

Study on non-catalytic and catalytic reactivity of Biodiesel and model soot

Hailong Zhang

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Sichuan University

School of Chemical Engineering

Study on non-catalytic and catalytic reactivity of Biodiesel and model soot

Etude sur la r éactivit é catalytique et non catalytique du biodiesel et de suies mod des

生物柴油和模型碳烟的非催化与催化活性研究

By Mr. Hailong ZHANG

Doctoral thesis in Chemical Engineering - Chemical Technology

Supervised by Prof. Patrick DA COSTA and Prof. Yaoqiang CHEN

Presented in public on 27 May 2019

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D édicace

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1. Introduction

1.1 Overview

Diesel engines have extensive usage compared to gasoline engines due to their improved fuel economy, energy efficiency, high durability and reliability. They can also effectively reduce CO_2 emissions. Thus, Diesel engines as the power source of commercial transport have been widely employed in trucks, cars, buses, trains and ships as well as off-road industrial vehicles. However, the high emissions of Diesel exhaust pollutants such as NO_x and particulate matter (PM) have become a severe environmental problem worldwide, and the pollutants have a potential threat to human health. In order to protect the environment and improve human health level, many countries in the world have paid much attention to Diesel emission control. Thus, in Europe, North America and China, the government has enacted restrictive legislation to limit the pollutants emissions.

To comply with the restrictive standards, soot particulate emission from Diesel vehicles exhaust and control technology have attracted much attention in recent years. The most effective method to reduce soot particulate emissions is to apply wall-flow Diesel particulate filter (DPF) in exhaust post-treatment system. As soot particles pass through the filter, they are intercepted and collected in the wall-flow substrates by physical filtration and then burned by chemical method. The regeneration of DPF has two ways: active regeneration and passive regeneration. Active regeneration can be periodically applied to DPF by burning soot with O₂ at higher temperatures (> 550 °C). Its serious problem is higher regeneration temperature and energy supply. However, passive regeneration can allow the oxidation of soot particulates to occur at the low exhaust temperature through a catalytic reaction process. It can provide a more effective regeneration and reduce the cost of vehicle operator and engine management.

Precious metal catalysts and ceria-based oxides materials have been widely studied

and applied in DPF passive regeneration and show an excellent performance in decreasing soot oxidation temperature. Small amounts of NO in Diesel exhaust gas can be effectively oxidized into NO₂ on the precious metal catalysts especially platinum catalysts, the NO₂ will promote the oxidation of soot under a temperature range of 200-450 °C. However, precious metals as rare resource are very expensive. Furthermore, the optimization of modern engine combustion technology has decreased the concentration of NO_x in exhaust gas. These would limit the application of precious metal catalysts. On the other hand, Ce-based mixed oxides have strong oxygen storage capacity and redox ability, they are able to transfer O₂ into active oxygen species and then oxidize NO and soot at low temperatures, showing high catalytic performance. Due to relatively low cost of Ce-based catalyst, it is promising to be a commercial catalyst for DPF passive regeneration. Therefore, in my PhD work, MnO_x-CeO₂ mixed oxides as catalyst was used to evaluate the catalytic oxidation reaction of soot.

Many studies reported that the use of Biofuel/Biodiesel induces significantly lower soot deposits in DPF, which might decrease the need of active regeneration and thus the fuel consumption. So Biodiesel as a new energy has also become a focus of soot emission control. It would be a trend of energy market for Diesel vehicles. Based on this case, the effect of the use of Biodiesel on DPF active regeneration and passive regeneration should be studied in details, including soot nanostructure, soot surface property, soot noncatalytic and catalytic oxidation reactivity as well as impact of Biodiesel impurities, and so on. Thus these are also main works in my PhD research. In this research, the structure and reactivity of model soot and real Biodiesel soot were studied and compared to look for suitable model soot used for correct experimental simulation.

The thesis presents 7 chapters. The first three chapters include the general introduction, research background and materials characterizations and soot reactivity tests, respectively. The fourth, fifth, sixth and seventh chapter present the main experimental results, including structure-reactivity study of model and Biodiesel soot,

NO adsorption/desorption influence on MnO_x -CeO₂ catalyst, Biodiesel soot activation study and impact of Biodiesel impurities on soot reactivity. The last chapter is a summary of the PhD works.

The first chapter introduces the general content of various chapters and the PhD research objectives and experimental methods, it is a general introduction of the thesis.

The second chapter is a literature review of the research background. The first part describes Diesel exhaust emissions, environment pollution and health impacts. It illustrates that Diesel exhaust emissions, especially NO_x and particulate matter (PM) emissions, severely affect air environment and human health. The second part introduces Diesel particulate filter (DPF), including DPF filtration process and DPF regeneration and illustrates that it is the most effective way to control PM emissions. The third part is to introduce soot structure that shows an important role in soot oxidation reactions. The soot structure can be characterized through TEM, Raman and XRD methods. The fourth part mainly introduces the precious metal Pt catalysts and Ce-based mixed oxide catalysts. The fifth part presents the reaction mechanisms for soot oxidation with O_2 and/or NO_2 . It also illustrates that the reaction mechanisms are different under different reaction conditions and catalyst systems.

The third chapter introduces the main experimental methods, including different characterizations such as Laser Granulometry, BET, XRD, HRTEM, Raman, TGA, Temperature-Programmed Reduction (TPR), Temperature-Programmed Desorption (TPD), Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS), X-ray Photoelectron Spectra (XPS) and reactivity evaluation of soot by TPO method. Their experimental equipment and operating conditions are also described. Moreover, the calculation equations of some characterization parameters and soot oxidation rate are also introduced. Some materials used for soot and catalyst preparation are presented in this chapter.

The fourth chapter mainly focuses on the effect of NO adsorption/desorption on catalytic performance of MnO_x -CeO₂ catalyst for soot oxidation. Firstly, materials preparation method is described, MnO_x -CeO₂ mixed oxides are prepared through co-precipitation and then high-temperature calcination. The mixed oxides are treated in 600 ppm NO/10% O₂/N₂ at 350 °C for 30 min to obtain NO-adsorbed sample. The next part is the characterization of NO-adsorbed MnO_x -CeO₂ catalyst by DRIFTS, XPS, Raman, NO_x-TPD and Soot-TPR, and the effect of NO adsorption and desorption on physicochemical property of the catalyst is analyzed. In final, the soot oxidation activity is evaluated by TPO method and isothermal reactions and we also compares the catalytic reactivity of soot before and after the exposure of catalyst in NO. This chapter also discusses the reason why the presence of NO promotes soot oxidation reactions.

The work in chapter 5 mainly focuses on the study on structure and reactivity of model and Biodiesel soot samples. In the materials preparation, the real Biodiesel soot samples are obtained in an engine bench equipped with a Euro VI post-treatment system containing DOC and DPF, the model soot samples are prepared through the combustion of model fuels in an steady co-flow laminar diffusion flame burner. MnO_x-CeO₂ mixed oxides are also prepared by a co-precipitation and used to evaluate the catalytic reactivity of soot. In the characterizations, the physicochemical properties of Biodiesel and model soot samples are analyzed through laser granulometry, HR-TEM, XRD, Raman. In soot oxidation activity measurement, the non-catalytic and catalytic reactivity of Biodiesel and model soot samples are tested through temperature-programmed oxidation (TPO) method under model DPF regeneration conditions. Finally, the correlation of soot oxidation reactivity with the structure is also presented in this chapter.

In chapter 6, the activated Biodiesel and Printex U soot samples are prepared by temperature-programmed oxidation (TPO) with rising the temperature from 25 $^{\circ}$ C up to 500 or 600 $^{\circ}$ C. The aim of this work is to investigate the impact of activation process on the structure, surface and reactivity of soot. The structural property of

activated soot is analyzed by BET, Laser granulometry, HRTEM and Raman and the surface property is studied by DRIFTS and XPS. The oxidation reactivity of soot samples is evaluated through TPO method and isothermal experiments. In final, the factors that affect the reactivity of the activated soot samples are discussed based on the physicochemical characterizations.

In chapter 7, the study mainly focuses on the effect of Biodiesel impurities such as K, Na and P on the noncatalytic and catalytic reactivity of soot under model DPF regeneration conditions. A real engine soot is used for this experiment and these Biodiesel impurities are doped into this soot by a saturated impregnation method. Then the reactivity of the doped soot samples is measured by TPO method under different reaction conditions, and this research also presents different activity effects of K, Na and P doping. The physicochemical properties of the doped soot are characterized by BET, Raman, HRTEM and XPS and correlated to their reactivity.

The last part is a summary of all works and the perspectives for future study on Biodiesel/Diesel soot oxidation. The main results of the experimental chapters including chapter 4, chapter 5, chapter 6, chapter 7 are presented, which would contribute to the further study on DPF active regeneration and passive regeneration. In addition, based on these conclusions, some suggestions are provided for further research on soot particulate combustion.

1.2 Objectives of Ph.D. work

My PhD research mainly focuses on the structure, surface and reactivity of Biodiesel soot as well as the effect of NO adsorption/desorption on the catalytic performance of MnO_x -CeO₂ mixed oxides. The related work is as follows:

(1) Real Biodiesel soot and model soot were prepared through a real engine bench and a laminar burner, respectively. Printex U model soot that is often used for experimental study was also considered as a comparison. This work investigated and compared their non-catalytic and catalytic reactivities and structural properties by a series of characterizations and TPO measurements. Furthermore, the relationship between the structure and the reactivity was also analyzed.

(2) The previous work (1) revealed that the presence of NO apparently promoted the catalytic reactivity of MnO_x -CeO₂ catalyst for soot oxidation. Thus, this work studied the role of NO adsorption/desorption in MnO_x -CeO₂ catalyst on soot oxidation activity. It was found that NO adsorption/desorption promoted low-temperature soot oxidation reactivity. The result was further analyzed through a series of characterizations such as DRIFTS, XPS, Raman, NO_x-TPD, Soot-TPR, TPD-MS, and so on.

(3) The activated/oxidized Biodiesel soot and Printex U model soot were prepared by TPO method, and then their non-catalytic and catalytic reactivities were studied. TPO gave an evidence that the activated Printex U exhibited more apparent promotion on the reactivity than the activated Biodiesel soot. A series of characterizations such as XPS, HRTEM, DRIFTS, Raman were tested to analyze the structure and surface of the activated soot samples.

(4) A real Biodiesel soot was impregnated by an aqueous solution of NaNO₃, KNO₃ or NH₄H₂PO₄. Then the non-catalytic and catalytic reactivities of the doped soot samples were evaluated through TPO method under model exhaust gas conditions. The results confirmed the impact of Biodiesel impurities on the reactivity. The physico-chemical properties of the doped soot were also analyzed by BET, Raman, HRTEM and XPS.

2. Literature review on soot emission control

2.1 Diesel exhaust emissions, environment pollution and health impact

With the fast development of social economy and continuous progress of industrialization, the rapid increase of motor vehicles has led to the severe air pollution and climate impact due to high emissions of vehicle exhaust gas [1-10]. Transport has become a larger source of urban air pollution, which arouses a serious public health problem in many cities of the developing world. It has been reported that air pollution in developing countries account for tens of thousands of excess deaths and billions of dollars in medical costs and loses productivity every year [5,11]. The World Health Organization (WTO) estimated that air pollution arouses the death of around 2.4 million people each year [12]. Nowadays, pollution control and environmental protection have become important subjects and are widely concerned by many countries. In order to prevent air pollution and pollutant emissions, many agencies and organizations (EPA, OECD, IPCC, IEA, EEA, etc.) were established worldwide [4,13-17]. These organizations reported that around the 20-30% of pollutant emissions originates from transport. To control pollutant emissions, they have made several legal arrangements, created several model structures, developed control systems and organized the structure of traffic.

Compared with gasoline engines, Diesel engines have lower operating costs, high energy efficiency, high durability and reliability and thus are widely employed in trucks, buses, trains, ships and off-road industrial vehicles. However, the emissions of pollutants from Diesel exhaust gas have resulted in significant environmental pollution and health problems. In fact, according to ideal thermodynamic equilibrium, the complete combustion of diesel fuel would only produce CO_2 and H_2O in combustion chambers of engine [18]. But many factors such as the air-fuel ratio, air-fuel concentration, ignition timing, turbulence in the combustion chamber, combustion form and temperature lead to the generation of harmful products during

fuel combustion [19]. As shown in Figure 2-1, the most significant harmful products in Diesel exhaust gas are CO, HC, NO_x and PM. Pollutant emissions occupy around 1% in the Diesel exhaust gas, NO_x and PM emissions have the highest proportion of Diesel pollutant emissions [19-22]. Due to the lean combustion condition of Diesel engines, the concentration of CO and HC is minimal. Besides, the emission of SO_2 depends on the specifications and quality of fuel. In this section, the four main pollutant emissions (CO, HC, NO_x , PM) are introduced, their impacts on environment and health are also illustrated.



Figure 2-1. The compositions of Diesel exhaust gas [19].

(1) Carbon monoxide (CO) emissions

The incomplete combustion process of fuel in Diesel engines results in CO emissions. Diesel engines are lean combustion engines which have a high air-fuel ratio ($\lambda > 1$), so the formation of CO is minimal. Carbon monoxide is an odorless and colorless gas. In humans, CO in the air is inhaled by the lungs and transmitted into the bloodstream. It binds to hemoglobin and decreases its capacity to transfer oxygen. Higher CO concentration in the air would lead to asphyxiation, thus affecting the function of different organs and resulting in impaired concentration, slow reflexes, and confusion [10,19,23-25].

(2) Hydrocarbon (HC) emissions

Hydrocarbon emissions consist of unburned fuels resulting from insufficient temperature which occurs near the cylinder wall. At this point, the temperature of air-fuel mixture is apparently lower than the center of the cylinder [26,27]. These HC species include alkanes, alkenes, aromatics, and so on. In Diesel engines, the fuel type, engine adjustment, and design can affect the emissions of hydrocarbons [19]. Besides, HC emissions in the exhaust gas depend on irregular operating conditions [28,29]. the hydrocarbon emissions affect environment and human health. They can react with the other pollutants in air to form ground-level ozone. About 50% of the vehicle exhaust emissions are contributed to form ozone. Hydrocarbons are toxic with the potential to respiratory tract irritation and cause cancer [7,30].

(3) Nitrogen oxides (NO_x) emissions

It is well known that the fuel in Diesel engines is ignited by highly compressed hot air. Air is mainly composed of oxygen and nitrogen, it is drawn into the combustion chamber and mixed with fuel, the combustion of fuel releases a large amount of heat. When the temperature reaches more than 1600 °C in the cylinders, it can cause the reaction between nitrogen and oxygen and thereby lead to generate NO_x emissions [19]. The amount of NO_x emissions is related to the maximum temperature in the cylinder, oxygen concentrations and residence time. Most of the emitted NO_x is formed early in the combustion process due to the highest flame temperature [19]. Nitrogen oxides (NO_x) include nitrogen oxide (NO) and nitrogen dioxide (NO₂), and NO generally constitutes 85-95% of NO_x. The two pollutants are distinctively different. NO is a colorless and odorless gas, while NO₂ is a reddish brown gas with pungent odor [31,32].

Nitrogen oxides emissions from Diesel exhaust gas are responsible for environmental pollution and health hazard. It was reported that NO_x emissions result in the acidification, ozone formation, nutrient enrichment and smog formation, which have

become important issues in many major cities worldwide [33]. In the atmosphere, NO_x would react with other pollutants to form tropospheric ozone (the main component of photochemical smog) and other toxic pollutants. Besides, NO and NO_2 are considered to be toxic, but NO_2 has five times greater toxicity than NO and it is also a direct concern of human lung disease. NO_2 can irritate the lungs and decrease resistance to respiratory infection (such as influenza). NO_x emissions are favorable for forming acid rain, which will affect both terrestrial and aquatic ecosystems. Nitrogen dioxide and airborne nitrate are also the components of pollutant haze that may decrease visibility [9,34].

(4) Particulate matter (PM) emissions

The combustion process in Diesel engines also causes a large number of particulate matter (PM) emissions, these particulates mainly result from the agglomeration of fine particles which include unburned fuel and lube oil, ash, sulfates and water [26,34]. The diameter size of Diesel particulates is generally in a range of 15-40 nm, and the size of most of PM (> 90%) is less than 1 μ m in diameter [19]. PM emissions are related to many factors, including combustion process, fuel and lube oil quality, exhaust gas cooling, etc. [35]. In general, the amount of Diesel particulate matter emissions are 6-10 times higher than that of Gasoline particulate matter emissions. Diesel particulate matter is composed of three main components: soot, soluble organic fraction (SOF) and inorganic ash [34,36-39]. More than 50% of particulate matter is soot (carbon black), the SOF components are often adsorbed and/or condensed on the surface of soot.

Many researchers have reported that Diesel particulate matter emissions apparently affect environment and human health [19,40-43]. In many major cities, a large number of PM emissions have led to low visibility, which severely affects people's production and life. Furthermore, the fine particles emitted to air also result in a change of the climate. Besides, fine particulate matters containing toxic components such as polycyclic aromatic hydrocarbons (PAHs) may cause lung damage and

respiratory problems and even cancers when they go into human body through the respiration [8,17,44].

2.2 Diesel Particulate filter (DPF)

In order to control Diesel exhaust pollutant emissions and protect environment and human health, the exhaust post-treatment system has been designed and widely employed in Diesel vehicles. The pollutant control system mainly includes Diesel oxidation catalyst (DOC), Diesel particulate filter (DPF) and selective catalytic reduction (SCR) [19,45,46]. As shown in Figure 2-2, DOC unit is placed in the upstream of DPF and closer to DPF. The main function of DOC unit is to reduce hydrocarbons (HCs) and carbon oxide (CO) through catalytic combustion. Besides, a small part of fine soot particles and condensed HC droplets may be also oxidized in DOC unit. The catalysts in DOC are also able to oxidize NO to NO₂, which has stronger oxidation ability than O₂ and can be used to regenerate the DPF. DPF is mainly applied to trap the particulate matters (PMs) in the exhaust gas and then regenerated periodically through physical and/or chemical methods. The role of the downstream SCR is to selectively reduce NO_x pollutant to nitrogen by using ammonia.



Figure 2-2. Diesel exhaust post-treatment system.

2.2.1 DPF filtration

As previously mentioned, one of the roles of DOC unit in exhaust post-treatment

system is to oxidize soluble organic fractions (SOFs) of Diesel exhaust PM. As a result, particulate matter emissions would be reduced to a lower level. The introduction of DPF to the post-treatment system greatly improves the efficiency of PM emission control, and it becomes the best choice to fulfil Euro 6 standard.

DPF has been applied in Diesel PM emission control since 2000. Ceramic wall-flow filters show the highest filtration efficiency (> 95%) and then received the most attention [19,47-49]. DPF is usually made of cordierite $(2MgO-2Al_2O_3-5SiO_2)$ or silicon carbide (SiC) honeycomb monolithic structure, with the channels being blocked at alternate ends [19,50]. Thus, the exhaust gas containing PM is forced through the porous channel walls (Figure 2-3) and the PM are trapped on the substrate walls by a physical process or diffused into the pore walls where they adhere.



Figure 2-3. Wall-flow filter of PM from diesel exhaust [19].

When the exhaust gas is forced to pass through the wall-flow substrates, the PM are retained on the porous channel walls. In this filtration process, there are two PM filtration mechanisms: deep bed filtration and cake bed filtration. Deep bed filtration often occurs at the initial stage of filtration. The PM with smaller size than filter pore size are forced by flow inertia and concentration gradients into wall pores. They are deposited in the wall pores by diffusion and flow line interception as exhaust gas passes through the channel walls [51]. An example of deep filtration can be seen in Figure 2-4. With the deep bed filtration, the pore size in wall substrates becomes

smaller and smaller, so that the PM cannot penetrate through the wall pores and cake bed filtration takes place. The PM deposition occurs on the surface of wall-flow substrates, so cake bed filtration is also called surface filtration. The formation of a "cake" layer is favorable for improving the filtration efficiency, thus cake bed filtration is very important, especially, at high PM emission rates [51].



