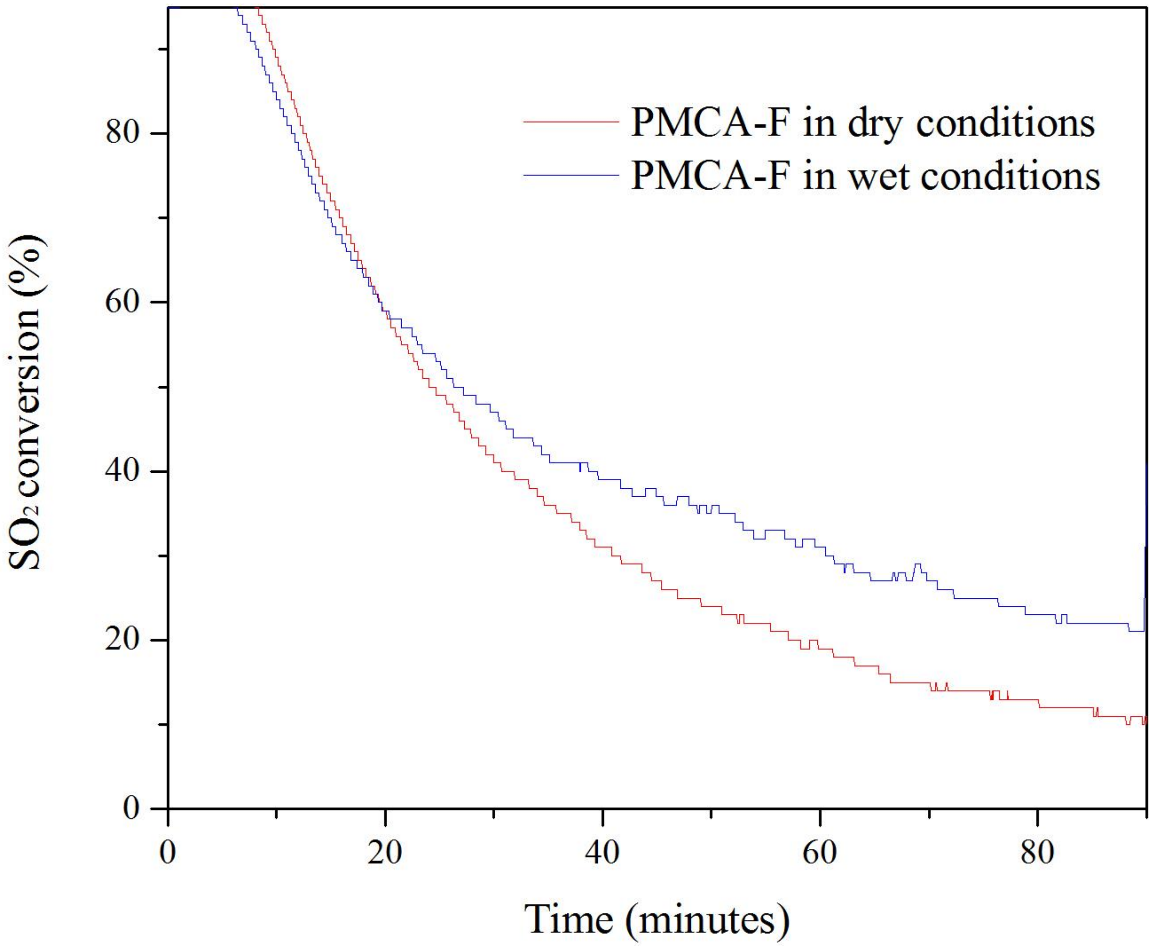

Figure 4. SO_2-TPO performed on PMCA-F in both wet (HS) and dry conditions (DS). The reactions were performed in 100 ppm SO_2, 10% H_2O and air in the wet conditions,

and 100 ppm SO_2 and air in dry conditions.

From Figure 4 it is seen that SO_2 oxidation during wet conditions (HS) show higher conversion of SO_2 than during wet conditions (DS). The first 20 minutes the oxidation of SO_2 is slightly better for DS, however, after 20 minutes HS is better.

NO-TPO: This technique describes the amount of NO that is being oxidized and relates to the catalytic activity. NO_2, formed through oxidation of NO, could assist soot oxidation and preferably should occur at a low temperature [5]. Hence, oxidation of NO to NO_2 (NO + O_2) is an important step in catalytic soot oxidation and NO_2 plays an important role in soot oxidation [41]. Figure 5 shows the formation of NO_2 during the NO-TPO measurements.