Figure 2-4. Soot deep bed and cake filtration on DPF wall-flow substrates [51].

2.2.2 DPF regeneration

As the filter becomes increasingly saturated with soot, more PM are deposited on the surface of channel walls and result in the formation of PM cake layers. Consequently, excessive saturation of PM filtration leads to pore-plugging phenomena and builds up a backpressure, thereby pressure drop increasing (see Figure 2-5), which is negative for Diesel engine operation because of increasing fuel consumption, causing engine failure and high stress in the filter. In order to prevent the negative effects, the DPF has to be continuously or periodically regenerated by burning the collected PM.



Figure 2-5. Pressure drop increasing with particulate matter deposition during PM filtration [51].

In general, there are two types of regeneration methods: active regeneration and passive regeneration [19,52,53]. As shown in Figure 2-6, the active regeneration needs extra energy supply, for example, fuel combustion, electrical heat or other ways, to increase the exhaust heat. While the passive regeneration occurs under normal exhaust heat conditions through adding catalysts to the filter or fuel additives.



Figure 2-6. Active and passive regeneration methods of filter system.

The main role of DPF regeneration is to oxidize soot particles that are retained on the flow-wall substrates. On the one hand, during active regeneration, the trapped soot particles can be periodically removed through a controlled oxidation with excessive O_2 in the exhaust gas [54]. Unfortunately, the soot combustion with O_2 needs a higher temperature (> 550 °C), which is higher than Diesel exhaust temperatures [50,52,53,55]. Therefore, many strategies such as engine management, outside

sources heat and fuel injection are used to increase the exhaust temperature. However, the higher regeneration temperature arouses high fuel consumption and large amount of energy supply and thereby increases the cost of post-treatment system.

On the other hand, unlike the active regeneration, passive regeneration takes place at real exhaust gas temperatures, it does not need external heat sources or additional fuel injection to increase the exhaust temperature [56]. Main approaches used for passive regeneration have: continuously regeneration trap (CRT) with DOC + DPF, catalyzed CRT (CCRT) with adding catalysts to DPF (Figure 2-7), and fuel additives which can decrease soot combustion temperature [54,56-59].



Figure 2-7. DPF passive regeneration system [59].

CRT technology is a two-stage and full-time passive regeneration system, the soot particles accumulated in the uncatalyzed DPF are oxidized by using the NO₂ that generates from the upstream DOC unit. In view of stronger oxidizing ability of NO₂ than O₂, the passive generation temperature can be decreased to 250-300 % [54,58]. In order to further improve regeneration efficiency of DPF, some advanced catalysts

are coated onto the filter surface. NO_2 is reduced by soot particles into NO, which can be reoxidized to NO_2 on the catalysts. The increase of NO_2 concentration can not only increase the oxidation rate of soot but also enhance the fast SCR reaction [54,58]. It was reported that ceria-based materials that are coated onto DPF are able to generate a large number of active oxygen species under excessive O_2 , these active oxygen species can also effectively decrease the soot oxidation temperature [60].

Another method of passive regeneration is dosing a very small amount of fuel additives such as cerium, iron or platinum into the fuel on-board [61]. The fuel combustion in the engine results in the formation of small metallic oxide particles, they afterwards are trapped by the DPF. These metallic oxides are also able to decrease the soot combustion temperature [54,62].

2.3 Soot structure

Soot particulates are the main component of particulate matter from Diesel exhaust gas. In general, the soot particulates are collected on DPF channel wall and then removed through soot combustion. The regeneration efficiency of DPF and oxidative activity of soot are related to the structural property of soot particles [63-65]. Diesel soot particles are generally composed of 10-30 nm sphere-like particles [66], which aggregate in chain-like structures [67]. Each of the soot particles contains the carbon nucleus, which are composed of graphitic carbons. The elemental carbon is arranged in graphene sheets, which form the turbostratic particles with a wavy and multi-layered structure [68].

In fact, the oxidation activity of soot particles depends on their chemical structure or nanostructure (in particular the degree of graphitisation), and bulk properties such as proposity, H/C ratio and inorganic impurities. These bulk properties also affect the nanostructure of soot [69]. In general, the carbonaceous materials are mainly composed of highly ordered graphite and disordered amorphous carbon. Graphite is a form of pure carbon which consists of layers of hexagonally arranged carbon atoms in

a plane. The interlayer spacing of graphite is 0.0335 nm [66,69] and the chemical bonds within the carbon layers are covalent with sp^2 hybridisation [70]. On the other side, amorphous carbon is a form of carbon material without long-range crystalline order. There are also different forms of carbon structures which exist in between graphite and amorphous carbon. Graphitised carbons have more orderly stacked crystalline layers and thus expose fewer active sites, while the disordered amorphous carbons exist more active sites. It was reported that the disordered structure may evolve to become more ordered structure at higher temperatures (\geq 700-1100 °C), this process is called as graphitisation [68,71,72]. As shown in Figure 2-8. the isolated basic structural units (BSUs) gradually tend to accumulation and then form layer-like and ordered graphitised carbons.



Figure 2-8. Various steps of graphitisation [68].

Figure 2-9 shows the TEM images of Diesel soot particles, an onion-like turbostratic structure can be clearly observed. From this TEM result, it is known that soot particle is composed of relatively disordered amorphous carbon core and an external shell of neatly arranged crystalline layers. The carbon core consists of 3-4 nm fine particles and the external shell looks more disordered than carbon core [66,69,73]. Some researchers also used X-ray diffraction (XRD) to study the structure of soot particles [66,74]. As shown in Figure 2-10 [66], the XRD patterns of graphitised carbon materials show four narrow bands, which can be identified in 002 (26.8 °), 100 (42.3 °),

101 (44.5 °) and 102 (54.9 °) positions. For Diesel model soot Printex 90 and Printex XE2, their XRD patterns only show two bands appearing at 24.9 ° and 43.6 ° of Printex XE2 as well as 24.2 ° and 43.4 ° of Printex 90. The graphitisation of soot particles can be evaluated by the full width at half maximum (FWHM) and crystallite size [66]. For example, in Figure 2-10, the crystalline size of Diesel model soot is 2-4 nm and that of graphitised carbon is around 250 nm, this illustrates that Diesel model soot has lower degree of graphitization [66].



Figure 2-9. Structure of soot particles characterized by TEM [73]



Figure 2-10. X-ray diffractograms of graphite, Printex 90, and Printex XE2 [66].

Raman is also usually used to characterized the nanostructural features of soot particles, much information on the nanostructure of soot has been reported through Raman characterization [63,66,68,74-81], which provides a better understanding of soot structure. As shown in Figure 2-11, the Raman spectra of soot can be

characterized as two bands: G band and D band, which represent the content of graphitised carbon and non-graphitised carbon, respectively [68,73,75]. The degree of graphitisation of soot is generally related to the intensity and the full width at half maximum (FWHM) of G band at 1580 cm⁻¹. The D band as defect band is divided into D1, D2, D3 and D4, which appear at 1350, 1620, 1500 and 1200 cm⁻¹, respectively. D1 band and D3 band are separately related to the disordered graphite and amorphous and molecular carbons. The full width at half maximum (FWHM) of D1 and the relative intensity of D3 are considered to be important parameters, since they can provide more information on the structure of graphite-like carbon and amorphous carbon [63,75].



Figure 2-11. Raman spectrum of untreated EURO VI soot [73].

2.4 Catalyst materials

An important role of the catalysts coated on DPF channel-wall substrates is to decrease the temperature of soot oxidation, as a result, the DPF passive generation occurs under real exhaust temperatures, which apparently decreases the cost of energy consumption resulting from active generation. With the development of passive generation technology, many catalysts have been widely studied and applied in soot oxidation, which include alkali metal or alkaline-earth metal catalysts, perovskite-type catalysts, precious metal catalysts and ceria-based mixed oxide catalysts. The latter two have excellent NO oxidation ability into NO₂, redox ability, structural and

textural property and high thermal stability, thus they are extensively applied in DPF passive regeneration. In this thesis, the precious metal catalysts and ceria-based mixed oxide catalysts are mainly introduced as follows.

2.4.1 Precious metal catalysts

Precious metal catalysts are usually used for DPF passive regeneration and received much attention in catalytic field for DPF passive regeneration. Precious metal catalysts consist of two main parts: active components and support oxides. The former mainly refers to Pt, Pd, Rh and Au, and the latter includes CeO₂, CeO₂-ZrO₂, SiO₂, TiO₂, Al₂O₃, etc. materials with vesicular structure and high thermal stability. In the previous section, it is mentioned that a role of DOC is to oxidize NO in Diesel exhaust gas into NO₂ and then NO₂ is used for DPF passive regeneration, this process is called as CRT technology [82]. Some precious metal catalysts are coated onto the DPF substrate and can further oxidize NO from NO₂ reduction by soot into NO₂, thus increasing NO₂ concentration. This is favourable for the improvement of DPF passive regeneration efficiency [83,84].

Among all the precious metal catalysts, Pt catalysts show the best catalytic performance for NO oxidation into NO₂ and thus are often applied in Diesel exhaust post-treatment system. Certainly, the excellent performance of Pt catalysts is not only related to active Pt atoms but also to the dispersion, particle size and chemical state of Pt [84-87]. For the Pt catalysts, the physicochemical performance of active component Pt highly depends on the properties of the support, for example, surface area, thermal stability, and the interaction between Pt and the support, etc. [85,86,88]. The thermal sintering of the support oxides at higher temperatures would lead to the decrease of surface area and Pt dispersion, aggregation of Pt atoms and Pt particle growth, and thereby a loss of catalytic activity [88]. Moreover, the activity of Pt catalyst is affected by the composition of exhaust gas. For example, SO₂ in exhaust gas is absorbed on Pt atoms and then oxidized into SO₃, which reacts with H₂O that presents in exhaust gas into sulfuric acid, and the reaction between sulfuric acid and

some metallic ash forms sulfate. These sulfuric acid and sulfates then cover the surface of Pt atoms, leading to the deactivation of Pt [88]. Thus, Pt catalysts are generally applied in the exhaust gas system with low content of sulfur or without sulfur.

In general, thermal stability and sulfur resistance of Pt catalysts are important factors in actual application and many researchers have done a lot of works to improve the performance of the catalysts. There are two methods to optimize the precious metal catalysts and improve their catalytic performances, one is the optimization of the active component to improve the sulfur resistance, thermal stability and the dispersion of Pt. The other one is the optimization of the support oxides to better the structural and textual properties, thermal stability and the interaction between Pt and the support, and so on. For example, it was reported that the introduction of Rh into Pt catalysts can decrease the formation of SO_3 on Pt surface and thereby improve the sulfur resistance of Pt catalysts [89]. It was also found that the addition of La, Y, Ce, etc. into active components or support oxides would greatly improve the dispersion of Pt and the thermal stability of the catalysts [90-92].

In Oi-Uchisawa's studies [85], the researchers studied the effect of different support oxides, which include TiO₂, ZrO₂, SiO₂, Al₂O₃ and their mixed oxides, on soot oxidation performance of Pt catalysts. It was found that the Pt catalyst with TiO₂-SiO₂ support showed the highest activity. Then Pt/TiO₂-SiO₂ catalyst was pretreated in SO₂ gas flow, it still showed the best activity, which illustrates higher sulfur resistance of the catalyst. They also studied the effect of different reaction gases on soot oxidation activity [83], it was confirmed an apparent role of Pt on oxidizing NO to NO₂ and revealed that the presence of NO visibly enhanced the activity of the catalysts for soot oxidation. The authors also studied the mechanism for soot oxidation under the reaction gas with a small amount of SO₂ and H₂O. They thought that the presence of SO₂ and H₂O enhanced the decomposition of anhydride species as CO_x precursors. In another work [84], it was found that the precursors of Pt is also an important factor that affects soot oxidation activity of Pt catalysts. Jeguirim et al. [93] studied and compared the soot-NO₂ and soot-O₂ reactions over Pt/Al_2O_3 catalyst, they found that the presence of Pt catalyst had no apparent influence on C-NO₂ and C-O₂ reactions. While Pt catalyst showed visible catalytic activity under NO₂ + O₂ mixture. The authors suggested that the NO generating from NO₂ reduction by soot could be reoxidized into NO₂ on the Pt catalyst and thus promote catalytic activity. They also proposed C + NO₂ + O₂ cooperative reaction and thought that the presence of Pt catalyst increased the rate of the cooperative reaction.

Liu et al. [94] studied the impact of the sulfurization of Pt/Al_2O_3 catalyst on its soot oxidation activity through doping a small amount of H_2SO_4 into Pt/Al_2O_3 catalyst. The result was found that the catalyst showed better activity in the presence of NO, which would be ascribed to the interaction between Pt and sulfates. The authors discussed three reasons: (i) the formation of sulfates prevented the oxidation of Pt under high concentration of O_2 , which benefits the oxidation of NO into NO_2 over the Pt; (ii) the sulfurization of the support oxides could inhibit the adsorption of NO_x on the surface of the support, thus there are more NO_2 react with soot particles; (iii) the presence of sulfates would promote the decomposition of surface oxygenated complexes (SOCs) into CO_x .

However, the use of precious metal catalysts results in a high cost due to the expensive precious metals. Moreover, in the SO₂-containing exhaust gas, the presence of Pt catalysts would promote the formation of sulfates and increase their emissions. Therefore, many researchers have also been studying the catalysts with lower content of precious metals or without precious metals.

2.4.2 Ce-based mixed oxide catalyst

Ce-based mixed oxide catalyst is mainly composed of CeO_2 oxides and transition metal oxides such as MnO_x , Co_2O_3 , NiO, CuO, ZrO_2 , La_2O_3 and Y_2O_3 . Rare-earth metal CeO_2 oxides as cheaper materials have been confirmed to have excellent redox

ability and oxygen storage/release capacity and thus received much attention. In order to further improve the thermal stability, oxygen storage/release capacity and structural and textual properties, those transition metals are often doped into CeO_2 oxides to form Ce-based mixed oxides, thereby improving the catalytic activity. Besides, the interaction between CeO_2 and transition metal oxides can also enhance the redox ability and oxygen storage capacity of the catalysts.

Atribak et al. [95] studied a series of Ce-Zr mixed oxide catalysts with different Ce/Zr ratios and found that NO could be effectively oxidized into NO₂ by the active oxygen species presented in CeZrO₂ catalysts. They also confirmed that the catalytic activity of the catalyst is apparently related to the concentration of NO₂, and the production of NO₂ depends on the content of CeO₂ in the mixed oxides, higher content of CeO₂ would cause the production of more NO₂. In another work [96], they studied the thermal stability of CeO₂ and CeZrO₂ catalysts and found that CeZrO₂ catalyst showed higher thermal stability after calcination at 1000 $^{\circ}$ C. Subsequently, the authors added Y into CeZrO₂ and found that there was no apparent effect on soot oxidation activity, this is because ZrO₂ in Ce-Zr mixed oxides plays an important role on increasing thermal stability [97].

Krishna et al. [86] studied the impact of La, Pr, Y, Sm four rare-earth elements on the catalytic activity of CeO₂ catalyst under NO + O₂ mixture. It was found that Pr- and La-modified CeO₂ catalysts showed higher activity, which should be attributed to their increased surface area and redox ability. Besides, they also found that the lattice oxygen in CeO₂ took part in the oxidation reaction of NO into NO₂. The authors also impregnated 2.5 wt% Pt into these Ce-based mixed oxides, the experimental results showed that the presence of Pt greatly improved the redox property of the catalysts, and thereby soot oxidation activity and CO₂ selectivity. Some researchers studied the effect of Nd on physicochemical property and catalytic performances of Ce-Zr mixed oxide catalysts [98]. It was found the addition of Nd into Ce-Zr mixed oxides increased the oxygen vacancies and redox ability as well as thermal stability.

Furthermore, the presence of Nd enhanced the formation of unstable nitrites on the surface of the catalysts under NO, thus improving NO₂ production.

Wu and Liu et al. [99-101] studied the catalytic performance of MnO_x-CeO₂ mixed oxides during soot oxidation. It was confirmed the mixed oxides showed better catalytic performance under both NO + O_2 and O_2 , which should be ascribed to their strong redox ability, oxygen storage capacity and low-temperature NO_x storage capacity as well as high oxidation ability of NO into NO₂. It was also found that Mn^{x+} could enter into CeO₂ lattice and form Mn-Ce solid solution, thereby increasing the amount of oxygen defects. The authors thought that the interaction between MnO_x and CeO₂ could inhibit crystalline growth of the oxides and increase surface area. It was also revealed that under NO, the formation and decomposition of surface nitrates and NO₂ production on the Mn-Ce catalyst are very important in promoting soot oxidation reactions. In some works [102,103], Mn-Ce mixed oxides were modified by adding Ba. As a result, the modified catalyst showed higher NO_x storage in the form of surface nitrates and thereby produced more NO₂ at higher temperatures due to the decomposition of surface nitrates, thus improving soot oxidation activity. Some authors studied that the effect of the introduction of Al₂O₃ on the catalytic activity and thermal stability of Mn-Ce mixed oxides [104]. The result was found that the introduction of Al₂O₃ increased surface area of the mixed oxides and the dispersion of active species. Thus, Mn-Ce-Al mixed oxide catalyst exhibited higher activity and thermal stability after aging at high temperatures.

2.5 Soot oxidation reaction mechanism

For the mechanism of soot oxidation reaction, it might be extremely complex in view of a fact for the solid-solid-gas reaction under different contact and gas phase conditions. In our previous work [105], it was reported that the soot oxidation over Pt/MnO_x -CeO₂ under tight contact occurred at lower temperatures (250-450 °C) and showed a higher reaction rate in comparison with that under loose contact. The results should be ascribed to the accelerated oxidation mechanism of soot under tight contact.

In Jeguirim's works [106,107], it has been reported that the carbon-oxygen complexes (-C(O)) such as carboxylates and phenols could form by the chemisorption of O_2 presented in reaction gas on the carbon surface at 300-400 °C. Based on the literature [108,109], the tight contact between CeO₂ catalyst and soot can provide more contact sites on the interface between soot and the catalyst and more active oxygen species (O*) easily reach carbon surface to further oxidize -C(O) into CO₂. Furthermore, the formation of -C(O) complexes is easier under tight contact due to the involvement of more active oxygen generated from CeO₂. These facts might determine lower oxidation temperatures and enhanced oxidation rate of soot under tight contact. The reaction mechanism for the interaction of carbon and oxygen would be proposed as follows:

$$C + O_2 \rightarrow -C(O)$$

$$C + O^* \rightarrow -C(O)$$

$$-C(O) \rightarrow CO$$

$$-C(O) + O_2 \rightarrow CO_2$$

$$-C(O) + O^* \rightarrow CO_2$$

On the other hand, NO₂ plays an important role during soot oxidation due to its stronger oxidation ability than O₂. According to the publications [83,105-107,110], NO₂ can directly attack the carbon surface and the attack would first produce the surface -C(O) species, these -C(O) species then further react with NO₂ to form -C(O-NO₂) intermediate complex. In fact, the -C(O) complexes can not decompose at a significant rate below 400 °C [111]. The -C(O) complexes need to be destabilized by NO₂ attack at low temperatures and then decompose into CO and NO₂. Thus, the authors proposed the following mechanism for C-NO₂ reactions:

 $C + NO_2 \rightarrow -C(O) + NO$ $-C(O) + NO_2 \rightarrow -C(O-NO_2)$ $-C(O-NO_2) \rightarrow CO + NO_2$ $-C(O-NO_2) \rightarrow CO_2 + NO$

In fact, in the C-NO₂-O₂ reaction system, the two reactions $(C + O_2/O^* \text{ and } C + NO_2)$ mentioned above should be cooperative but not isolated during soot oxidation. The cooperative reaction may be schematically presented as follows [105]:

$$C + O_2 + O^* + NO_2 \rightarrow CO + CO_2 + NO + NO_2$$

Moreover, in Ce-based catalyst system, under $NO_x + O_2$ mixture, the formation and decomposition of surface nitrites and nitrates play an important role on the promotion of soot oxidation reactions. In Setiabudi's study [112], as shown in Figure 2-12, it was found that the formation and desorption of active oxygen, especially super-oxygen species ($-O_2^-$), originating from NO₂ chemisorptions and the decomposition of surface nitrates (such as bidentate and bridging nitrates) might accelerate the CeO₂ catalyzed soot oxidation. Setiabudi et al. thought that the gas-phase NO₂ could be adsorbed to the oxygen vacant sites of CeO₂ and then form cerium nitrates, their decomposition would lead to the production of peroxide or super-oxide species.



Figure 2-12. Reaction scheme showing oxygen transfer from NO₂ to CeO₂ [112].

3. Materials and experimental methods

3.1 List of materials

3.1.1 Materials for soot preparation

Aref model fuel Methydecanoate (C₁₁H₂₂O₂) Methyl ester (Biodiesel fuel) Standard Euro VI fuel (EN 590) Degussa Printex U soot

3.1.2 Materials for catalyst preparation

Ce(NO₃)₃·6H₂O (solid, 95% pure) Mn(NO₃)₂ (liquid, 50 wt.%) Polyvinyl alcohol (PVA) Polyethylene glycol (PEG) NH₃H₂O (NH₄)₂CO₃

3.2 Physicochemical characterization

3.2.1 Brunauer-Emmett-Teller (BET)

The textural characterization was conducted by N_2 adsorption at -196 $^{\circ}$ C in a BelSorb-Mini II (BEL-Japan) device. The BJH method was used for the calculation of the specific surface area and mean pore size.

3.2.2 Laser Granulometry

FRITSCH laser particle sizer (ANALYSETTE 22 Nano Tec) was used to measure the particle size distributions of soot under wet dispersion in which water was used as a suitable liquid. Before each measurement, the aggregated soot sample was well dispersed into individual particles by a close circulatory system and an integrated ultrasonic generator.

3.2.3 X-Ray Diffraction (XRD)

The X-ray diffraction was performed on PANalytical-Empyrean diffractometer (Japan Science) with CuK α radiation ($\lambda = 0.154056$ nm) to obtain some information about internal lattice parameters of soot. The X-ray tube was operated at 40 kV and 40 mA. The XRD patterns of samples were recorded in the range of $10^{\circ} \leq 2\theta \leq 90^{\circ}$ with a scanning step size of 0.02° . The stacking thickness of crystallites (D) and the crystalline length (L) as crystallite dimensions of soot samples can be calculated by applying the Scherrer equation to the bands 002 and 100, respectively, where *K* and *K* are the shape factors and β_{002} and β_{100} are the full widths at half maximum of the bands.

$$D = \frac{K\lambda}{\beta_{002}\cos\theta_{002}}, K = 0.89$$
$$L = \frac{K'\lambda}{\beta_{100}\cos\theta_{100}}, K' = 1.84$$

3.2.4 Temperature-Programmed Reduction (TPR)

3.2.4.1 H₂-TPR

The hydrogen temperature-programmed reduction (H₂-TPR) profiles were obtained using a BELCAT-M (BEL-Japan) apparatus, equipped with a TCD. The materials were outgassed and activated at 400 $^{\circ}$ C for 1 h in Ar, then cooled down to room temperature and reduced until 700 $^{\circ}$ C in 5 vol.% H₂/Ar at a heating rate of 8 $^{\circ}$ C/min.
3.2.4.2 Soot-TPR

30 mg of soot-catalyst mixture in tight contact was used for soot temperature-programmed reduction (soot-TPR). The sample was heated from 80 to 650 $\$ at a ramp rate of 5 $\$ /min in a pure Ar flow (100 ml/min). The consumption signals (CO_x concentration) of soot were monitored by a MS (mass spectrometry) detector (Figure 3-2).

3.2.5 Temperature-Programmed Desorption (TPD)

3.2.5.1 NO_x-TPD coupled to MS

The catalyst (50 mg) was outgassed at 450 °C under O₂/Ar flow for 30 min to clean the surface and then cooled down to 350 °C. NO and NO₂ adsorptions in the catalyst were separately performed in a U-shaped quartz reactor by the exposure in 400 ppm NO/9% O₂/Ar and 400 ppm NO₂/9% O₂/Ar for 1 h. After that, the sample was kept at 80 °C in pure Ar flow for 1 h for proper degassing. The desorption profiles of NO_x and O₂ were obtained by heating the sample from 80 to 550 °C at 10 °C/min in Ar flow (100 ml/min). The concentrations of desorption species were calculated by the m/z = 30 (NO), 32 (O₂) and 46 (NO₂) on a mass spectrometer (MS) (Figure 3-2).

3.2.5.2 NO_x-TPD coupled to IR

The prepared MnO_x-CeO₂ mixed oxides were treated at 350 °C for 30 min in 600 ppm NO/10% O₂/N₂, and then cooled down to 100 °C, the gas mixture was replaced by pure N₂ and the sample was maintained for 1 h to remove the weakly adsorbed NO_x species. The NO_x (NO and NO₂) temperature-programmed desorption (NO_x-TPD) tests were carried out in a fixed-bed reactor. 50 mg of pretreated sample was heated to 650 °C from 100 °C at a heating rate of 10 °C/min in N₂ or 10% O₂/N₂ flow with a flow rate of 500 ml/min. The concentration of NO_x desorbed from the catalyst was

recorded on an IR detector.

3.2.6 Thermal Gravimetric Analysis (TGA)

The SOFs content of soot samples was evaluated by means of thermogravimetric oxidation in a SDT Q600 apparatus (TA Instruments), under air flow, heating from ambient temperature to 800 % at a rate of 10 %/min.

The soot oxidation reactivity of the catalysts was also measured through means of thermogravimetric oxidation in a HCT-2 apparatus, in 10% O_2/N_2 flow (50 ml/min), heating from ambient temperature to 700 °C at a rate of 10 °C/min.

3.2.7 Transmission Electron Microscope (TEM)

High-resolution transmission electron microscopy (HR-TEM) (JEOL JEM 100CX) with a point resolution of 0.3 nm was utilized for an analysis of the internal structure of soot particles. The high-resolution images were acquired under 500,000 magnification. The carbon fringes lengths of different soot samples were also measured and analyzed by a software *Image J* in this work. The carbon fringe length distribution (f(x)) of soot was obtained by the following:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{\frac{-(x-\mu)^2}{2\sigma^2}}, \ \sigma > 0$$

where μ is the mean value of fringe lengths, σ is the standard deviation and σ^2 is the variance.

3.2.8 Raman Spectroscopy (Raman)

Raman spectra of soot were obtained on a micro-Raman system (Horiba Jobin Yvon HR 800 UV) with an exciting source of 532 nm. The output power of 0.1 mW was chosen in the scanning range of 800-2000 cm⁻¹. The spectrometer includes a grating

with 600 grooves mm^{-1} and a CCD detector with $50 \times magnification$ objective lens.

3.2.9 Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS)

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of soot were measured by using a Nicolet 6700 spectrometer with a DTGS detector and a high temperature cell. Soot sample was diluted by KBr at a soot/KBr ratio of 1/40, then the mixture was placed in a reaction cell and pretreated at 100 $^{\circ}$ C in pure N₂ for 10 min. After that, the IR spectra were recorded.

The diffuse reflectance infrared Fourier transform spectra (DRIFTS) of catalyst were measured by using the same equipment. MnO_x -CeO₂ powder sample was diluted by KBr and placed in a reaction cell and then pretreated at 500 °C in pure N₂, the background spectra were recorded at 250, 350 and 450 °C. The sample was finally exposed in 600 ppm NO/10% O₂/N₂ at each temperature for 30 min for DRIFTS measurements.

3.2.10 X-ray Photoelectron Spectra (XPS)

XPS measurement was conducted on an AXIS Ultra DLD spectrometer (Kratos, England) by using AlK α radiation as the excitation source (300 W). All binding energies (B.E.) were referenced to carbon C 1s line at 284.6 eV.

3.3 Reactivity evaluation by TPOs

3.3.1 Soot oxidation reactivity

The catalyzed and non-catalyzed oxidation activities of soot samples were studied by temperature program oxidation (TPO) tests under different reaction gases: 9% b.v. O_2/Ar , 400 ppmv NO + 9% b.v. O_2 in Ar, 400 ppmv NO₂ + 9% b.v. O_2 in Ar. It is well

known that one of important functions of Diesel oxidation catalyst (DOC) placed the up-stream of DPF is to convert NO into NO_2 and assist the DPF passive regeneration. Thus, NO_2 as reaction gas was added into gas mixtures in order to simulate real DPF regeneration conditions.

Soot-TPOs were performed in a U-shaped quartz reactor (internal diameter 8 mm) with a porous frit as reaction bed (Figure 3-1). Each sample was placed in the reactor and heated by a thermally isolated furnace at a ramp rate of 10 °C. As shown in Figure 3-1, the reaction temperature was monitored by K-type thermocouple located in a thermowell in the reaction bed. The temperature program was controlled by a heating controller (E'EUROTHERM 2404). All gas flows were controlled with the mass flow meters (Brooks 5850S and Brooks Delta II). The gas mixtures passed through the reactor at a total flow rate of 15 Nl/h (GHSV \approx 100,000 h⁻¹). Concentrations of CO and CO₂ (ppmv) in the outlet were measured by a Siemens Ultramat6 analyzer (Figure 3-2).

Soot and MnO_x-CeO₂ catalyst powder were mixed by a spatula in an agate mortar for 2 min with a weight ratio of 1/10 (2.0 mg/20 mg) to obtain so-called loose-contact mixtures [105,109,113]. In order to compare the soot oxidation activity in different contact cases, the tight-contact and pressure-contact samples with same soot/catalyst ratio were prepared via using a pestle grinding for 2 min and loading about 60 bar pressure in a pneumatic press, respectively [105,113]. Tight contact was used in this work to study the intrinsic activity of soot catalytic combustion. In fact, in real catalytic wall-flow DPF, the formation of soot cake during soot filtration can lead to the increase of flow pressure, which promotes the interface contact between soot and catalyst. Base this case, pressure contact was selected to evaluate the catalytic reactivity of soot. To minimize the impact of hot spots, the soot-catalyst mixtures (22 mg) were diluted with 80 mg SiC pellets. In the obtained soot-TPO curves, T_i and T_m separately represent the ignition temperature at which the CO_x (CO + CO₂) concentration reaches 100 ppm and the temperatures at which 5% and 50% of soot

conversion.

For each experiment, based on the reaction $C(\text{soot}) + (1 + x)/2O_2 \rightarrow xCO_2 + (1-x)CO$, the specific reaction rates were normalized to initial soot mass (2.0 mg) or the catalyst quality (20 mg) and thus calculated by the following:

$$V_{spec} = \frac{(X_{CO} + X_{CO2}) \times D \times 10^{-3}}{3600 \times V_M \times m_{soot,ini}}$$
(Eq. a)

$$V_{spec} = \frac{(X_{co} + X_{co2}) \times D}{3600 \times V_M \times m_{cat}}$$
(Eq. b)

Where V_{spec} : the specific reaction rate in mmol_{soot}/s/g_{soot,ini} (Eq. a) or μ mol_{soot}/s/g_{cat}. (Eq. b),

 X_{CO} and X_{CO2} : molar fractions of CO and CO₂ in ppmv,

D: flow rate (15 Nl/h),

 V_M : molar volume (22.4 L/mol),

 $m_{soot,ini}$ and m_{cat} : initial quality of soot (0.002 g) and mass of catalyst (0.02 g).

Moreover, the selectivity of CO_2 (S_{CO2}) in soot oxidation reaction was obtained through the following equation:

$$S_{CO2} = \frac{X_{CO2}}{X_{CO} + X_{CO2}} \times 100\%$$

3.3.2 NO oxidation reactivity (NO-TPO)

The NO temperature-programmed oxidation (NO-TPO) tests were conducted in a fixed-bed reactor. The reaction gases including 600 ppm NO, 10% O_2 , N_2 were fed to the fixed-bed reactor at a flow rate of 500 ml/min. 50 mg of MnO_x -CeO₂ sample was firstly mixed with 200 mg SiC powder and the mixture was then used in NO-TPO test. In order to a comparison, the mixture of 50 mg catalyst and 5 mg soot was also used

for NO-TPO under same conditions. The reactor temperature was heated to 650 °C at a heating rate of 10 °C/min. The effluent gases were detected on an infrared (IR) spectrometer (Thermo scientific).

3.4 Isothermal experiment

Isothermal experiments of soot oxidation were conducted at 350 °C or 400 °C under 9% b.v. O_2/Ar and 400 ppm $NO_x/9\%$ b.v. O_2/Ar , respectively, to obtain the specific reaction rate of soot. There is no apparent increase in soot conversion at 350-400 °C, thus soot oxidation reaction is in a relatively stable state. High space velocity and mixing SiC powder effectively inhibit the mass and heat transfer, and thereby soot oxidation reaction can be mostly controlled by the chemical kinetics [114,115]. After isothermal reaction for 1800 s, The "initial soot oxidation rate" at the starting of isothermal reaction and the "final soot oxidation rate" at the end were recorded.





Figure 3-1. The physical profile of TPO equipment.



Figure 3-2. The physical profiles of exhaust gas detectors.

4.1 Introduction

In order to avoid the emission of soot from diesel vehicles and serious air pollution, one effective method is to trap the soot by a Diesel Particulate Filter (DPF) and then to burn soot at lower temperatures by a catalytic technology [116-118]. MnO_x -CeO₂ mixed oxides as a cheap and effective candidate for diesel soot oxidation have been widely studied because of their high redox properties and oxygen storage capacity [92,119,120]. Moreover, higher NO_x storage capacity and better oxidation ability of NO to NO₂ make the soot oxidation reaction easier [92,118].

NO-assisted soot oxidation reactions are complex since they involve two main oxidants: NO₂ and oxygen, both oxidants playing a dominant role during soot oxidation. It is well known that NO_2 has a stronger oxidation ability than O_2 , and it often plays a key oxidizing role in Pt catalyst system. For example, in Pt/Al₂O₃ catalyst system, the NO in exhaust gas can be oxidized into NO₂ on Pt active sites, and soot oxidation activity greatly depends on the production of NO₂ [87,94]. It has been reported that there are two fundamental reactions during soot oxidation in the presence of NO_2 and O_2 : the direct and cooperative reactions [106,107,121]. The direct oxidation reactions (Eqs. (1) and (2)) are triggered when O₂ or NO₂ reaches the carbon surface along with the C-NO₂-O₂ cooperative reactions (Eqs. (3) and (4)). For the cooperative reactions, firstly, the soot reacts with O_2 and forms -C(O) complexes (Eq. (5)), then the presence of NO₂ would lead to the formation of intermediate nitro-oxygenated species (-C(ONO₂)) (Eq. (6)), and their decomposition finally produces CO and CO₂ (Eqs. (7) and (8)) [100,106,110,122]. However, for Ce-based oxygen storage materials, the generation of active oxygen species (O*) and NO_x storage play an important role during soot oxidation and thus make the case of soot oxidation different with that of Pt/Al_2O_3 [92,105,123]. Except for the cooperative C +

 $NO_2 + O_2$ reactions, the oxidizing role of active oxygen from Ce-based oxides would make soot oxidation reaction easier, because the presence of active oxygen effectively enhances the formation and oxidation of -C(O) complexes (Eq. (9)) and thus the cooperative reaction (Eq. (10)).

$C + NO_2 \rightarrow CO_x + NO$	Eq. (1)	
$C + O_2 \rightarrow CO_x$	Eq. (2)	
$C + NO_2 + O_2 \rightarrow CO_2 + NO$	Eq. (3)	
$C + NO_2 + O_2 \rightarrow CO + NO_2$	Eq. (4)	
$C + O_2 \rightarrow -C(O)$	Eq. (5)	
$-C(O) + NO_2 \rightarrow -C(ONO_2)$	Eq.(6)	
$\text{-C(ONO_2)} \rightarrow \text{CO} + \text{NO}_2$	Eq. (7)	
$-\mathrm{C(ONO_2)} \rightarrow \mathrm{CO_2} + \mathrm{NO}$	Eq. (8)	
$C + O^* \rightarrow CO + CO_2$	Eq. (9)	
$C + O_2 + O^* + NO_2 \rightarrow CO + C$	$O_2 + NO + NO_2$	Eq. (10)

It has been reported that the low-temperature (20-50 °C) adsorption of NO on CeO₂ and CeO₂/ZrO₂ could promote the formation of surface O₂⁻ species and vacant site (\Box) of Ce³⁺ [124]. Atribak et al. [95] proposed that NO could be adsorbed in oxygen vacancies (\Box) of ceria and then formed transient species (NO⁻) (Eq. (11)), these species were oxidized into nitrites and nitrates by an active oxygen transfer process in ceria, which also led to the formation of Ce³⁺ (Eqs. (12) and (13)). Setiabudi et al. [112] reported that CeO₂-accelerated soot oxidation reaction under NO + O₂ was because the decomposition of surface nitrates led to the generation of surface peroxides (-O₂⁻) as more active oxygen species (Eq. (14)). It was also confirmed that the decomposition of the nitrates formed on Ce-based catalysts led to the desorption of oxygen and NO_x [95,112]. In the previous work [105], it was found that nitrates decomposition on Pt/MnO_x-CeO₂ catalyst greatly enhanced oxygen desorption.

$$Ce^{3+}$$
-□ + NO → Ce^{4+} -NO⁻ Eq. (11)
 Ce^{4+} -NO⁻ + Ce^{4+} -O* → Ce^{4+} -NO₂⁻ + Ce^{3+} -□ Eq. (12)

 $Ce^{4+}-NO_{2}^{-} + Ce^{4+}-O^{*} \rightarrow Ce^{4+}-NO_{3}^{-} + Ce^{3+}-\square \qquad \text{Eq. (13)}$ $Ce^{4+}-NO_{3}^{-} \rightarrow Ce^{4+}-O_{2}^{-} + NO \qquad \text{Eq. (14)}$

In Wu's works [100], the effect of adsorbed NO_x species (surface nitrates) on soot oxidation activity over MnO_x -CeO₂ was investigated. The authors thought that the high promotion of NO on soot oxidation activity was mainly attributed to the role of NO₂ from nitrate decomposition and NO catalytic oxidation. However, in our previous works [105], we analyzed the emissions of all products during NO_x-assisted soot oxidation over Pt/MnO_x-CeO₂ and found that the oxygen, which results from the catalyst and NO desorption, also showed an apparent role in promoting soot oxidation. In fact, the adsorption/desorption performances of NO in MnO_x-CeO₂ mixed oxides exist in NO_x-assisted soot oxidation process. Thus a question remains: what are the effects of NO adsorption/desorption on the surface properties of MnO_x-CeO₂ catalyst and soot oxidation activity?

The main goal of this work is to investigate the influence of NO adsorption on surface properties of MnO_x -CeO₂ catalyst, including surface nitrates formation and decomposition, surface element content and state, active oxygen species and oxygen vacancies. Furthermore, we also studied the effects of NO desorption on oxygen desorption property and the oxygen availability of MnO_x -CeO₂ catalyst. The isothermal method was also used to evaluate the soot oxidation rate at 400 °C.

4.2 Materials preparation

 MnO_x -CeO₂ mixed oxides (CM) (Mn/Ce = 1/4 (mol/mol)) as the catalyst were prepared via a co-precipitation method as previously reported [105]. Ce(NO₃)₃ 6H₂O (solid, 95% pure) and Mn(NO₃)₂ (liquid, 50 wt.%) as the precursors were firstly dissolved in deionized water, then adding the dispersants PVA (*polyvinyl alcohol*) and PEG (*polyethylene glycol*) into the mixed solution. Finally, the mixture solution was mixed with the precipitant (pH > 9.0) consisting of NH₃·H₂O and (NH₄)₂CO₃ (chemical reagents, Beijing). The obtained precipitates were filtered and dried by a spraying apparatus, then calcined in static air at 500 $\,^{\circ}$ C for 3 h in a muffle furnace.