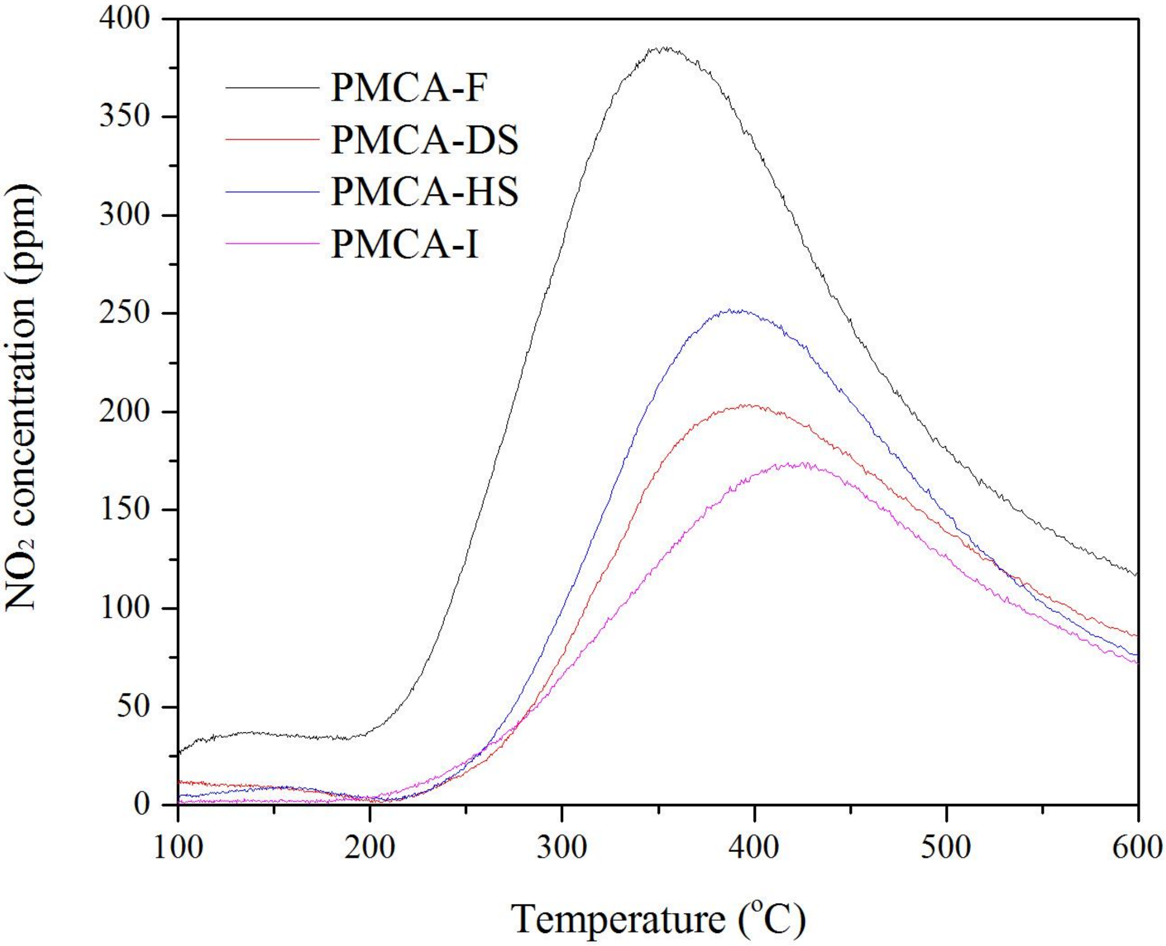

Figure 5. NO-TPO performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I. the

reactions were performed under 1 000 ppm NO, 10% O_2 and N_2 in balance with a total flow rate of 500 ml/minute. The temperature increased with a rate of 10℃/minute up until 600℃.

The PMCA-F sample showed the best NO oxidation ability, followed by PMCA-HS. For the fresh sample the soot oxidation activity correlates well with the NO oxidation activity. All the sulfated samples shows a significant inhibition of the NO oxidation ability. The results indicate that PMCA-HS has better activity than PMCA-DS, however PMCA-I did not show high conversion to NO_2 while it has a good soot oxidation activity.