The prepared sample was treated at 350 °C for 30 min in 600 ppm NO/10% O_2/N_2 , and then cooled down to 100 °C, the gas mixture was replaced by pure N_2 and the sample was maintained for 1 h to remove the weakly adsorbed NO_x species. The NO-adsorbed sample was labeled as CM-NO.

Printex U (Degussa) carbon was used as the model soot in soot oxidation activity measurement.

4.3 Physicochemical properties

4.3.1 DRIFTS tests

Figure 4-1 shows *in situ* DRIFTS of CM after the adsorption of NO, the strong NO_x storage capacity can be seen here. According to the literature [100,105,112,125], the bands of monodentate nitrates appear at 1040, 1237, 1290, 1440 and 1510 cm⁻¹ and those of bidentate nitrates can be seen at 1040, 1270, 1310, 1540 and 1580 cm⁻¹. And ionic nitrates (1030, 1280, 1380 cm⁻¹), chelating nitrites (1205 cm⁻¹), nitro compounds (1410 cm⁻¹) and a N₂O₄ compound (1750 cm⁻¹) are also observed in Figure 4-1. It can be noticed that at lower temperatures (250 and 350 °C) the NO_x is stored as various NO-adsorbed species, but at higher temperature (450 °C) most of NO adsorbed species are decomposed except for ionic nitrates. This illustrates ionic nitrates are more stable than others at high temperatures [126].



Figure 4-1. In situ DRIFTS of CM exposed to 600 ppm NO/10% O₂/N₂ at different temperatures.

4.3.2 XPS analysis

Figure 4-2 shows the XPS spectra of CM-NO and CM, and the XPS results are summarized in Table 4-1. According to the publications [92,127], the peaks at v, v', v" and u, u', u''' are assigned to Ce^{4+} and the peaks at v'' and u'' to Ce^{3+} ; the fitted XPS spectra of Mn 2p give the peaks of Mn^{4+} (643.0-644.5 eV), Mn^{3+} (641.6-642.9 eV) and Mn^{2+} (640.8 eV); the lattice oxygen at 529.1 eV (O²⁻) and surface adsorbed oxygen at 531.6 eV $(O_2^{2^2}, O^2, O_2^2, etc.)$ can be also observed in O 1s XPS spectra. The in situ DRIFTS tests confirm the formation of surface nitrates and nitrites on the catalyst during NO adsorption (Figure 4-1). Based on the mechanisms for nitrites/nitrates formation [95,128,129], the adsorption of NO and NO_x storage in ceria leads to a change in surface element states. For example, some bidentate nitrites formed on ceria can be oxidized by the activated O* surface species (Ce⁴⁺-O*) into nitrates, this thereby makes Ce⁴⁺ transfer to Ce³⁺ [128]. Thus, NO adsorption on CM surface should arouse the changes in the relative content of surface element components. As shown in Table 4-1, after NO adsorption, the relative content of surface Ce visibly decreases from 29.5 to 27.9%, but Ce³⁺/Ce has no a change. A slight decrease in surface Mn content can be observed. The results are also confirmed in UV-vis DR spectra (Figure 4-3) in view of the decrease of UV adsorbance intensity at ~302 nm ($O^{2-} \rightarrow Ce^{4+}$ electronic transition) and ~605 nm (electronic transition in MnO_x) [127,130,131]. However, it is interesting to note that the relative content of

surface Mn^{4+} obviously decreases from 1.17 to 0.56% and that of surface Mn^{3+} increases from 1.7 to 2.0%. This result illustrates that NO adsorption on CM greatly affects the chemical states of Mn. Moreover, NO-adsorbed sample shows apparently increased surface adsorbed oxygen (O_{ads}) (from 15.8 to 21.8%) due to the formation of NO_x-adsorbed species such as nitrites/nitrates.



Figure 4-2. XPS spectra of CM-NO (a) and CM (b).

Table 4-1. XPS results of CM-NO and CM.

Catalyst	Element (at.%)		Ce	Ce (at.%)		Mn (at.%)		O (at.%)		
	Ce	Mn	0	Ce ³⁺	Ce ³⁺ /Ce	Mn^{4+}	Mn^{3+}	Mn^{2+}	O _{ads}	\mathbf{O}_{latt}
СМ	29.5	6.0	64.5	3.8	12.9	1.17	1.7	1.35	15.8	48.7
CM-NO	27.9	5.8	66.3	3.6	12.9	0.56	2.0	1.21	21.8	44.5



Figure 4-3. UV-vis RD spectra of CM and CM-NO.



Figure 4-4. XRD pattern of MnO_x -CeO₂ mixed oxides.

Thus, based on the changes in the chemical states of Mn and Ce, the possible pathways leading to the formation of nitrites/nitrates can be mentioned, as suggested by Eq. (11) and Eqs. (15)-(19). Firstly, the NO molecules absorbed on active sites $(Ce^{4+}-O^*)$ are oxidized into NO₂ and then stored at the form of nitrites, and those absorbed in the vacancies $(Ce^{3+} - \Box)$ form transient species (NO⁻) by the electron transfer process and then are oxidized by CeO₂/MnO₂ to nitrites [95,112]. The formation of many nitrates (Figure 4-1) on CM should be the oxidation of these nitrites by active oxygen (O*). It has been confirmed that MnO_x-CeO₂ mixed oxides show fluorite-like structure and decreased lattice constant (0.5392 nm) compared to pure CeO₂ (0.5418 nm) (Figure 4-4) [92,132]. Furthermore, their lower wavenumber of F_{2g} model (455 cm⁻¹) than that of pure CeO₂ (463 cm⁻¹) illustrates the formation of Mn-Ce solid solution (see Figure 4-3) [132]. In fact, on the surface of Mn-Ce solid solution, Ce-O and Mn-O adjacent sites are present. Thus, the labile oxygen in MnO_x phase can take part in the transformations of Ce⁴⁺-NO⁻ to Ce⁴⁺-NO₂⁻ and Ce⁴⁺-NO₂⁻ to $Ce^{4+}-NO_3^-$ and $Ce^{3+}-\Box$ can be oxidized by the active oxygen in MnO_x phase (Eq. (20)). A great decrease in Mn⁴⁺ content for CM-NO sample might be ascribed to its stronger oxidizing role than Ce⁴⁺ during nitrites/nitrates formation.

$$\operatorname{Ce}^{4+}-\operatorname{O*} + \operatorname{NO} \to \operatorname{Ce}^{4+}-\operatorname{NO}_2^{-}$$
 Eq. (15)

$$Ce^{3+} - \Box + NO \rightarrow Ce^{4+} - NO^{-}$$
 Eq.(11)

$$Ce^{4+}-NO^{-} + Ce^{4+}-O^{*} \rightarrow Ce^{4+}-NO_{2}^{-} + Ce^{3+}-\Box$$
 Eq. (16)

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$Ce^{4+}-NO^{-} + Mn^{4+}-O^{*} \rightarrow Ce^{4+}-NO_{2}^{-} + Mn^{3+}-\Box$	Eq. (17)	
$Ce^{4+}-NO_2^- + Ce^{4+}-O^* \rightarrow Ce^{4+}-NO_3^- + Ce^{3+}-\Box$	Eq. (18)	
$Ce^{4+}-NO_2^- + Mn^{4+}-O^* \rightarrow Ce^{4+}-NO_3^- + Mn^{3+}-\Box$	Eq. (19)	
Ce^{3+} - \Box + Mn^{4+} - $\operatorname{O*}$ \rightarrow Ce^{4+} - $\operatorname{O*}$ + Mn^{3+} - \Box	Eq. (20)	

4.3.3 Raman analysis

The Raman spectra of CM and CM-NO are shown in Figure 4-5. A prominent band at ~455 cm⁻¹ should be assigned to the F_{2g} mode in fluorite-like structure. The weak band centered at ~600 cm⁻¹ is ascribed to the oxygen vacancies in CeO₂ lattice [133,134] and that at 644 cm⁻¹ to oxygen defects in the doped CeO₂ [127]. To obtain the relative amount of O-vacancies, the correct method is calculated the ratio between the areas of O-vacancy (A_{OV}) band and F_{2g} band (A_{F2g}). The higher ratio reveals a larger O-vacancies concentration. As shown in Figure 4-5, CM-NO shows an increased A_{OV}/A_{F2g} ratio (0.75) compared to CM (0.68), which illustrates that NO adsorption increases the O-vacancies in the sample. It is worth noting that NO adsorption more apparently influences the states of Mn ions in Mn-Ce oxides (Table 4-1), thus it is likely that the increase in O-vacancies is related to the change of Mn.



Figure 4-5. Raman spectra of CM and CM-NO. A_{OV} : area of the bands at 600 and 644 cm⁻¹, A_{F2g} : area of F_{2g} band.

4.3.4 TPD analysis with IR and MS



Figure 4-6. (a) NO- and (b) NO₂-TPD profiles of CM-NO sample in N_2 and 10% O_2/N_2 .

The NO_x desorption experiments of CM-NO sample were carried out by means of TPD with an IR detector in N₂ and 10% O₂/N₂, respectively, to investigate the desorption cases of NO and NO₂ and the results are shown in Figure 4-6. In the case of NO-TPD (Figure 6-4a), the desorption profile in N₂ flow shows a larger NO desorption peak than that in 10% O₂/N₂, this illustrates that NO-TPD in N₂ is more favorable for the desorption of NO. In the other case of NO₂-TPD (Figure 6-4b), a contrary result compared to NO-TPD can be seen, the NO₂-TPD profile in 10% O₂/N₂ exhibits more apparent NO₂ desorption peak than that in N₂. This may be because the desorbed NO₂ is more easily decomposed into NO in N₂ due to thermal control of the balance reaction: NO₂ \leftrightarrow NO + 1/2O₂ at high temperatures. However, the decomposition of NO should be mainly based on the decomposition of nitrates (Eq. (21)) [112]. Thus the increase in NO₂ desorption in the presence of O₂ more likely results from the oxidation of the produced NO over the catalyst.

$$Ce(NO_3)_4 \rightarrow CeO_2 + 4NO + 3O_2$$
 Eq. (21)

TPD-MS profiles were also obtained by heating the samples CM and CM-NO at 5 °C/min under pure Ar flow. It can be observed in Figure 4-7 that NO-adsorbed CM shows a stronger NO desorption (> 200 ppm) and a smaller NO₂ emission (< 20 ppm) during TPD experiment. This illustrates that NO is the main product in the decomposition of NO_x-adsorbed species. It has to be noted that the O₂ desorption

profile of CM-NO shows a much lager amount of O_2 during NO desorption. However, for the blank sample (CM), there is no apparent O_2 desorption (< 20 ppm). The results indicate that the NO adsorption/desorption enhances the yield of oxygen species in the CM catalyst and further confirm that nitrates decomposition follows Eq. (21). Based on the literature [112], the decomposition of nitrates would lead to the production of cerium peroxides and super-oxides (Ce- O_2^-), the emission of partial O_2 should be attributed to their decomposition.



*Figure 4-7. Mass spectrometry of NO, NO*² *and O*² *emissions during TPD tests of CM (blank) and CM-NO. The sample was heated from 50 to 500 ℃ at 5 ℃/min in pure Ar flow (100 ml/min).*

4.3.5 Soot-TPR tests coupled to MS

To know the real reduction ability of CM and CM-NO used for soot oxidation, soot-TPR was conducted in pure Ar flow based on carbon-catalyst redox reactions. As shown in Figure 4-8, it can be seen that the TPR profiles (CO_x) show some continuous reduction peaks. According to the publications [135,136], the peak at about 200 $^{\circ}$ C should be ascribed to the reduction of the outer layer and that at 250-600 $^{\circ}$ C might be assigned to the reduction of the second outer layer. By comparison, CM-NO shows larger soot consumption and decreased reduction temperatures. This illustrates that the NO adsorption/desorption enhances the redox property of CM. As revealed in the previous results, NO adsorption arouses the changes in Ce/Mn valence states and increases the oxygen vacancies, which would improve oxygen storage capacity and

mobility of oxygen in CM. Besides, NO desorption greatly promotes the generation of surface oxygen species. These should play a crucial role on promoting the redox property of CM.



Figure 4-8. Soot-TPR results of CM (dash line) and CM-NO (solid line) with NO and O₂ emissions. The mass of soot-catalyst mixture was 30 mg, the sample was heated from 80 to 650 °C at a ramp rate of 5 °C/min in pure Ar flow (100 ml/min).

Moreover, it should be noticed in Figure 4-8 that the desorption of O_2 can hardly be observed during soot-TPR, while the previous TPD results show an obvious O_2 desorption of CM-NO. This reveals the consumption of surface oxygen species in soot-catalyst redox reactions and thus confirms a key role of oxygen in NO-assisted soot oxidation reactions.

4.4 Soot oxidation activity

4.4.1 Soot-TPO

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Figure 4-9. The soot oxidation reaction with CM catalyst. The mass of soot-catalyst mixture was 20 mg, 80 mg SiC powder was used for dilution. The flow rate of reaction gas was 500 ml/min, heating rate was 10 °C/min.



Figure 4-10. NO oxidation to NO₂ over CM catalyst in 600 ppm NO/10% O₂. 50 mg catalyst and 5 mg soot were used here, the flow rate of 600 ppm NO/10% O₂/N₂ was 500 ml/min, heating rate was 10 °C/min.

It was proposed in the literature that the promoting role of NO on soot oxidation with Ce-based materials should be attributed to NO₂ from NO oxidation [100,118,119,135], while other authors proposed that active oxygen in Ce-based oxides played a key role on the acceleration of NO_x-assisted soot oxidation [105,112]. In our works, the consumption of oxygen was detected during NO-assisted soot oxidation and the result shows that oxygen exhibits a larger contribution on oxidizing soot (Figure 4-9). NO₂ production of CM (50 mg) with/without soot was measured on IR analyzer (NO-TPO), the results (Figure 4-10) show that NO₂ production of CM with soot is close to that of

bare CM. This seems to illustrate that the consumption of NO_2 is not apparent during soot oxidation.



Figure 4-11. Soot oxidation activities of CM and CM-NO in 10% O₂/N₂. The mass of soot-catalyst mixture was 20 mg, 80 mg SiC powder was used for dilution. The flow rate of reaction gas was 500 ml/min, heating rate was 10 °C/min.

To compare soot oxidation activities of CM and CM-NO, the soot-TPO was conducted in 10% O_2 and the results are shown in Figure 4-11. By comparison with CM, CM-NO shows an apparently accelerated soot oxidation activity at 350-550 °C. The TG tests (Figure 4-12) can also evidence this point. The previous results (Figure 4-6) have revealed that NO desorption of CM-NO effectively promotes the desorption of oxygen, which may be an important factor that promotes the low-temperature activity. In Wu's work [100], the Mn-Ce mixed oxides were pretreated in NO + O₂ at 350 °C and then used for TPO test in O₂, the same results can be observed. The authors thought that the promotion on soot oxidation activity should be ascribed to the nitrate-derived NO₂. However, in the present work, the production of NO₂ is very little during NO_x desorption (Figure 4-6), thus the oxidizing role of NO₂ is very weak.



Figure 4-12. Soot-TG result of CM and CM-NO in 10% O₂/N₂ with a flow rate of 50 ml/min.

25 600 Soot + 10% O₂ Soot + 400 ppm NO₂ + 10% O₂ Soot oxidation rate (µmol_{soo}/s.g_{ini}) 2 00 07 07 500 Soot + 400 ppm NO₂ Soot + 10% O₂ + CM-NO Soot + 400 ppm NO + 10% O₂ + CM 400 Soot + $10\% O_2 + CM$ 300 200 100 0 0 20 60 t (min) 100 120 40 80

ŝ

emperature

4.4.2 Isothermal reaction at 400 °C

Figure 4-13. The profiles of isothermal reactions at 400 °C. The masses of soot and catalyst were 2.0 mg and 20 mg, respectively, 80 mg SiC was used for dilution, flow rate was 15 Nl/h.

Ponotion conditions	Initial soot oxidation activity	Final soot oxidation acitivity	
Reaction conditions	$(\mu mol_{soot}/s/g_{ini})$	$(\mu mol_{soot}/s/g_{ini})$	
Soot + 10% O ₂	0.9658	0.4967	
$Soot + 400 \text{ ppm } NO_2$	0.8146	0.6137	
Soot + 400 ppm NO ₂ + 10% O ₂	1.8788	1.0791	
Soot + 10% O_2 + CM-NO	3.9335	1.4943	
$Soot + 400 \text{ ppm NO} + 10\% \text{ O}_2 + \text{CM}$	12.950	12.355	
Soot + 10% $O_2 + CM$	3.7050	1.1089	

Table 4-2. The results of isothermal reactions at 400 $\,$ °C.

Figure 4-13 and Table 4-2 illustrate the oxidation performances of soot under isothermal conditions at 400 °C. In the absence of the catalyst, the oxidation reactions of soot show lower reaction rate in both the presence and absence of NO₂. It can be seen in Table 4-2 that the oxidation rate under 10% O₂ and 400 ppm NO₂ is lower than that under 400 ppm NO₂ + 10% O₂ and only 400 ppm NO₂ in reaction gas cannot show a high soot oxidation rate. This fact indicates a cooperative oxidation reaction of NO₂ and O₂. Generally, the chemisorption of O₂ on the surface of soot leads to the formation of -C(O) complexes (Eq. (5)), then the NO₂ reacts with -C(O) complexes and forms nitro-oxygenated species (-C(ONO₂)) (Eq. (6)), their decomposition thereby produces gas-phase CO and CO₂ (Eqs. (22) and (23)) [100,105,106]. This cooperative reaction also confirms an importance of oxygen during soot oxidation.

$C + O_2 \rightarrow -C(O)$	Eq. (5)
$-C(O) + NO_2 \rightarrow -C(ONO_2)$	Eq. (6)
$-\mathrm{C(ONO_2)} \rightarrow \mathrm{CO} + \mathrm{NO_2}$	Eq. (22)
$-C(ONO_2) \rightarrow CO_2 + NO$	Eq. (23)

On the other hand, in the case of catalytic reactions, it can be observed that in 10% O₂, the soot oxidation rate has a greater increase in both the initial and final soot oxidation activities compared to non-catalytic reaction. This is because CM catalyst provides many active oxygen species (O*) and thus greatly enhances soot oxidation rate (Eqs. (24) and (25)). For the pretreated sample CM-NO, it shows larger soot oxidation rate than CM sample in 10% O₂. In the previous sections, it has been proved that the adsorption/desorption of NO in the catalyst promotes the formation of oxygen vacancies and the desorption of active oxygen. This should be an important role on promoting soot oxidation rate for C + O₂ and C + NO₂ + O₂ reactions. When adding 400 ppm NO into 10% O₂, the catalytic reaction rate apparently increases to a higher value (12.355-12.950 μ mol_{soot}/s/g_{ini}). The result should be attributed not only to the adsorption/desorption of NO but to a cooperative oxidizing role of NO₂ and oxygen species (O₂/O*) (Eq. (10)).

$C + O^* \rightarrow -C(O)$	Eq. (24)
$-C(O) + O^*/O_2 \rightarrow CO + CO_2$	Eq. (25)
$C + O_2 + O^* + NO_2 \rightarrow CO + CO_2 + N$	$NO + NO_2$ Eq. (10)

4.5 Summary

NO adsorption on Mn-Ce mixed oxides leads to the formation of various adsorbed species (especially nitrates), which arouses a visible change in chemical states of surface Ce and Mn ions and thereby increases the oxygen vacancies. More interesting, TPD-MS indicates that NO desorption effectively enhances the generation of surface oxygen species and NO is main product during nitrates decomposition. Soot-TPR-MS confirms that NO adsorption/desorption improves the availability of oxygen during redox reactions. Isothermal experiments reveal soot-catalyst that the adsorption/desorption of NO promotes soot oxidation rate, this is mainly ascribed to the role of active oxygen and a cooperative $C + NO_2 + O_2$ reaction.

5. Structure-reactivity study of model and Biodiesel soot in model DPF regeneration conditions

5.1 Introduction

It is well known nowadays that Diesel engines have high power output and improved fuel economy, reasons why they are widely used by car and truck manufacturers. Moreover, Diesel engines can play an important role on the reduction of anthropogenic CO_2 emissions [137]. However, the excessive amount of soot particles emitted to the environment remain a significant issue, due to their potential threat to human health [116,137-139]. Accordingly, the new Euro VI emission normative contains more stringent emission limits regarding soot (particulate matter), in order to protect the environment and human health [140,141].

Consequently, soot emission control has become a subject of major concern for both scientists and automobile makers. On one hand, the application of Biodiesel and Biodiesel blends in diesel engines is known to play a positive role on reducing pollutant emissions, especially soot [142-144]. Therefore, commercial Diesel fuels already contain small amounts of Biodiesel, and the aim is to increase its content in future blends. On the other hand, the regeneration efficiency of the DPF (Diesel Particulate Filter) can see a great development through the use of highly performing advanced catalysts for soot oxidation [118,145].

Previous studies have proved that adding oxygenated hydrocarbons (such as ethers, alcohols, methyl esters, methyldecanoate) into the surrogate fuels can effectively decrease the sooting tendencies during fuel combustion [63,143,146,147]. Indeed, the formation of combustion intermediates promoting soot generation is inhibited, while the presence of radical species (-O and -OH) favors soot combustion rather than its formation [148,149]. Seong and Boehman studied the impact of oxygenate additives on the formation and oxidation activity of soot particles, they found that the presence of oxygenate additives in fuels enhanced the formation of oxygenated soot and

thereby increased soot oxidative reactivity [149]. Song et al. [150] found that the use of Biodiesel in fuels led to the incorporation of oxygen into soot particles and thus improved soot oxidative reactivity.

Furthermore, many studies have revealed that soot oxidation activity is related to the structural features of soot particles and soot structure generally depends on the type and origin of fuels [64,151,152]. Different oxygenate additives in fuels can affect the nature of fuels and combustion cases and thereby govern the structure of soot particles [63,146]. It has been reported that ester components in Biodiesel have a larger impact on the structure and oxidative reactivity of soot [147]. The authors confirmed that the presence of shorter alkyl chains of methyl esters in Biodiesel led to the formation of the soot particles with lower structural order and thus increased soot oxidation reactivity. They also found that the increase in carbon chain length inhibited the reactivity of soot. Moreover, It was also reported that soot oxidative reactivity is in fact dependent on the nanostructure especially the degree of graphitization [69]. Graphene layers in soot are a form of pure carbon and arranged by carbon atoms in a plane with higher order. This chemical structure can decrease the reactivity of soot due to its an apparent influence on number and location of active sites exposed on carbon surfaces [69,152,153]. However, amorphous carbon with lower crystalline order has many exposed edge sites and defects, showing lower degree of graphitization, and thus leads to a higher soot oxidation reactivity [69,153].

The use of catalytic DPFs placed the downstream of DOC (Diesel Oxidation Catalyst) has been applied to soot emission control and can play an important role on the enhancement in soot oxidative reactivity [145,154]. The use of advanced catalysts (e.g., [85,100,118,155,156]) coated on DPF can visibly decrease the temperature of soot combustion based on the reactions Eqs. (1) and (2). Moreover, the NO₂ contained in the exhaust gases can more easily oxidize soot at low temperatures in the range of 250-400 \degree C due to its stronger oxidizing strength in comparison to O₂ [94,157]. However, the reaction rate of Eq. (1) greatly depends on the amount of NO₂, thus it is difficult to achieve an optimal usage of NO₂ during continuous regeneration of DPF

because of lower NO_x emissions in modern engine combustion modes [82,158]. Ce-based catalysts have been paid special attention for the past few years as they can provide a mass of active oxygen species (O*) for low-temperature soot oxidation and as a result increase the availability of O_2 in exhaust gas [105,159].

$$C + NO_2 \rightarrow CO_x + NO$$
 Eq. (1)
 $C + O^* \rightarrow CO_x$ Eq. (2)

 MnO_x -CeO₂ mixed oxides are a relatively cheap and a convenient candidate for soot oxidation, they possess excellent oxygen storage capacity and redox ability and have shown to highly promote soot reactivity towards oxidation [100,105,118]. Moreover, it has been proved that MnO_x -CeO₂ mixed oxides have high oxidation activity of NO into NO₂ and better NO_x storage ability at low temperatures, which is favorable for the oxidizing role of NO₂ [160,161]. Besides, MnO_x -CeO₂ mixed oxides can release a large amount of active oxygen species that can directly oxidize soot and thus apparently improve the catalytic activity for soot oxidation [105].

Many researchers often use carbon blacks (such as Printex-U) as Diesel soot surrogates, in order to study its reactivity. However, the soot from a real Diesel engine may considerably differ from such carbon blacks, in terms of nanostructure and reactivity. In this work, real soot samples were prepared by burning Biodiesel surrogates in a real Diesel engine whereas the model soot samples were obtained through burning the surrogate fuels in a co-flow diffusion burner [63]. MnO_x-CeO₂ mixed oxides were used as catalyst in order to investigate the catalytic oxidation of the different soot samples. The originality of this work indeed the use of Biodiesel surrogates in a burner and the comparison of the structure and reactivity of the soots generated to the soot obtained in an engine bench. All the materials have been also compared to a Printex-U carbon black. The structural features of the soot samples were characterized by laser granulometry, high-resolution transmission electron microscopy (HR-TEM), XRD and Raman spectroscopy. Their catalytic and non-catalytic oxidation were assessed by means of temperature-programmed oxidation (TPO) analysis under typical DPF regeneration conditions. A correlation between soot structure and oxidation activity is also presented.

5.2 Materials preparation

5.2.1 Soot samples preparation

Sc	oot	Fuel composition	Soot preparation method
M. J.1	M1	Aref + 7 mol% $C_{11}H_{22}O_2$	Coflow diffusion flame burner [63]
soot	M2	Aref + 30 mol% $C_{11}H_{22}O_2$	Coflow diffusion flame burner [63]
	M3		Degussa
Real	R 1	7 vol.% methyl ester + EN 590	Diesel engine
soot	R2	100 vol.% methyl ester	Diesel engine

Table 5-1. The preparation methods of model and real soot samples.

In the present work, the model Biodiesel soot was prepared by the combustion of a model fuel. The Diesel surrogate Aref consists of 70 mol% of n-decane and 30 mol% of α -methylnaphthalene and is often used as a model fuel to simulate the combustion of commercial Diesel in Diesel engine [162,163]. Two model Biodiesels were prepared by separately adding 7 mol% and 30 mol% methyldecanoate ($C_{11}H_{22}O_2$) into the model fuel Aref [63,164]. An steady co-flow laminar diffusion flame burner [63,164-166] was used for the combustion of the model Biodiesels. This setup enables the release of soot to be investigated at conditions that are strictly controlled [165,166]. In turn, this allows the fine numerical simulations of soot production, therefore the understanding of soot history along the processes of formation and potential partial oxidation [167,168]. This history highly affects the nanostructure of released soot [169]. With the burner, two types of model soot were obtained, separately noted M1 and M2. A carbon black, Printex-U (Degussa), noted M3, was also considered in this study, since it has been often used frequently as Diesel soot surrogate. Real soot samples were provided by Volvo Group Trucks Technology. An engine bench (8L Diesel engine) equipped with a Euro VI post-treatment system containing DOC and DPF was used for soot production. The system worked with a low loaded cycle operating at low temperatures, simulating very severe cold drive cycles. During this cycle, the average temperature of exhaust gases upstream the filter was around 160 $\,^\circ$ C. The real soot particles were obtained through the combustion of fuel with 7 vol% and 100 vol%, respectively, of methyl ester from rapeseed oil. The used fuel was a standard Euro VI fuel (EN 590). The obtained real soot samples were labeled as R1 and R2. Some information about soot preparation can be seen in Table 5-1.

5.2.2 Catalyst preparation

MnO_x-CeO₂ mixed oxides (Mn/Ce = 1/4 (mol/mol)) were prepared via a co-precipitation method as previously reported [105]. Ce(NO₃)₃ 6H₂O (solid, 95% pure) and Mn(NO₃)₂ (liquid, 50 wt.%) as the precursors were firstly dissolved in deionized water, then adding the dispersants PVA (*polyvinyl alcohol*) and PEG (*polyethylene glycol*) into the mixed solution. Finally, the mixture solution was mixed with the precipitant (pH > 9.0) consisting of NH₃·H₂O and (NH₄)₂CO₃ (chemical reagents, Beijing). The obtained precipitates were filtered and dried by a spraying apparatus, then calcined in static air at 500 °C for 3 h in a muffle furnace.

5.3 Physicochemical properties of soot

5.3.1 Laser granulometry

The size distributions of particles aggregates of real and model soot samples are shown in Figure 5-1. It can be visibly seen that the different soot samples show different size distribution profiles. Among the two types of real soot produced in a real Diesel engine, R1 presents a wide particle size distribution (0.1-15 μ m), with two peaks separately centered at about 1.5 μ m and 8.0 μ m. The particle sizes of R2 aggregates are mainly distributed in 0.3-20 μ m, the diameters of a majority of particles are close to around 2.6 μ m. It is also noted that R1 has more small-size particles (< 1.0 μ m) than R2 generated from neat Biodiesel. This may indicate that

increasing Biodiesel content in Diesel fuels is favorable for the aggregation of soot particles. On the other hand, for the model soot M1 and M2 from the burner, they present a smaller particle-size distribution than real soot samples. M1 shows two continuous peaks centered at about 0.4 µm and 2.0 µm, respectively. Most of M2 particles are distributed in a narrow range of particle size $(0.1-1 \mu m)$ with a lager distribution at around 0.4 µm. Another two smaller peaks of M2 appear at about 6 µm and 24 µm, respectively. In the previous Table 5-1, M2 soot was generated from the combustion of the fuel with more $C_{11}H_{22}O_2$ additive (30 mol%). This illustrates that the addition of $C_{11}H_{22}O_2$ affects the aggregation of soot particles. Finally, for Degussa Printex U (M3) as a Diesel soot surrogate, it shows only one peak centered on the particles whose diameters are close to 8 µm. A lager percent of M3 particles present the largest particle size in comparison with others. In fact, fuel components are one of important factors that affect the particle size distribution. Different fuel compositions would evoke a great difference in soot formation pathways. It was reported that adding the oxygenate compounds into Diesel can lead to the production of more radical species (-O and -OH) during soot formation [149]. These species as the core structure of soot impact the growth and aggregate of carbon particles. In the present work, M2 shows more small-diameter particles (0.4 µm) than M1, which may be due to an increase in the percentage of Biodiesel surrogate [63]. Most of Diesel soot M3 particles show larger sizes than the other soot samples generated from Biodiesel and Biodiesel surrogates. This illustrates that the combustion of Biodiesel surrogates is beneficial to the formation of smaller soot particles aggregates [63].



Figure 5-1. Particle size distribution of real and model soot samples.

5.3.2 HRTEM analysis

HRTEM was applied to characterize the morphologies and nanostructures of different soot samples. The results are illustrated in Figure 5-2. All soot samples show highly ordered carbon layers and a characteristic of disordered structure, which indicates the existence of graphite and amorphous carbons in soot samples. The graphene segments exhibit strongly bent ribbons and long chain-like agglomerates. Moreover, some edge defective sites are also present in soot. In the case of real soot, it can be seen that R1 shows more visible carbon layers and higher structural order than R2, this seems to reveal that R1 soot particles show higher degree of graphitization.



Figure 5-2. HRTEM images of real and model soot samples.

Observations on the R2 the micrographs of this sample display less chainlike orientation and the carbon particles of R2 seem to be less connected than those of R1.

In the case of model soot, they seem to appear more compact stacked crystallites in comparison with real soot. A blurry and highly disordered surface can be observed on the M1 soot. M2 and M3 exhibit more obvious carbon layers than M1, revealing their higher order. The morphology of M2 illustrates that the agglomerates of small nano-particles are happening, this leads to an intersection of different chainlike orientations. On the surface of M3, the fullerenoid nano-particles with an onion-like structure can be seen and the carbon particles are "tighter" connected than M1 and M2. Furthermore, M3 has a larger number of parallel stacked graphene layers. This fact points to highest graphitic order in M3 carbon-black in comparison to the other two model soot samples. In addition, the interlayer spacing was measured by TEM images. It is found that the real soot samples show larger interlayer spacings (3.7-4.0 nm) than model ones (3.3-3.7 nm). This result also shows that model carbon particles have more compact graphene layers than real carbon particles.



Figure 5-3. Carbon fringe length distributions of real and model soot samples.

Based on the HRTEM results, the carbon fringe lengths of real and model soot samples were measured by the software *Image J* and their distributions were obtained. As shown in Figure 5-3, for the real soot, R1 and R2 show a similar shape of fringe length distribution profiles. The distribution profile of R2 shifts towards lower fringe length values, with a decreased mean fringe length (about 1.6 nm) compared to R1. It has been reported that larger fringe length of the ordered carbon layers indicates higher degree of carbon graphitization and lower proportion of reactive edge atoms [152,153]. Thus, R2 presents higher disordered nano-structure and more reactive edge

atoms than R1. On the other side, M1 and M2, which are the soot generated from surrogate Diesel with oxygenated additives, show narrower fringes length distribution (1.5-2.8 nm) and M2 has a lower mean fringe length than M1. M3 carbon-black presents a wider distribution (1.2-3.2 nm) with a higher mean value of fringe lengths. Thus, the degree of graphitization in graphene segments for model soot samples may follow the order: M3 > M1 > M2.

Besides, nano-particle sizes of real and model soot samples were measured by TEM images and the particle-size distribution and mean nano-particle size are separately shown in Figure 5-4a and Figure 5-4b. For the real soot R1 and R2, R1 has a very wide distribution of particle sizes (< 13 nm and 15-25 nm) and the sizes of a half of nano-particles are centered on 19-21 nm (25%) and 23-25 nm (25%). R2 shows a narrow particle-size distribution and most of nano-particles (about 80%) are centered on 17-21 nm. Figure 5-4b also illustrates that R2 presents smaller mean nano-particle size (18.97 nm) than R1 (20.92 nm). In the case of model soot, it can be observed in Figure 5-4a that most of M1 soot particles show smaller sizes (13-19 nm) and the nano-particle sizes of M2 and M3 apparently shift towards higher values (17-25 nm and 23-27 nm, respectively). Thus the mean nano-particle size of model soot follows the order: M1 (17.94 nm) < M2 (19.67 nm) < M3 (25.44 nm).



Figure 5-4. Nano-particles sizes of real and model soot samples. (a) particles size distribution and (b) mean nanoparticle size.

5.3.3 XRD analysis

Figure 5-5 shows the XRD patterns of real and model soot samples. All the soot samples display the diffraction peaks of graphite-like structure. The bands can be identified in 002, 100, 004 and 110 positions [170]. Table 5-2 lists the diffraction angle of the band 002 and fringe dimensions of the soot samples. It can be observed that the diffraction angle $2\theta_{002}$ of these samples exhibits a lower value (around 25 $^{\circ}$) than that of graphite carbon (26.8 $^{\circ}$) [171], illustrating lower degree of graphitization. Furthermore, the crystallite thickness (or crystallite size) of all the soot samples shows a very small value (14-17 Å), which is also a characterization of low graphitization degree [171]. By comparison, R2 and M1 soot samples have a lower crystallite size (14 Å) than the others (16-17 Å), this reveals their lower degree of graphitization. M3 soot presents the largest crystallite size and the highest diffraction intensity in Figure 5-5, the result indicates that M3 sample shows the highest degree of graphitization among all the samples. Besides, the crystallite lengths of soot samples have a similar and larger crystallite length (37-38 Å) compared with that of M1 (30 Å) and M3 (23 Å).



Figure 5-5. XRD patterns of real and model soot samples.

Table 5-2. Diffraction angle of the band 002 and crystallite dimensions of the soot samples.							
_	Sect	Diffraction angle	Crystallite thickness	Crystallite length			
	5001	$2 heta_{002}$ ()	D (Å)	L (Å)			
-	R1	24.6	16	37			
	R2	25.0	14	38			
	M1	24.9	14	30			
	M2	25.1	16	38			
	M3	24.8	17	23			

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5.3.4 Raman spectra analysis

Figure 5-6 shows the Raman spectrum of real soot R1 and the result is analyzed by a curve fitting method (as an example of a typical Raman spectra obtained for these materials). The other samples show similar Raman curves (no shown). It can be observed that the Raman spectrum of R1 consists of four Lorentzian-shaped bands (G', D1, D2, D4) at around 1587, 1342, 1620 and 1232 cm⁻¹, respectively, and a Gaussian-shaped band D3 at around 1512 cm⁻¹ [63,171]. The G band should be assigned to an ideal graphitic structure and the entire D band (including D1, D2, D3 and D4) is ascribed to the defective structure of carbon [63]. D1 band with the largest intensity implies the presence of disordered graphitic carbon and D3 band represents the amorphous carbon. In Raman spectra, the structural defects in carbonaceous materials depend on the intensity ratio of D and G bands (I_D/I_G) . It has been reported that the ratio of I_D/I_G increases with the order for amorphous and disordered carbon with smaller crystallite size (< 2 nm) and decreases with the increase of order for graphitic carbon with larger crystallite size (> 2 nm) [172,173]. Based on the previous XRD results, the crystallite sizes of all soot samples are less than 2 nm. Thus, a higher $I_{\rm D}/I_{\rm G}$ ratio indicates an increase in the structural order [63,170].

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Figure 5-6. Analysis of the Raman spectra and curve fit of real soot R1.

Soot —	Relative intensity		Raman sh	I /I	
	D	G	D	G	$I_{\rm D}/I_{\rm G}$
R1	1.53	1.61	1342	1587	0.95
R2	1.52	1.61	1341	1585	0.95
M 1	1.81	2.03	1337	1586	0.89
M2	1.89	2.03	1335	1586	0.93
M3	1.44	1.40	1347	1580	1.03

Table 5-3. Raman results of different soot samples.

All the Raman spectra of real and model soot samples illustrate a similar structure. The Raman results of all samples are summarized in Table 5-3. For the real soot generated from a real engine, R1 and R2 show a very similar result. The same ratio of I_D/I_G (0.95) seems to illustrate that both the real soot samples have a similar nanostructural property. However, the previous HRTEM and XRD results illustrate some apparent differences between the structures of R1 and R2. For example, R1 shows more visible and "tighter" connected carbon layers than R2, and the two real soot samples have different distributions of carbon fringe lengths as well as different crystallite sizes. Sadezky et al. proposed that the measurement of Raman parameters as distinguishing structural features may be limited by the heterogeneity of carbon materials [171]. Therefore, the structural features of soot are not only determined by Raman results. For the three model soot samples, although M3 exhibits the lowest D-band intensity, it has the largest I_D/I_G ratio (0.89) in comparison with M2 (0.93).
Concerning model soots, these results point to increasing structural order as follows: M3 > M2 > M1. A lower I_D/I_G ratio of soot samples also illustrates that there is higher amorphous and disordered carbon concentration in soot. Moreover, it was reported that the graphitic G-peak of the ideal graphite structures occurs at around 1580 cm⁻¹ and an increase of the distance of G band from 1580 cm⁻¹ indicates a less graphitic structure [63]. It can be noted that the G band of M3 is at around 1580 cm⁻¹ and does not shift to higher wavenumber compared with the others, this also illustrates a higher degree of graphitization of M3.

5.4 Soot oxidation activity analysis by TPOs

5.4.1 Non-catalytic soot oxidation

The non-catalytic oxidation of real and model soot samples was assessed in 9% b.v. O_2 and 400 ppmv NO₂ + 9% b.v. O_2 , respectively. The oxidation reactivity and CO_2 selectivity of different types of soot are compared and the promoting role of NO₂ during soot oxidation is also discussed here.