H_2-TPR: This technique is used to investigate the redox properties of the catalyst were obtained. In Figure 6 the results from the H_2-experiments are shown. The alumina support is irreducible in the operating temperature range, therefore the reduction peaks correspond to different types of species on platinum, manganese and cerium [5].

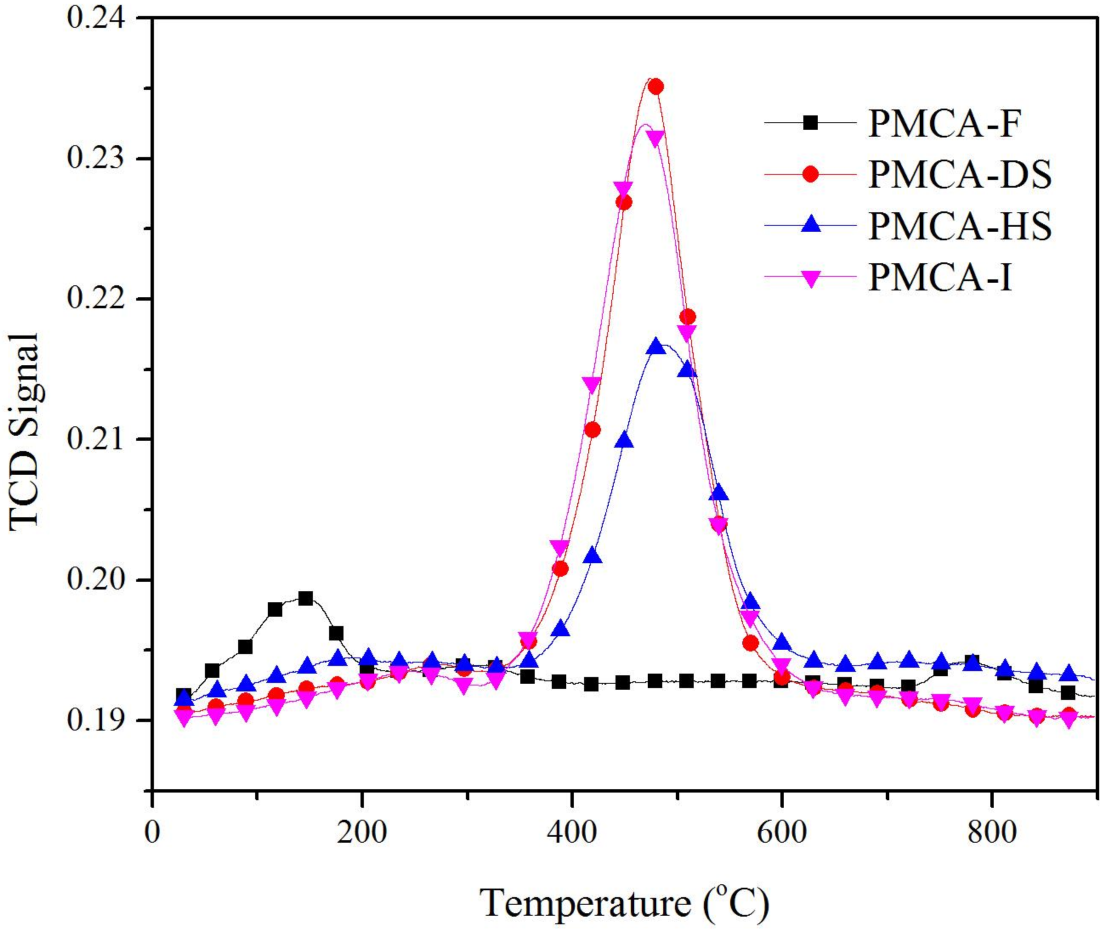

Figure 6. H_2-TPR performed on PMCA-F, PMCA-DS, PMCA-HS and PMCA-I. The

reaction conditions were 10% H_2 and N_2 in balance with a total flow rate of 50 ml/minute. The temperature increased with a rate of 10℃/minute up until 850℃.

In general the reduction of ceria is promoted by platinum. In the high temperature range the peaks can be ascribed to ceria not promoted by platinum. The PMCA-F sample shows distinct peaks at 140 ℃ and 780℃. The figure indicates that ceria reduction takes place in the high temperature range, which the reduction of platinum occurred in the low temperature range. Also visible as "bump" at 300℃, which can correspond to reduction of MnO_x clusters [42][5]. The PMCA-DS sample has a strong peak at 480℃, which can be ascribed to sulfates. The corresponding peak of sulfates in the PMCA-HS sample is weaker and shifted (10℃) to a higher temperature. There is also a small bump at 280℃, which can correspond to MnO_x clusters. The curve shows that cerium is reduced during sulfur poisoning and more sulfates are formed than over PMCA-HS, which is in accordance with the TGA data. The deactivation of active sites on platinum is more prominent when going from low to high temperature and the reduction of platinum becomes more noticeable. At high temperature there is no reduction of ceria as it has converted to soot. The PMCA-I sample is very similar to the PMCA–DS sample, the only difference is the peak temperature. At high temperature no reduction of ceria is found [5].

7. Discussion

The impregnated sample (with H_2SO_4) was designed to be similar to the PMCA-DS sample, the amount of sulfates were approximately the same but in different forms. However, the graph from the soot-TPO shows different results. The impregnated sample is significantly better in oxidizing soot than the PMCA-DS sample. The IR spectra for the PMCA-I and PMCA-DS samples are almost identical, while the NO-TPO for the PMCA-I and PMCA-DS samples are not comparable. The reason is not concluded yet, and more research needs to be done. The results from the TGA and H_2-TPR experiments are as expected, showing that the impregnated sample is similar to the dry sample. However, the NO oxidation ability is low for the impregnated sample, which was not expected, as the soot oxidation ability is good. One speculation is that this is due to the redox property of the surface. The surface of the PMCA-I sample might have more acidic sites and hence has a higher NO_2–conversion efficiency during soot oxidation in $NO+O_2$ atmosphere.

As stated in the results, the sample in dry conditions shows a better SO_2 conversion during the first 20 minutes than the sample in wet conditions, however the dry sample is reduced faster than the wet sample. After 20 minutes, the conversion of the wet sample has surpassed the dry sample. This trend indicates that water may occupy the active sites and cause the conversion to be slower than the dry sulfur poisoning in the beginning. As the TGA result show that the PMCA-HS sample has the least severe sulfur poisoning and the PMCA-DS sample has the most severe. This may indicate that in wet conditions the catalyst adsorbs even less than in dry conditions, although it converts more SO_2 to SO_3. The occupation of the active sites by water needs however to be confirmed.

With the IR technique it was expected to receive information about the different sulfates, which form they were in and whether they were bulk or dispersed sulfates. However, the results are too similar to make a distinction and it might indicate that they have the same structure. All the samples show a band at 950 cm^{-1}; one possibility is that this band relates to OH-groups. The difference in surface OH-groups may explain the activities. More research should be done for verification of these groups and also to receive information about the different sulfate forms on the samples.

As mentioned earlier in the theory part the results from SEM were not clear and therefor not published. As future work SEM should be performed again. This was not possible during the project timeframe since the machine was under reparation. Also NO_x-TPD should be performed on the samples to receive information about how much NO_x is adsorbed on the surface and in what form. To be able to exclude the effect of surface area BET could be performed, this could either confirm the hypothesis that the specific surface area do affect the result, or not.

The wet and impregnated samples show the lowest T_{50}, which means that these samples are the most active for soot oxidation at lower temperature. The conclusions that can be drawn from the experiments are that the PMCA-HS sample is a promising catalyst for soot oxidation, however more research needs to be done.

8. Conclusions

Pt/MnO_x-CeO_2-Al_2O_3 in wet conditions is a promising catalyst for soot oxidation with high catalytic activity and hydrothermal stability. However, more evaluation is needed and further experiments need to be performed. If the catalyst is promising it needs to be performed in real conditions (in a vehicle) before producing it in larger scale.

9. Acknowledgements

The author wishes to thank Professor Xiaodong Wu, Doctor Dongmei Zhao and Yuxi Gao for all the encouragement and help. This work was supported by Department of Material Science and Engineering, Tsinghua University and Department of Chemical and Biological Engineering, Chalmers University of Technology.

10. Bibliography

[1] I. N. Krivoshto, J. R. Richards, T. E. Albertson, and R. W. Derlet, “The Toxicity of Diesel Exhaust: Implications for Primary Care,” *J. Am. Board Fam. Med.*, vol. 21, no. 1, pp. 55–62, Jan. 2008.

[2] “Under the Dome –China’s Smog,” *earthsharing.org*. .

[3] P. G. Harrison, I. K. Ball, W. Daniell, P. Lukinskas, M. Céspedes, E. E. Miró, and M. A. Ulla, “Cobalt catalysts for the oxidation of diesel soot particulate,” *Chem. Eng. J.*, vol. 95, no. 1–3, pp. 47–55, Sep. 2003.