5.4.1.1 TPOs in 9% b.v. O₂/Ar

Figure 5-7 and Table 5-4 illustrate the oxidative performances of the different soot samples under 9% O₂/Ar. It can be observed in Figure 5-7a that the oxidation reactions of all the soot samples occur at more than 450 °C and M3 shows the largest soot oxidation rate at peak temperature ($T_{\rm m}$). As shown in Table 5-4, for the real soot



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Figure 5-7. TPO profiles under 9% b.v. O₂ of different soot samples. (a) soot oxidative reactivity;
(b) CO production; (c) CO₂ selectivity. Initial quality of soot was 0.002 g, 80 mg SiC powder was used for dilution, heating rate was 10 °C/min, total flow rate was 15 Nl/h.

Table 5-4. TPO results in 9% b.v. O_2 and 400 ppmv NO_2 + 9% b.v. O_2 .

Soot	9% O ₂			400	400 ppm NO ₂ + 9% O ₂			
	$T_{\rm i}/{\rm C}^{\rm a}$	$T_{\rm m}/{\rm C}^{\rm b}$	$S_{\rm CO2}/\%^{\rm c}$	$T_{\rm i}/{\rm C}^{\rm a}$	$T_{\rm m}/{\rm C}^{\rm b}$	$S_{\rm CO2}/\%^{\rm c}$		
R1	523	670	56	503	667	51		
R2	505	656	69	477	654	65		
M1	503	650	49	497	648	35		
M2	515	658	47	515	664	35		
M3	535	673	64	531	669	50		

^aIgnition temperature at which CO_x concentration reaches 100 ppm.

^bThe temperature of maximal soot oxidation rate.

^cWhich is the CO₂ selectivity at $T_{\rm m}$.

samples that were prepared in a real engine, R2 has lower T_i and T_m values and thus shows better oxidative reactivity than R1. The reactivities of model soot samples follow the order: M1 > M2 > M3. Figure 5-7b displays the production of CO during soot combustion. It is noted that the real soot R1 and R2 have lower CO emissions than model soot and thereby show a relatively higher CO₂ selectivity (Figure 5-7c). In the real soot samples R2 exhibits higher CO₂ selectivity compared to R1. A slight lower CO₂ selectivity than M1 can be found in M2. M3 shows the highest CO₂ selectivity among model soot, but it has a more serious CO emission. Moreover, by comparison, with the increase of soot oxidation rate (500-670 °C), the model soot shows a decreased CO₂ selectivity and the real soot shows a relatively stable result.



Figure 5-8. TPO profiles under 400 ppmv $NO_2 + 9\%$ b.v. O_2 of different soot samples. (a) soot oxidative reactivity; (b) CO_2 selectivity.

5.4.1.2 TPOs in 400 ppmv NO₂ + 9% b.v. O₂ in Ar

Figure 5-8 shows the soot conversion profiles under NO₂ + O₂ and CO₂ selectivity and Table 5-4 lists the TPO results. All the TPO profiles seem to be similar with those under O₂ (Figure 5-7a). As shown in Table 5-4, by comparison with the results under O₂ the model soot exhibits very similar T_i and T_m values and the real soot also has close T_m values. However, a visible decrease in T_i can be observed for the real soot. This result reveals that NO₂ promotes the oxidation of real soot at ignition temperatures. An apparent promotion of NO₂ at T_m cannot be seen, which is due to the decomposition of NO₂ into NO at high temperatures [95]. Moreover, CO₂ selectivity of model soot slightly decreases after adding NO₂ into reaction gas and that of real soot has almost no changes compared to the results under only O₂.



Figure 5-9. TPO profiles under 400/1000 ppmv NO₂ + 9% b.v. O_2 of R1 and M2 samples. The inset presents the T_i values of TPO profiles.

In general, the promoting effect of NO₂ strongly depends on its concentration. As shown in Figure 5-9, the oxidation reactivity of R1 and M2 was tested under 1000 ppmv NO₂, a more apparent promotion on soot oxidation can be seen at low temperatures compared to that observed at 400 ppmv NO2. Let us note here that increasing NO₂ concentration from 400 ppm to 1000 ppm leads to an important decrease of T_i for the real soot R1, i.e. from 503 °C to around 400 °C, whereas the T_i value for the model soot M2 is only about 30 °C lower. The result also confirms that real soot shows higher promotion on soot ignition than model soot. According to the previous XRD and Raman results, R1 and M2 show similar degree of graphitization in view of their similar crystallite sizes and I_D/I_G values. But R1 exhibits a larger promotion on the reactivity than M2 under NO₂. There is a fact that the reactivity of soot depends not only on nano-structrual property but also on the composition of soot [63]. The real soot samples generated from a real engine contain higher SOFs content due to the presence of lube oils compared to model soot produced from a burner. Based on the TGA tests (not shown). the SOFs contents of R1 and R2 have much higher values (5.7% and 8.7%) than that of M1 and M2 (1.8% and 1.3%), which might be one factor that leads to a higher ignition activity of real soot under NO_2 + **O**₂.

5.4.2 Catalytic soot oxidation

The catalytic oxidation reactivity of real and model soot was investigated in 9% b.v. O_2 , 400 ppmv NO + 9% b.v. O_2 and 400 ppmv NO₂ + 9% b.v. O_2 , respectively. The promoting roles of NO and NO₂ on catalytic reactivity are compared here. Besides, the contact between catalyst and soot is moreover considered.

5.4.2.1 TPOs in 9% b.v. O₂/Ar



Figure 5-10. TPO profiles under 9% b.v. O₂ of different soot samples with the catalyst. 2.0 mg soot and 20.0 mg catalyst were mixed by loose contact.

Table 5-5. TPO results in 9% b.v. O_2 , 400 ppmv NO + 9% b.v. O_2 and 400 ppmv NO₂ + 9% b.v. O_2 .

Soot	O_2		NO	$+ O_2$	$NO_2 + O_2$		
	$T_{\rm i}/{\rm C}^{\rm a}$	$T_{\rm m}/{\rm C}^{\rm b}$	$T_{\rm i}/{\rm \ C}^{\rm a}$	$T_{\rm m}/{\rm C}^{\rm b}$	$T_{\rm i}/{\rm C}^{\rm a}$	$T_{\mathrm{m}} / \mathbb{C}^{\mathrm{b}}$	
R1	493	665	346	540	401	554	
R2	440	649	311	563	358	601	
M1	480	623	348	556			
M2	490	630	371	574	377	600	
M3	506	636	386	590	380	605	

^aIgnition temperature at which CO_x concentration reaches 100 ppm.

^bThe temperature of maximal soot oxidation rate.

Figure 5-10 and Table 5-5 summarize the results of the catalytic oxidation of the different real and model soot samples under O_2 . All of them show high CO_2

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selectivity (> 98%), proving that the presence of the catalyst effectively decreases the production CO. It is noted that all soot samples can be oxidized at lower temperatures in the presence of this catalysts, as pointed out by the decrease of T_i and T_m values compared with the results obtained in the absence of a catalyst. Regarding the real soot samples, R2 shows higher reactivity together with a more evident promotion of its ignition than R1. This can be ascribed to the lower degree of graphitization of R2 in comparison to R1. It can be observed that there is a shoulder peak at around 550 °C in TPO profiles of real soot, which may be attributed to the oxidation of soot particles in improved contact with the catalytic material, i.e. closer to catalytically active sites, and/or to the relative presence of an amorphous carbon phase in these samples. Indeed, these real soot samples possess high-content SOFs, which can promote the contact between soot particles and the catalyst, and trigger the initiation of soot oxidation. For the model soot, the catalytic oxidation activity follows the order: M1 > M2 > M3, this result is in well agreement with their nano-structural properties.

5.4.2.1 TPOs in 400 ppmv NO/NO₂ + 9% b.v. O₂ in Ar



Figure 5-11. TPO profiles of different soot samples with the catalyst under 400 ppmv NO + 9% b.v. O₂. 2.0 mg soot and 20.0 mg catalyst were mixed by loose contact.

Figure 5-11 presents the TPO profiles of real and model soot under 400 ppmv NO + 9% b.v. O_2 . It can be seen that the oxidation of all soot samples occurs within a wider temperature window (200–700 °C) and all the TPO profiles shift towards lower

temperatures in comparison with the results in only O₂. As shown in Table 5-5, after adding NO into O₂, T_i and T_m values of all the soot samples greatly decrease to 311–386 $^{\circ}$ and 540–590 $^{\circ}$, respectively. This apparently shows the strong promoting role of NO during soot oxidation. Additionally, for real soot, it can be observed that R2 generated from neat Biodiesel has lower T_i value and higher T_m value than R1. At the sight of the results of the HRTEM, XRD and Raman characterization of these materials we concluded that R2 contains more amorphous and disordered carbon particles that are thereby more prompt to oxidation thus leading lower ignition temperature under NO + O₂ than for R1. However, thought R1 possesses a higher degree of graphitization it shows lower $T_{\rm m}$ value (540 °C) than R2 (563 $^{\circ}$ C), what illustrates that nano-structure of soot is just one of factors that impacts soot oxidation reactivity, but may not be the only one. For the model soot generated in the burner, their catalytic activity order is very similar to that observed in O₂, M1 shows the best reactivity and M3 displays the worst one. The result is consistent with their nano-structural properties. This also indicates that the catalytic reactivity of model soot produced in the burner depends more strongly on their nano-structural properties than the real soots produced in an engine bench.



Figure 5-12. TPO profiles of different soot samples with the catalyst under 400 ppmv $NO_2 + 9\%$ b.v. O_2 . 2.0 mg soot and 20.0 mg catalyst (S/C = 1/10) were mixed by loose contact.

Figure 5-12 and Table 5-5 show the catalytic oxidation activities of real and model soot samples under 400 ppmv NO₂ + 9% b.v. O₂. The $T_{\rm m}$ values of all soot samples

move to higher temperatures compared to the results obtained in NO + O_2 , even the T_i of real soot visibly shifts towards higher values. This fact confirms that, in the presence of a catalyst, NO₂ promotes soot oxidation to a lower extent than NO.



Figure 5-13. T_i versus T_m for catalytic oxidation of soot.

In summary, the presence of MnO_x-CeO₂ catalyst effectively enhances the oxidation reactivity of the soots in O_2 and $NO_x + O_2$. It has been reported that Mn-Ce mixed oxides are excellent oxygen storage materials, they can transfer O₂ in gas phase into active species O_{cat.}* and then provide these active oxygen species for soot oxidation, thus promoting soot oxidation activity [100,105,118,160,161]. The temperatures T_i and $T_{\rm m}$ measured during the different catalytic oxidation experiments are plotted together in Figure 5-13. The results further evidence that the addition of NO/NO₂ greatly promotes the soot oxidation activity, and more interestingly, NO shows higher promotion than NO₂. Some researchers thought that the promoting role of NO should be ascribed to the production of NO₂ [100,160]. Certainly, NO₂ has rather higher oxidation ability than O₂ and is able to oxidize soot at lower temperatures. However, as shown in the previous section (5.4.1.2), low-temperature promotion of NO₂ strongly depends on its concentration. Furthermore, in the absence of catalyst, the addition of NO₂ cannot make the whole TPO profiles shift to lower temperatures. The NO₂ production in the presence of the MnO_x-CeO₂ catalyst (20 mg) was tested in 400 ppmv NO + 9% b.v. O₂, yielding only very small amounts of NO₂ (< 50 ppm) (results not shown). This relatively low amounts cannot be apparently responsible for the enhancement of the oxidation of soot by NO_2 . In fact, the presence of NO_x makes soot oxidation reactions more complex. In this work, the promotion of NO_x on catalytic soot oxidation might be attributed to the following two reasons: the desorption capacity of oxygen in the catalyst and the co-operative reactions involving active oxygen and NO_2 .



Figure 5-14. Ar-TPD results of the samples separately pretreated in 400 ppm NO/9% O₂/Ar (solid line), 400 ppm NO₂/9% O₂/Ar (dash line) and 9% O₂/Ar (red line) at 350 °C.

Based on the previous works [105,125], it is well known that the adsorption of NO and NO₂ on Mn-Ce catalyst leads to the formation of various nitrate species. An important fact has been confirmed that the decomposition of these nitrates not only causes the generation of NO_x but, simultaneously, increases the desorption capacity of oxygen [82,105,112]. In order to prove this point in this work, the Mn-Ce catalyst-soot mixture was pretreated either in NO and NO₂ and then analyzed by means of temperature programmed desorption (TPD). The results obtained are presented in Figure 5-14. The NO_x-pretreated samples show a visibly increased desorption of oxygen compared to the non-pretreated sample. This may be a key factor leading to soot oxidation promotion in the presence of NO_x. In addition, NO-pretreated sample has larger desorption capacity of oxygen than the NO₂-pretreated sample, which is a reasonable evidence to explain the larger promoting role of NO than NO₂ during soot oxidation. Moreover, it can be also observed that the main product of nitrates decomposition is NO rather than NO₂. Thus,

the nitrates decomposition may be written as follows [112]:

$$-NO_3 \rightarrow NO + O_2$$
 Eq. (3)

The cooperative effect of NO₂ and O₂ during soot oxidation also plays an important role on improving soot oxidation rate. Jeguirim et al. [121] have reported that the C-NO₂-O₂ cooperative reactions (Eqs. (4) and (5)) with Pt/Al₂O₃ catalyst effectively enhance the oxidation rate of soot. Schobing and Zhu et al. [144,174] also reported the existence of C-NO₂-O₂ cooperative reactions when the concentration of O₂ is excessive. In Mn-Ce catalyst system, an excess of active oxygen species (O_{cat.}*) generated from the catalyst would greatly promote the cooperative reactions, and the reaction may be written as Eq. (6) [105].

$$C + NO_2 + O_2 \rightarrow CO_2 + NO$$

$$C + NO_2 + O_2 \rightarrow CO + NO_2$$

$$C + O_{cat.}^* + NO_2 + O_2 \rightarrow CO + CO_2 + NO + NO_2$$

$$Eq. (6)$$

5.4.3 Effect of soot-catalyst contact

In general, soot catalytic oxidation reactions occur on the soot-catalyst interface and the soot-catalyst contact is an important factor that determines soot oxidation rate [105,109]. Based on the literature [109,113,175], three contact modes have been reported: tight, loose and pressure. Loose contact is thought to be close to the real soot-catalyst contact in DPF and thereby widely used for the study of soot oxidation catalysts, but it is really the poorest contact among the three modes. The best soot-catalyst contact can be obtained by tight mode and soot oxidation shows higher rate and reactivity due to more soot-catalyst contact sites (or active sites). The contact level of pressure mode is between the first two.

Chapter V. Structure-reactivity study of model and Biodiesel soot in model DPF regeneration conditions



Figure 5-15. Catalytic activities of different soot particles in 9 b.v.% O_2 under tight contact (a) and pressure contact (b).



Figure 5-16. Catalytic activities of real soot R1 and R2 in $NO + O_2(a)$ and $NO_2 + O_2(b)$ under tight/pressure contact.

Departies and	R1	R2	R1	R2	R1	R2
Reaction gas	Tight/ °C		Pressure/ °C		Loose/ °C	
O ₂	216	209	321	323	493	440
$NO + O_2$	215	205	321	290	346	311
$NO_2 + O_2$	215	205	324	313	401	358

Table 5-6. Ignition temperatures (T_i) of R1 and R2 under different contacts.

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Figure 5-17. Ignition temperature (T_i) of different soot samples under tight, pressure and loose contact conditions.

In this work, the oxidation reactivities of real and model soot under the three contact modes were investigated and compared and the results are shown in Figures 5-15-17 and Table 5-6. The case of loose contact has been presented in the previous sections. Figure 5-15a illustrates the catalytic activities of different soot samples under tight contact in 9% O₂. It can be seen that soot oxidation temperatures of all the samples shift to much lower values and the peaks in TPO curves become narrower compared to those under loose contact, showing higher oxidation rate and reactivity. For real soot, R2 exhibits slightly lower ignition temperature ($T_i = 209$ °C) than R1 ($T_i =$ 216 °C), but they have a similar peak temperature (T_m) . Thus the oxidative reactivity of real soot should be similar. For model soot, the reactivity follows the order of $T_{\rm m}$: M1 (355 $^{\circ}$ C) > M2 (378 $^{\circ}$ C) > M3 (388 $^{\circ}$ C), this result agrees well with their nano-structural properties. Figure 5-15b shows the reactivity results under pressure contact in 9% O₂. The oxidation reactions of all the soot samples present a wider temperature window (200-700 $^{\circ}$ C) and a lower reaction rate. These TPO curves seem to be a superposition of tight-TPO and loose-TPO. It is observed that real soot shows better reactivity at around 400 $^{\circ}$ C but poorer reactivity at high temperatures (> 500 $^{\circ}$ C) than model soot, which is different with the cases of tight and loose modes. For R1 and R2, they show a similar T_i (Table 5-6) but the peak temperatures of R1 slightly move to higher values under pressure contact. Among these model soot samples, M3 shows the best reactivity and M1 presents the poorest one at around 400 $^{\circ}$ C, and the reactivity at high temperatures displays the order: $M1 > M2 \approx M3$ (Figure 5-15b).

Figure 5-16 shows the catalytic activities of real soot samples under tight and pressure modes in $NO_x + O_2$. It can be observed that the TPO profiles is similar with those in O₂ (Figure 5-15). In the previous results under loose contact, it has been confirmed that the addition of NO/NO₂ can effectively promote the catalytic oxidation of soot. However, under tight contact, as shown in Table 5-6, this promoting role of NO/NO₂ cannot be seen in view of their similar T_i values compared with that in O₂. For the pressure mode, R1 exhibits a similar result in different reaction gases, but R2 presents a visible promotion in NO/NO₂ + O₂. This may indicate that the oxidation of R2 is more easily promoted by NO/NO₂ than that of R1. Table 5-6 also illustrates that the promoting role of NO/NO₂ would become weaker in a better contact and the reactivity under the three contact modes follows the order: tight > pressure > loose. These facts confirm that soot-catalyst contact is an important factor that affects soot oxidation activity. This point is also revealed in Figure 5-17. For example, R2 exhibits an apparently lower T_i value than R1 under loose contact, but their T_i values are very similar under tight and pressure conditions. For model soot, under loose contact the T_i value follows this order: M1 < M2 < M3, however, a different result is found under tight and pressure contact conditions.

5.5 Structure and reactivity correlation

Previous works linked the soot oxidation activity to the nanostructure and it was found that the reactivity of soot is closely related to its nanostructure. Lapuerta and Sadezky [170,171] used XRD and Raman to illustrate the differences in the structure, i,e. length scale and carbon fringe as well as the concentration of amorphous carbon, of different types of soot generated under various conditions. Some researchers studied the relationship between nanostructural properties and the oxidation reactivity of soot and they found that the reactivity of soot strongly depends on its nanostructure and high degree of graphitization of the graphene segments affects the oxidation activity of soot particles [63,64,152]. Knauer et al. [176] also confirmed a strong dependency of soot oxidation activity on the nanostructure by Raman and HRTEM

measurements.

In the present work, the oxidation reactivity of soot was measured by TPO under different reaction gases and shows differences in T_i and T_m when various types of soot generated from a real engine and a burner. The structural properties of soot were characterized by laser granulometry, HRTEM, XRD and Raman and exhibit different features in the particle and crystallite sizes, particle morphology and the degree of graphitization. In order to connect the soot reactivity with the soot structure, the initiation temperature T_i which represents the reactivity is used to analyze the relationship between the both.

Figure 5-18 presents the correlation of the reactivity of real and model soot with the structural features. The mean values of nanoparticle sizes, crystallite sizes and particles aggregate sizes were obtained by HRTEM, XRD and laser granulometry, respectively, and the relationship between these dimensions and the reactivity are summarized in Figure 5-18a. In the case of real soot, R2 soot generated from the combustion of neat Biofuel (methyl ester) shows lower mean crystallite and nanoparticle sizes (14 Å and 18.97 nm) than R1 soot (16 Å and 20.92 nm) from the combustion of a fuel blend (7% methyl ester). It is also observed that R2 has higher oxidation reactivity than R1 both with and without catalyst under only O_2 or NO + O_2 . Similarly, for the model soot, the crystallite and nanoparticle sizes follow the order: M1 < M2 < M3, which well agrees with their reactivity order. These results indicate that the catalytic and non-catalytic oxidation reactivities are closely related to the nanostructure of soot. Moreover, it is also seen in Figure 5-18a that R2 shows larger mean size of soot particles aggregates and presents better oxidation reactivity than R1. However, the model soot sample with larger soot particles aggregates presents poorer reactivity. These soot samples except R2 have an order of the reactivity under only O₂: M1 > M2 > R1 > M3, which is consistent with the change in particles aggregate size. This shows that smaller particles aggregate is favorable for the oxidation of soot because it might benefit the exposition to oxygen [170] and a better contact between soot particles and the catalyst. In addition, it should be noted that M2 shows a similar

catalytic reactivity in O_2 but apparently poorer reactivity in NO + O_2 compared with R1. The result illustrates that the oxidation reactivity of soot is related not only to the structure but to the reaction conditions.



Figure 5-18. Correlation of the non-catalytic and catalytic reactivities of real and model soot with the structural parameters including mean nanoparticle size (a), mean crystallite size (a), mean soot aggregate size (a), mean carbon fringe length (b) and I_D/I_G ratio (b).

Figure 5-18b presents the correlation of oxidation reactivity with mean carbon fringe length and I_D/I_G . It has been reported that smaller fringe length of the ordered carbon layers indicates a higher proportion of reactive edge atoms in soot [152,153]. For the real soot, it can be observed that R2 exhibits smaller fringe length (1.64 nm) than R1 (1.87 nm), thus showing a better oxidation reactivity. However, for model soot, the carbon fringe length follows the order: M2 (2.06 nm) < M1 (2.17 nm) \approx M3 (2.16 nm), which cannot well correlate with the reactivity. In Raman spectra, the structural defects in carbonaceous materials are related to the ratio between the intensities of D band and G band (I_D/I_G) , a higher I_D/I_G value indicates a higher degree of graphitization. Therefore, the model soot presents this order in the degree of graphitization: M1 < M2 < M3, this is well linked to their oxidation reactivity. But the real soot samples R1 and R2 show a very similar I_D/I_G ratio, which cannot be connected with the reactivity. In fact, the nanostructure of soot is not the only factor that determines the oxidation reactivity. Ye et al. [177] studied the oxidation reactivity of Biodiesel soot samples generated from a diesel engine and found that there is no correlation between the reactivity and the nanostructure analyzed by Raman. Many researchers have reported the other factors that influence the soot reactivity such as ash content and composition [179-180] as well as oxygen content in soot [100].

Besides, in this study, the particle morphology of soot also plays an important role in affecting soot oxidation reactivity. This result has been found in the previous works [177,181]. Figure 5-18a has confirmed that the correlation between nanoparticle and soot aggregates sizes and the oxidation reactivity. On the other hand, in the previous HRTEM images, it can be observed that R2 soot presents less chainlike orientation and "looser" connected carbon particles than R1, which seems to show higher disorder of R2. Thus, R2 has a better oxidation reactivity than R1. The morphology of the model soot also presents various features and can be linked to the reactivity. For example, M1 soot shows a blurry and highly disordered surface, M2 and M3 exhibit more obvious carbon layers than M1, and M3 has the largest number of parallel stacked graphene layers. By comparison with the reactivity, it indicates that the blurry and less carbon layers, revealing higher disordered surface, are connected with higher reactivity of M1 and M3 with more graphene layers displays lower reactivity. These results all prove a visible relationship between soot reactivity and particle morphology. This study provides valuable findings on the soot oxidation rate and the parameters influencing it, which could contribute to develop accurate soot models that are required for robust regeneration strategies. The use of 100% biofuel induces significantly lower soot deposits in DPF that being correctly estimated (adapted biofuel soot models) might reduce the need of active regenerations and therefore the fuel consumption and the catalyst ageing. Therefore, the understanding of how the

fuel type and engine operation affects the particle morphology and its reactivity are crucial for optimizing the DPF regeneration strategy.

For the development of new coating formulations, the selection of model soot to be used in synthetic gas benches shall be taken with care, as it was shown in that study the risk of having different behaviors for example for the carbon-black Printex often reported in literature. The catalyst evaluation studies shall therefore take into account the use of burner and real engine soot samples as well as realistic operating conditions in terms of gas composition and soot/catalyst contact in order to perform an accurate benchmark.

5.6 Summary

In this work, real soot generated in a real Diesel engine and the model soot generated in a burner were studied using laser granulometry, HRTEM, XRD and Raman, as characterization techniques. A MnOx-CeO2 catalyst was used for the measurement of catalytic reactivity. The results of the temperature programmed oxidation (TPO) experiments point to increased oxidation reactivity for the real soot generated with 100% Biodiesel than the one obtained using the 7% Biodiesel mixture. The carbon-black Printex U soot showed the poorest reactivity of the series, whereas the reactivity of the soot prepared from the 7% oxygenated in the laminar flame burner was higher than the one observed for the model soot generated from the 30% oxygenated addictivated fuel. Characterizations illustrate that the real and model soot samples show different nanostructure and morphology features. The reactivity of soot was found to be closely related to its nanoparticle size, crystallite size, particles aggregates and the degree of graphitization. The oxidation reactivity of soot in the presence of the MnO_x-CeO₂ catalyst depended not only on its nanostructure but also on the reactant gas composition, as well as soot-catalyst contact. Furthermore, it was found that the presence of NO_x cannot affect the reactivity of soot under tight contact, whereas NO_x can clearly enhance the reactivity under loose contact. Thus, the promotion of NO_x on catalytic activity depends on the contact between soot and the

catalytic DPF.

6. Structure, surface and reactivity of activated carbon: From model soot to Bio Diesel soot

6.1 Introduction

The high efficiency and durability of diesel engines have motivated their wide applications in passenger cars and heavy-duty trucks in the world. However, the high emission of fine soot nanoparticles for example PM_{2.5} has caused serious public health and environment pollution [182-184]. These fine soot particles as an important fraction of aerosols present in the air around urban area with big influences on the climate, biosphere and citizen health [185-187]. Nowadays, the emissions of diesel soot particles are limited all around world [188-190]. For example, the emissions of particulate matters from cars and heavy-duty vehicles are limited to 4.5 mg/km and 10 mg/kWh, respectively [188-190]. Thus, the soot removal technology has become an important topic of improving environment level and protecting human health. Diesel particulate filter (DPF) used as an exhaust after-treatment unit has been confirmed to be an effective way to remove soot emission [191-193]. Of course, the regeneration (active or passive regeneration) of the filter unit is crucial to controlling soot emission. The soot is oxidized periodically by O₂ at higher temperatures during active regeneration and also oxidized continuously over the catalysts by active oxygen and NO₂ during passive regeneration [94,187,125,194,195]. The regeneration efficiency strongly depends on the reactivity of soot, because the combustion of high-activity soot occurs at lower temperatures with small energy demand [187]. Many studies also confirmed that the reactivity of soot is related to the soot nanostructure [170,196], soot morphology [196,197], fuels [164,170,198], catalyst materials [93,94,125,194,195,199] and engine operation conditions [200,201].

The main composition of soot is carbon (> 80 wt.%) with a particle of soluble organic fraction (SOF) and ash [171,202,203]. The formation steps can be performed in diesel engines through nucleation, nanoparticles aggregation and surface growth mechanisms [171,204]. The primary soot particles are composed of ordered and

amorphous carbons. The ordered carbon surface shows a graphite-like structure with higher crystalline order and the amorphous carbon presents lower degree of graphitization with many active edge sites and defects [69,152,205]. The different structural features of soot determine its physical and chemical properties and thereby its reactivity [69,205-207].

Boehman et al. [208] reported that the disordered carbon with more amorphous structure had more defects and thus exhibited higher reactivity. Knauer et al. [196] studied the relationship between soot structure and reactivity by Raman microspectroscopy and high-resolution transmission electron microscopy (HRTEM), it was found that the higher reactivity of soot was attributed to a higher degree of disorder and a higher content of molecular carbon. It was also reported that the reactivity of soot would be dependent on its primary particle size characterized by TEM [170]. On the other side, Seong and Boehman found that the presence of oxygenated additives in fuels enhanced the formation of oxygenated soot and thereby increased the oxidative reactivity of soot [149]. Song et al. [150] illustrated that the use of Biodiesel fuels would increase the content of oxygen in soot particles and thus improved soot reactivity.

Moreover, the catalytic materials on the catalyzed DPF also play an important role on determining soot reactivity. Bueno-L \dot{q} pez et al. [209] found that active oxygen from ceria lattice is able to oxidize soot particulates at lower temperatures. It was also reported that MnO_x-CeO₂ mixed oxides could exhibit a higher catalytic activity for soot oxidation, this is due to the presence of a great quantity of active oxygen [105,210]. Many authors studied ceria-zirconia mixed oxides for soot oxidation and revealed that the reactivity of soot depends on oxygen vacancies, oxygen storage capacity (OSC) and redox ability of the catalysts [195,156,158,211,212]. The oxidative reactivity of soot can be also increased by precious metal Pt catalysts such as Pt/Al₂O₃ and Pt/SiO₂ as they have a strong ability to oxidize NO to NO₂ which is able to oxidize soot at lower temperatures [83,93,94].

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In Knauer's work [196], the authors prepared the oxidized soot through an oxidation process in a temperature range from 25 to 600 °C and studied the differences in nanostructure between raw and oxidized/activated soot samples, they found the changes in chemical homogeneity and structural order in different soot samples are different during soot oxidation at increasing temperatures. In real exhaust aftertreatment system, soot particles which were generated from diesel engine follow thermal gas-flow and go through DOC unit, where the soot particulates experience a partial oxidation or an activating process. Besides, for the catalytic soot oxidation, the reactivity of soot is only ascribed to the role of catalysts, which may not be a full understanding of soot oxidation. During soot activation in DOC or catalytic oxidation in DPF, the changes in structure and surface property of soot itself should be also an important aspect for understanding soot oxidation. Thus, the present work presents results on activated soot presented in temperature-programmed oxidation (TPO) and mainly studied the changes in nanostructure and surface properties of the activated soot by BET, Raman spectra, HRTEM, diffuse reflectance infrared Fourier transform spectra (DRIFTS) and XPS as well as linked them to their noncatalytic/catalytic reactivity. The originality of this work is to use the real Bio Diesel soot obtained in an engine bench and study its activation influence on oxidation reactivity, with being compared to Printex U model soot which is usually used for experimental model.

6.2 Materials preparation

6.2.1 Soot samples preparation

The oxidized/activated soot samples were prepared by Temperature Programmed Oxidation (TPO) method under 9% b.v. O_2/Ar (250 ml/min). A carbon black (Printex-U) from Degussa as a representative of model soot and biodiesel derived soot B7 and B100, which separately generated from the burning of 7% biodiesel-diesel blends and 100% biodiesel in a real diesel engine [159], were used for this study. As shown in Figure 6-1, when soot-TPO was performed till 500 °C (about 3-10% conversion) and 600 °C (about 20-30% conversion), respectively, the

oxidized/activated soot samples were taken out from the reactor and marked "soot-500" and "soot-600". The raw soot samples were used as a reference.



Figure 6-1. Soot conversion in TPO under 9% b.v. O₂/Ar at a heating rate of 10 °C/min.

6.2.2 Catalyst preparation

MnO_x-CeO₂ mixed oxides (CM) (Mn/Ce = 1/4 (mol/mol)) were prepared through a co-precipitation method and used to evaluate the catalytic activity of soot. Ce(NO₃)₃ 6H₂O (solid, 95% pure) and Mn(NO₃)₂ (liquid, 50 wt.%) as the precursors were firstly dissolved in deionized water, then the mixture solution was mixed with the precipitant (pH > 9.0) consisting of NH₃·H₂O and (NH₄)₂CO₃ (chemical reagents, Beijing). The obtained precipitates were filtered and dried by a spraying apparatus, then calcined in static air at 500 °C for 3 h in a muffle furnace.

6.3 Reactivity analysis

6.3.1 TPO tests in O₂

To explore the effect of thermal activation or partial oxidation of soot on soot oxidation activity during DPF regeneration, the TPO experiments of raw and activated soot samples were conducted in 9% b.v. O_2/Ar . Figure 6-2a shows the noncatalytic activities of the raw and oxidized Printex U samples. By comparison, the oxidized

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soot Printex U-600 (about 20% of conversion) presents an apparently increased reactivity, its T_i and T_m values visibly decrease to 484 and 600 °C from 535 and 674 °C of raw soot, respectively (Table 6-1). However, the oxidized soot Printex U-500 (about 3% of conversion) has no apparent changes in reactivity compared to raw soot, Table 6-1 also lists their similar T_i and T_m values. Figure 6-2b presents the catalytic activities of Printex U samples. The same phenomenon can be observed that the conversion temperatures of Printex U-600 visibly shift towards lower values compared with raw soot, for example, the T_i and T_m separately shift to 458 and 560 °C from 483 and 644 °C (Table 6-1). While the TPO curve of Printex U-500 seems to be similar with that of raw soot and shows slightly increased T_i and T_m values. These results illustrate that the Printex U-600 is more reactive than Printex U-500 and raw Printex U.



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Figure 6-2. Noncatalytic (a, c, e) and catalytic (b, d, f) reactivities of raw and oxidized soot samples under 9% b.v. O₂/Ar. Reaction conditions: soot mass is 2.0 mg, catalyst mass is 20.0 mg, 80 mg SiC was used for dilution, the flow rate is 250 ml/min, heating rate is 10 °C/min.

B7 and B100 are real Biodiesel soot, which produced from a real diesel engine. The noncatalytic and catalytic activities of their raw and activated samples were also tested by TPO and the results are shown in Figure 6-2c-f. It can be seen that for the activated B7 and B100 samples, the low-temperature reactivity decreases compared to raw soot. Table 6-1 also illustrates that the T_i values of the activated B7 and B100 samples are higher than those of raw soot during both noncatalytic and catalytic oxidation. Besides, T_m values of B7-600 and B100-600 are similar with those of raw soot and do not visibly shift to lower temperatures (except for noncatalytic reactivity of B100-600). It is also observed that the high-temperature reactivity (T_m) of B7-500 and B100-500 slightly moves to higher temperatures compared to raw samples. Thus, the partial oxidation process of real Biodiesel soot decreases the low-temperature reactivity but cannot apparently affect the high-temperature reactivity. These results are contrary to those of Printex U samples.

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C 1	In	O_2	In NO + O_2		
Samples	$T_{\rm i}/^{\circ}{ m C}$	$T_{\rm m}/$ °C	$T_{\rm i}/{ m C}$	$T_{\rm m}/$ °C	
Printex U	535 ^a /483 ^b	674 ^a /644 ^b	412 ^b	609 ^b	
Printex U-500	540/508	672/662	382	580	
Printex U-600	484/458	600/560	338	490	
B7	511/379	676/662	370	556	
B7-500	534/479	681/673	378	553	
B7-600	540/483	672/664	374	543	
B100	490/414	662/644	339	565	
B100-500	527/480	667/662	404	590	
B100-600	528/477	647/646	382	561	

Table 6-1. T_i and T_m values of TPOs with different soot samples.

^aThe values were obtained without catalyst.

^bThe values were obtained with catalyst.

In order to confirm the influence of the activation step on the reactivity of soot, the raw soot samples were firstly oxidized in O_2/Ar through TPO step from 25 to 600 °C, then the oxidized soot was cooled down to 25 °C and the second TPO was performed to obtain the total soot conversion profile. As shown in Figure 6-3. For Printex U soot (Figure 6-3a), the soot oxidation temperatures for the second TPO curve visibly shift to lower values relative to the first TPO, which reveals a promoting role of the activation step on soot oxidation. For B7 and B100 samples (Figure 6-3b, c), it can be clearly observed that the second TPO profile presents a decreased low-temperature reactivity (< 600 °C) compared with the first TPO. These results above are in good agreement with those presented in Figure 6-2.



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Figure 6-3. TPO results of raw Printex U (a), B7 (b) and B100 (c) samples. Conditions: soot mass is 2.0 mg, SiC mass is 80 mg, without catalyst, the flow rate is 250 ml/min, heating rate is 10 °C/min.

6.3.2 TPO tests in NO + O₂

It was reported that the presence of NO can promote the oxidation of soot over Mn-Ce catalysts, which is due to the NO oxidation into NO₂ [105,118]. Moreover, the adsorption/desorption of NO on Mn-Ce mixed oxides can increase desorption of active oxygen [160]. TPO profiles of the catalytic oxidation of Printex U and Biodiesel soot samples under 400 ppm NO + 9% b.v. O_2/Ar are presented in Figure 6-4. An apparent promotion of NO on soot activity can be seen by comparing



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Figure 6-4. Catalytic reactivities of Printex U (a), B7 (b) and B100 (c) samples under 400 ppm NO + 9% O₂/Ar. Reaction conditions: soot mass is 2.0 mg, catalyst mass is 20.0 mg, 80 mg SiC was used for dilution, the flow rate is 250 ml/min, heating rate is 10 °C/min.

the TPO profiles in Figure 6-4 and Figure 6-2. In the case of Printex U, In comparison with raw soot, the oxidized samples especially for Printex U-600 show increased reactivity. It can be noted in Table 6-1 that the T_i and T_m of Printex U-500 slightly shift to lower values but those of Printex U-600 display a larger shift to lower temperatures. For the previous TPO with catalyst under O₂ (Figure 6-2b), Printex U-500 presents a similar TPO curve with the raw soot, and the T_i and T_m of Printex U-600 decrease by 25 and 84 °C, respectively, relative to those of raw Printex U. However, in NO + O_2 (Figure 6-4a), Printex U-500 exhibits a slight enhancement on soot oxidation activity and the T_i and T_m of Printex U-600 separately decrease by 74 and 119 °C compared to those of raw soot. The fact illustrates that the reactivity of the activated Printex U soot is more easily promoted in NO + O_2 . In the case of B7 and B100, it can be clearly seen that the low-temperature reactivity of oxidized soot samples decreases at about 200-350 °C. The results are also confirmed in Figure 6-2. For B7 soot, the high-temperature reactivities of raw B7 and B7-500 samples are almost similar in view of the close $T_{\rm m}$ values (556 and 553 °C), and that of B7-600 shows a slight promotion. For B100 soot, the $T_{\rm m}$ value of B100-500 shifts towards higher temperature (590 °C) and that of B100-600 (561 °C) is similar compared with raw soot (565 ℃).



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Figure 6-5. Isothermal catalytic reaction at 350 $\,^{\circ}$ C in 9% O₂/Ar (a, c, e) and 400 ppm NO + 9% O₂/Ar (b, d, f). Conditions: 2 mg soot and 20.0 mg catalyst, loose contact, 80 mg SiC pellets were used for dilution.

6.3.3 Isothermal reaction rate at 350 °C

Figure 6-5 and Table 6-2 illustrate the catalytic reaction rates of raw and activated soot samples under isothermal conditions. As shown in Figure 6-5a and Figure 6-5b, the catalytic reaction rates of raw and activated Printex U samples follow the order Printex U-600 > Printex U-500 > Printex U at 350 °C in both O₂ and NO + O₂. This, as same as the previous TPO results, reveals that the activated Printex U shows higher reactivity. Especially in the presence of NO, the increase in reaction rate of the

oxidized samples is more apparent (Table 6-2).

	9%	O ₂	$400 \text{ ppm NO} + 9\% \text{ O}_2$			
Soot sample	Initial oxidation rate	Final oxidation rate	Initial oxidation rate Final oxidation ra			
	$(\mu mol_{soot}/s/g_{cat.})$	$(\mu mol_{soot}/s/g_{cat.})$	$(\mu mol_{soot}/s/g_{cat.})$	$(\mu mol_{soot}/s/g_{cat.})$		
Printex U	0.1791	0.0082	0.3291	0.3484		
Printex U-500	0.2156	0.0082	0.7614	0.5066		
Printex U-600	0.3922	0.0538	1.3092	1.3532		
B7	0.3928	0.0251	0.6409	0.3055		
B7-500	0.2011	0.0433	0.5450	0.3146		
B7-600	0.1524	0.0480	0.6774	0.4604		
B100	0.4612	0.0814	0.7631	0.3238		
B100-500	0.1492	0.0243	0.7312	0.4077		
B100-600	0.0884	0.0243	0.6855	0.5471		

Table 6-2. The results of isothermal reaction at 350 °C.