[4] B. A. A. L. van Setten, M. Makkee, and J. A. Moulijn, “Science and technology of catalytic diesel particulate filters,” *Catal. Rev.*, vol. 43, no. 4, pp. 489–564, Nov. 2001.

[5] S. Liu, X. Wu, D. Weng, M. Li, and H.-R. Lee, “Combined promoting effects of platinum and MnOx–CeO2 supported on alumina on NOx-assisted soot oxidation: Thermal stability and sulfur resistance,” *2012*, vol. 25–35, no. 203.

[6] “The effect of catalysts on rates of reaction.” [Online]. Available: http://www.chemguide.co.uk/physical/basicrates/catalyst.html#top. [Accessed: 08-May-2015].

[7] M. Fadoni and L. Lucarelli, “Temperature programmed desorption, reduction, oxidation and flow chemisorption for the characterisation of heterogeneous catalysts. Theoretical aspects, instrumentation and applications.” .

[8] “types of catalysis.” [Online]. Available: http://www.chemguide.co.uk/physical/catalysis/introduction.html. [Accessed: 08-May-2015].

[9] “Catalytic converter - Wikipedia, the free encyclopedia.” [Online]. Available: http://en.wikipedia.org/wiki/Catalytic_converter. [Accessed: 07-May-2015].

[10] J. K. Dunleavy, “Final Analysis: Sulfur as a Catalyst Poison,” vol. 50, no. 2, pp. 110–110, 2006.

[11] W. B. Frank, W. E. Haupin, H. Vogt, M. Bruno, J. Thonstad, R. K. Dawless, H. Kvande, and O. A. Taiwo, “Aluminum,” in *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

[12] D. S. Maciver, H. H. Tobin, and R. T. Barth, “Catalytic Aluminas I. Surface Chemistry of Eta and Gamma Alumina,” *UW Gulf Res. Dev. Co. Pittsburgh Pa.*, Aug. 1963.

[13] R. B. Y. Rozita, “An investigation of commercial gamma-Al2O3 nanoparticles,” *J. Phys. Conf. Ser.*, vol. 241, no. 1, 2010.

[14] G. Rayner-Canham and T. Overton, *Descriptive Inorganic Chemistry*. Macmillan, 2003.

[15] J. E. Post, “Manganese oxide minerals: Crystal structures and economic and environmental significance,” *Proc. Natl. Acad. Sci.*, vol. 96, no. 7, pp. 3447–3454, Mar. 1999.

[16] T. Yamashita and A. Vannice, “NO Decomposition over Mn2O3and Mn3O4,” *J. Catal.*, vol. 163, no. 1, pp. 158–168, Sep. 1996.

[17] K. Frey, V. Iablokov, G. Sáfrán, J. Osán, I. Sajó, R. Szukiewicz, S. Chenakin, and N. Kruse,

"Nanostructured MnOx as highly active catalyst for CO oxidation," *J. Catal.*, vol. 287, pp. 30–36, Mar. 2012.

[18] R. Jain and R. Maric, "Synthesis of nano-Pt onto ceria support as catalyst for water–gas shift reaction by Reactive Spray Deposition Technology," *Appl. Catal. Gen.*, vol. 475, pp. 461–468, Apr. 2014.

[19] S. S. Lee, W. Song, M. Cho, H. L. Puppala, P. Nguyen, H. Zhu, L. Segatori, and V. L. Colvin, "Antioxidant Properties of Cerium Oxide Nanocrystals as a Function of Nanocrystal Diameter and Surface Coating," *ACS Nano*, vol. 7, no. 11, pp. 9693–9703, Nov. 2013.

[20] X. Wu, S. Liu, D. Weng, and Ran, "DESIGN AND PREPARATION OF MANGANESE-CERIUM OXIDES CATALYST FOR SOOT OXIDATION," p. 1.

[21] X. Wu, S. Liu, D. Weng, F. Lin, and R. Ran, "MnOx–CeO2–Al2O3 mixed oxides for soot oxidation: Activity and thermal stability," *J. Hazard. Mater.*, vol. 187, no. 1–3, pp. 283–290, Mar. 2011.

[22] "Brunauer, Emmett and Teller (BET) Theory | Particle Analytical." .

[23] X. Tiancun, A. Lidun, Z. Weimin, S. Shishan, and X. Guoxin, "Mechanism of sulfur poisoning on supported noble metal catalyst — The adsorption and transformation of sulfur on palladium catalysts with different supports," *Catal. Lett.*, vol. 12, no. 1–3, pp. 287–296, Mar. 1992.

[24] J. Oudar, "Sulfur Adsorption and Poisoning of Metallic Catalysts," *Catal. Rev.*, vol. 22, no. 2, pp. 171–195, Jan. 1980.

[25] G. Saracco, C. Badini, and V. Specchia, "Catalytic traps for diesel particulate control," *Chem. Eng. Sci.*, vol. 54, no. 15–16, pp. 3035–3041, Jul. 1999.

[26] D. Fino, P. Fino, G. Saracco, and V. Specchia, "Diesel particulate traps regenerated by catalytic combustion," *Korean J. Chem. Eng.*, vol. 20, no. 3, pp. 445–450, May 2003.

[27] C. Welder, "Rotary Evaporator (Rotovap)."

[28] T. Nicolet, "Introduction to Fourier Transform Infrared Spectrometry." Thermo Nicolet, 2001.

[29] M. Arenz, M. Lennartz, E. Vogler, C. Stuhlmann, and K. Wandelt, "Comparative in-situ and ex-situ FTIR spectroscopy of the electrochemical double layer," *Inst. Für Phys. Theor. Chem. Wegelerstr 12 53115 Bonn Ger.*

[30] K. Oura, V. G. Lifshits, A. A. Saranin, and M. Katayama, *Surface Science: An Introduction*, 1st ed. Springer-Verlag Berlin Heidelberg, 2003.

[31] P. Elmer, "Thermogravimetric Analysis (TGA), A Beginner's Guide." PerkinElmer, Inc., 2010.

[32] "Differential microcalorimeter."

[33] "Characterization by temperature programmed reduction." [Online]. Available: http://www.sciencedirect.com.proxy.lib.chalmers.se/science/article/pii/S0920586199002941. [Accessed: 12-May-2015].

[34] K. Nakai and K. Nakamura, "TPR measurement." 02-Jul-2003.

[35] S. Liu, X. Wu, D. Weng, M. Li, and R. Ran, "Roles of Acid Sites on Pt/H-ZSM5 Catalyst in Catalytic Oxidation of Diesel soot," *ACS Catal.*, vol. 5, no. 2, pp. 909–919, Feb. 2015.

[36] J. Jung, S. Song, and K. M. Chun, "Characterization of Catalyzed Soot Oxidation with NO2, NO and

O2 using a Lab-Scale Flow Reactor System," SAE International, Warrendale, PA, SAE Technical Paper 2008-01-0482, Apr. 2008.

[37] "Infrared Spectroscopy." [Online]. Available: http://www.umsl.edu/~orglab/documents/IR/IR.html. [Accessed: 31-May-2015].

[38] L. Kylhammar, P.-A. Carlsson, and M. Skoglundh, "Sulfur promoted low-temperature oxidation of methane over ceria supported platinum catalysts," *J. Catal.*, vol. 284, no. 1, pp. 50–59, Nov. 2011.

[39] M. Waqif, P. Bazin, O. Saur, J. C. Lavalley, G. Blanchard, and O. Touret, "Study of ceria sulfation," *Appl. Catal. B Environ.*, vol. 11, no. 2, pp. 193–205, Feb. 1997.

[40] P. D. Clark, N. I. Dowling, M. Huang, O. Okemona, G. D. Butlin, R. Hou, and W. S. Kijlstra, "Studies on sulfate formation during the conversion of H2S and SO2 to sulfur over activated alumina," *Appl. Catal. Gen.*, vol. 235, no. 1–2, pp. 61–69, Aug. 2002.

[41] F. E. López-Suárez, S. Parres-Esclapez, A. Bueno-López, M. J. Illán-Gómez, B. Ura, and J. Trawczynski, "Role of surface and lattice copper species in copper-containing (Mg/Sr)TiO3 perovskite catalysts for soot combustion," *Appl. Catal. B Environ.*, vol. 93, no. 1–2, pp. 82–89, Nov. 2009.

[42] M. Ferrandon, J. Carnö, S. Järås, and E. Björnbom, "Total oxidation catalysts based on manganese or copper oxides and platinum or palladium I: Characterisation," *Appl. Catal. Gen.*, vol. 180, no. 1–2, pp. 141–151, Apr. 1999.