It is interesting to undernote that, not all soot samples can show the same phenomenon with Printex U after activation. As shown in Figure 6-5c-f and Table 6-2, for real soot B7 and B100, the activated soot samples exhibit decreased oxidation rates in O_2 but increased results in NO + O_2 . In Table 6-2, it can be observed that the initial oxidation rates of the oxidized B7 and B100 samples visibly decrease in only O₂. A slight increase in final oxidation rates of the oxidized B7 samples can be also seen, but the oxidation rates are too small to illustrate the real case. In the case of the TPO results in NO + O_2 , the initial oxidation rates of B7 and B100 samples are ranked as follow: B7-600 (0.6774 μ mol_{soot}/s/g_{cat}) > B7 (0.6409 μ mol_{soot}/s/g_{cat}) > B7-500 $(0.5450 \ \mu mol_{soot}/s/g_{cat.})$ and B100 $(0.7631 \ \mu mol_{soot}/s/g_{cat.}) > B100-500 \ (0.7312)$ μ mol_{soot}/s/g_{cat.}) > B100-600 (0.6855 μ mol_{soot}/s/g_{cat.}), respectively. However, their final oxidation rates apparently increase with the activation. In previous TPO results, it can be seen that the activated B7 and B100 samples show a decreased in the low-temperature catalytic reactivity in both O₂ and NO + O₂ mixture. The results in isothermal reactions under O_2 (Figure 6-5c, e) are in agreement with this point, but those in NO + O_2 (Figure 6-5d, f) exhibit the contrary. The fact illustrates that under isothermal conditions the presence of NO is more favorable for the catalytic oxidation of activated Biodiesel soot.

Moreover, it can be noted that for the isothermal reactions in only O_2 the final reaction rates sharply decline relative to the initial reaction rates, but the addition of NO into O_2 apparently inhibits the decrease of reaction rates and makes the final reaction rates remain higher values. The result would be attributed to the following reasons: (1) MnO_x-CeO₂ mixed oxides have higher catalytic oxidation activity of NO into NO₂ [105,210,160], the produced NO₂ with stronger oxidizing ability than O₂ can promote the soot oxidation rate; (2) the production of NO₂ on MnO_x-CeO₂ catalyst would lead to a C + NO₂ + O₂ cooperative reaction [105,126]; (3) it was confirmed that NO adsorption/desorption on MnO_x-CeO₂ enhances the production of active oxygen in the oxides [160].

In Seong's work [213], the authors analyzed the burning process of soot through partially oxidizing Printex-U soot under O₂-NO₂ mixtures and found that the oxidation-derived maturing process was much dependent on NO₂ content. The presence of NO₂ during soot oxidation has been confirmed to have good promoting role on the reactivity of soot [92,94,82,105,213]. Thus, we suppose that the activated soot that was prepared under different reaction gases would have different oxidation cases. In the present work, Printex U soot was chosen and partially oxidized by TPO from 25 to 500 °C in 9% O_2/Ar , 400 ppm NO + 9% O_2/Ar and 400 ppm NO₂ + 9% O₂/Ar, respectively. Then these oxidized soot samples were used for isothermal catalytic reactions in NO + O_2 at 350 °C to compare their differences. As presented in Figure 6-6, the isothermal reaction curves of the oxidized soot samples seem to have no a more apparent difference. When the reaction rate reaches stabilized values, it can be clearly seen that the oxidized soot under $NO + O_2$ shows a similar oxidation rate (about 0.51 μ mol_{sot}/s/g_{cat}) compared to that one under only O₂, but the oxidized soot under NO₂ + O₂ exhibits a slightly increased oxidation rate (about 0.57 μ mol_{soot}/s/g_{cat.}). This might be because the presence of NO₂ affects the structure of soot particles and thereby the oxidation reactivity during the activation process [200,213].

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Figure 6-6. Isothermal catalytic reactions of Printex U soot samples that were partially oxidized with the TPO from 25 to 500 °C in O_2 , $NO + O_2$ and $NO_2 + O_2$, respectively, at 350 °C in $NO + O_2$.

6.4 Physicochemical properties of soot

6.4.1 Laser granulometry

Figure 6-7 presents the size distributions of particles aggregates of raw and activated soot samples. It can be clearly seen that the activated soot samples show different size distribution profiles compared to raw soot. For all the soot samples, it is found that the activation step leads to a decrease in the amount of smaller soot particles and the whole distribution profiles of activated soot shift towards higher values. As shown in Figure 6-8, the mean size of soot particles aggregates increases after the activation, with following the order: raw soot < soot-500 < soot-600. Especially for the real soot B7 and B100, the activated soot samples exhibit a larger increase in particles aggregates sizes than Printex U. These results also illustrate that the soot particles with smaller aggregates sizes would be firstly oxidized during soot oxidation.

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Figure 6-7. Particles aggregates size distribution of Printex U (a), B100 (b) and B7 (c) samples.



Figure 6-8. Mean size of particles aggregates of different soot samples.

6.4.2 BET analysis

Table 6-3 lists the values of surface area (S_{BET}), mean pore size (R) and pore volume (V_p) of raw and activated soot samples. Partial oxidation of raw soot significant

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increases surface area and decreases mean pore size. This illustrates that the activation process led to a modification of textural property of soot. For Printex U samples, Printex U-500 (at about 3% partial oxidation) shows a slight increase in S_{BET} and R, while Printex U-600 (at about 20% partial oxidation) has a sharp increase in S_{BET} and decrease in R. The pore volume (V_p) of Printex U also exhibits an increased trend with the activation. For real Biodiesel soot B7 and B100, a similar change in S_{BET} and Rwith Printex U can be observed after activation, but one different point is that the V_p of activated soot decreases (for example B7-600 and B100-500). The sharp decrease of mean pore size for the activated soot indicates an apparent increase in the amount of smaller pores and a disappearance of large pores. It is speculated that the initial soot oxidation may occur in larger pores.

Soot sample	$S_{\rm BET} \left(m^2/g \right)^a$	Mean pore size R $(nm)^{a}$	Pore volume $V_{\rm p}$ $({\rm ml/g})^{\rm a}$
Printex U	97.8	18.94	0.90
Printex U-500	111.8	19.07	1.05
Printex U-600	321.3	1.21	1.30
B100	124.1	39.01	1.26
B100-500	154.9	1.64	0.92
B100-600	217.1	1.21	1.29
B7	231.6	25.55	2.73
B7-600	296.2	1.21	1.91

Table 6-3. Textual properties of raw and activated soot samples

^awhich was calculated by BJH method.

6.4.3 Raman analysis

The Raman spectra of raw and activated soot samples were measured to analyze the microstructural features and the results are presented in Figures 6-9, 6-10 and Table 6-4. Figure 6-10 presents the Raman analysis of Printex U samples (as an example). The Raman spectra of these soot are characterized by two overlapping peaks, which appear at around 1580 cm⁻¹ (G peak) and 1350 cm⁻¹ (D peak), respectively [63,171,196]. The D peak is generally related to defect sites or disordered carbon and

G peak involves the ordered carbon. As shown in Figure 6-9, in comparison with untreated raw soot, which has more separated D and G peaks, the Raman spectra for activated samples show more strongly overlapping peaks, this might imply an increase in the content of molecular carbon for the activated soot [196]. Moreover, in Figure 6-9, it is also observed that raw soot samples exhibit broad Raman signals in the range of about 2300-3200 cm⁻¹, these should be ascribed to second-order bands



Figure 6-9. Raman spectra of raw and partially oxidized Printex U (a), B7 (b) and B100 (c) samples.

due to (2*D) overtones and (D + G) combinations of graphitic lattice vibration modes [171]. The second-order signals become less pronounced after activation treatment for Printex U soot (Figure 6-9a), but the visible decrease in the second-order signals cannot be seen for the activated B7 and B100 soot (Figure 6-9b and c). The result may illustrate that Printex U soot becomes more disordered than B7 and B100 soot after activation.

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Figure 6-10. Analysis of the Raman spectra and curve fits of raw Printex U (a), Printex U-500 (b) and Printex U-600 (c).

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Sample	$FWHM_{D1}/cm^{-1}$	$FWHM_{D2}/cm^{-1}$	FWHM _G /cm ⁻¹	$I_{\rm D1}/I_{\rm G}$	$I_{\rm D2}/I_{\rm G}$	$I_{\rm D3}/I_{\rm G}$	$A_{\rm D1}/A_{\rm G}$	$A_{\rm D3}/A_{\rm G}$
Printex U	174	47	70	1.04	0.87	0.90	2.7	0.75
Printex U-500	182	57	81	1.04	0.97	0.98	3.1	1.09
Printex U-600	179	51	81	1.03	0.97	0.97	3.3	0.97
B7	153	42	70	1.01	0.30	0.42	2.3	0.39
B7-500	149	39	67	1.07	0.37	0.44	2.6	0.44
B7-600	151	47	71	1.10	0.42	0.43	2.6	0.42
B100	154	37	61	0.98	0.38	0.47	2.3	0.42
B100-500	145	31	63	1.10	0.41	0.51	2.4	0.51
B100-600	166	31	65	1.09	0.34	0.49	2.4	0.56

Table 6-4. Raman results of soot samples.

Figure 6-10 clearly illustrates the Raman spectrum of soot consists of four Lorentzian-shaped bands (G, D1, D2, D4) at around 1580, 1350, 1620 and 1200 cm⁻¹, respectively, and a Gaussian-shaped band D3 at about 1500 cm⁻¹ [62,196]. It has been reported that D1 band is associated with disordered graphitic lattice and D3 band is

related to amorphous carbon or molecular carbon, thus D1 FWHM (full width at half maximum) and D3 band intensity as important parameters can provide some information about chemical structure of graphite-like and amorphous carbon [170,196]. Many earlier works have also reported the FWHM of G and D bands and the D/G band intensity ratios (I_D/I_G) can correlate with degree of graphitization of carbonaceous materials [214-219]. The authors thought that an increase in G and D band FWHM and I_D/I_G values indicates a decrease in order. It was also published that the ratios between D bands and G band areas (A_D/A_G) are related to the structural defects in graphene layers [170]. Since it is unclear which of these parameters should be used for Raman analysis, most of parameters are used here for comparison.

Table 6-4 lists spectroscopic parameters of different soot samples. For Printex U soot, it can be observed that the partially oxidized soot samples (Printex U-500 and -600) exhibit an increased spectroscopic parameters including D and G band FWHM, I_D/I_G and A_D/A_G . This result illustrates that the activated soot has higher disorder and more structural defects. Among these parameters, D1 band FWHM and A_{D1}/A_G values of the activated soot samples increase with the activation, but their I_{D1}/I_G values are very similar with that of raw soot. Here D1 FWHM should be more important parameter for analyzing carbon structure. The relative intensity of D3 band (I_{D3}/I_G) is associated with amorphous carbon or molecular carbon. The increase of I_{D3}/I_G value of the oxidized soot samples indicates an increase in molecular carbon. However, by comparison, the two oxidized Printex U samples (Printex U-500 and -600) show similar spectroscopic parameters, which seems to imply their similar structural features.

In the previous work [159], it has been proposed that the noncatalytic and catalytic reactivities of soot are correlated to their structural properties. In the present work, the previous TPOs results have confirmed that the activated Printex U samples show improved reactivity compared to raw sample, this well agrees with the Raman results. Nonetheless, the similar Raman results of the two oxidized samples cannot explain much higher reactivity of Printex U-600 than the other one. This may illustrate that
the reactivity of soot cannot be only ascribed to the structure but also to particle morphology [159,220], ash content and composition [178,221] as well as oxygen content [149].

On the other hand, in the case of real soot B7 and B100, it can be seen in Table 6-4 that they have different structural features after activation compared with Printex U. For B7 soot, as listed in Table 6-4, the activated soot B7-500 (3-10% soot conversion) shows slightly decreased FWHM values, which appears to imply an increase in order. However, the I_D/I_G and A_D/A_G exhibit increased values, this seems to reveal an inverse result. It has been reported that D band FWHM and I_D/I_G have no significant correlation with each other [171]. Thus, it is difficult to well analyze the nanostructure of soot by Raman measurement and it may need more evidences to illustrate the nanostructural features. For B7-600 (20-30% soot conversion), D1 and G band FWHM values as well as I_{D3}/I_G ratio are very similar with those of raw B7 sample. But other parameters especially for D2 band FWHM and I_{D2}/I_G exhibit an increased tend. It was reported that the I_{D2}/I_G ratio and the D2 band FWHM should be inversely proportional to the thickness of graphitic domains in soot [171,216]. Therefore, the increase in D2 band FWHM and I_{D2}/I_G might indicate the decrease of graphitic carbon.

For B100 soot, it can be seen in Table 6-4 that B100-500 sample (3-10% soot conversion) shows apparently decreased D1 and D2 bands FWHM but increased G band FWHM, I_D/I_G and A_D/A_G values relative to raw soot. Generally, the intensity of G band, D1 and G band FWHM as well as I_{D1}/I_G are related to the graphitic order. The decrease in D1 band FWHM seems to reveal an increase in graphitic order. However, the G band FWHM and I_{D1}/I_G increase, this inversely indicates a decrease in order. Additionally, I_{D3}/I_G as important parameter is often used to evaluate the amorphous carbon content of soot. The increase of I_{D3}/I_G implies an increase in amorphous carbon content. Plus the increased tend of A_{D1}/A_G and A_{D3}/A_G , these results may illustrate an increase in disorder for B100-500. In the case of B100-600, it can be observed in Table 6-4 that D1 and G band FWHM as well as A_{D3}/A_G exhibit higher

values than both B100 and B100-500 samples, and I_{D1}/I_G , I_{D3}/I_G and A_{D1}/A_G show very close values with those of B100-500. The result illustrates B100-600 has a lower order compared to the raw and B100-500 samples in spite of the decreased D2 parameters.

6.4.4 HRTEM analysis



Figure 6-11. HRTEM images of Printex U (a, b), Printex U-500 (c) and Printex U-600 (d).

In order to better observe the structural changes of the activated soot samples, the morphology and nanostructural property of Printex U and B100 soot samples were characterized by HRTEM, and the results are shown in Figure 6-11 and Figure 6-12. In the case of Printex U soot, as shown in Figure 6-11a, the soot sample has turbostratic patterns and an onion-like structure, the "tight" fringe layers

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concentrically surround nucleus where the disordered carbon structure is observed. The raw Printex U also has a larger number of parallel stacked graphene layers with a larger thickness (19.5 nm) (Figure 6-11b). This reveals a higher order for raw Printex U. Moreover, some edge defective sites are also observed in Figure 6-11a. After the soot being partially oxidized, a decreased fringe-layer thickness can be clearly seen in



Figure 6-12. HRTEM images of B100 (a, b), B100-500 (c) and B100-600 (d).

Figure 6-11c and d (11.5 nm for Printex U-500 and 7.3 nm for Printex U-600). The result illustrates that the partial oxidation of Printex U decreases the degree of graphitization and Printex U-600 exhibits more apparent result. Besides, in comparison, it can be observed that the activated soot samples have an increased area of highly disordered carbon particles on the center. For example, for Printex U-600, the fringe patterns on the center become less noticeable, this is due to the oxidation of less-ordered nuclei through diffused oxygen into porous particles [222]. Thus, it is

also confirmed that Printex U experienced an internal burning-out process during partial oxidation under O_2 [200,213].

In the case of B100 sample as real biodiesel soot, it exhibits different structural and morphology changes after oxidation treatment compared with Printex U. As shown in Figure 6-12a and b, the raw soot displays less obvious fringe layers and thinner carbon-layers thickness (about 5-10 nm) than raw Printex U soot. A less chainlike orientation and looser fringe layers are also observed in Figure 6-12b. These results seem to illustrate that the real biodiesel soot has higher disorder and lower degree of graphitization than Printex U, which is also found in the previous work [159]. After partial oxidation, the activated soot samples (B100-500 and B100-600) all show unclear fringe layers. This might confirm that the partially oxidized samples become more disordered. In comparison in Figure 6-12c, the edge of the B100-500 soot particle shows vaguer fringe layers than the area inside. Some void areas on the outer surface of primary particle are also found in Figure 6-12d. Therefore, B100 soot tended to oxidize through an external burning process during oxidation treatment [213].

Moreover, 50 soot particles were used for nanoparticles size analysis for each sample and nanoparticle-size distribution was presented in Figure 6-13. With the soot being oxidized partially, the nanoparticles sizes of Printex U and B100 tend to decrease. Thus, the activated soot presents an smaller mean particle size than raw soot. This observation has been already reported in Al-Ourashi's work [200].



Figure 6-13. Nanoparticles size distribution of soot samples.

6.4.5 XPS analysis

Figure 6-14 presents the XP spectra of the raw Printex U and B100 samples in the C1s and O 1s energy regions, and those of the activated soot samples are shown in Figure 6-15 and Figure 6-16. It can be clearly seen in C 1s XPS that these soot samples mainly consist of graphene, aliphatic carbon and molecular carbon (R-OH, C-O-C, -COOH, -C(O)-O-C, -C=O, etc.) [223,224]. These molecular carbon species are also confirmed by the detection of O 1s spectra. Table 6-5 lists the relative contents of surface elements of the detected soot samples. It can be observed that the real Biodiesel soot shows higher oxygen content and lower content of graphene component than Printex U soot, this indicates that Biodiesel soot has a higher disorder, which was also confirmed in the previous work [159]. After the soot was activated at different temperatures, the activated soot samples show different XPS results. For both Printex U and B100, the activated samples all show an increased oxygen content and a decreased graphene content. By comparison, soot-600 has a more apparent increase in oxygen content and a larger decrease in graphene carbon than soot-500. In fact, the decrease of graphene content in the activated soot reveals the increase in disorder, this well agrees with the results of both Raman spectroscopy and HRTEM.



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Figure 6-14. XP spectra of C1s, O1s of the raw Printex U and B100 samples.



Figure 6-15. XP spectra of C1s, O1s of the activated Printex U samples.

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Figure 6-16. XP spectra of C1s, O1s of the activated B100 samples.

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Samples	Printex U (at.%)			B100 (at.%)			
	С	0	Graphene	С	0	Graphene	
Raw soot	90.3	9.7	59.4	80.9	19.1	49.1	
Soot-500	90.1	9.9	54.6	80.3	19.7	42.0	
Soot-600	89.2	10.8	45.1	78.0	22.0	37.7	

Table 6-5. XPS results of Printex U and B100 samples.

6.4.6 DRIFTS analysis

The DRIFT spectra of raw and activated Printex U and B100 soot samples were investigated to obtain more information about oxygen functional groups on the carbon surface. The obtained IR spectra are shown in Figure 6-17. According to the DRIFTS results and the previous reports [82,100,225,226], the bands at around 1205 and 1090 cm⁻¹ are assigned to the stretching of C-OH and the bands at 1550 and 1420 cm⁻¹ are ascribed to the symmetric and asymmetric stretching of COO in the aromatic carboxylate species, as well as some aromatic groups are very likely to be found at

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around 1515 cm⁻¹. The stretching of C=O in lactones and carboxylic anhydrides can be observed at 1745 cm⁻¹ as well as that in quinone and ceto-enol groups at 1610 cm⁻¹. The weak band at around 1250 cm⁻¹ may be associated with C-O stretching. It was reported that the formation of some surface oxygen complexes (SOCs) could be confirmed at 1730-1750 cm⁻¹ (carboxylic anhydrides and lactones), 1595 and 1615 cm⁻¹ (quinone and ceto-enol groups) as well as 1255 cm⁻¹ (ethers and phenols) [100]. Moreover, in another publication [197], it was reported that the band at 1726 cm⁻¹ is ascribed to the vibration of C=O in aromatic ester groups and the band at 1595 cm⁻¹ can be attributed to the stretching vibration of conjugated C=C bonds or the bending mode of H₂O. The apparent absorption bands between 1726 and 1615 cm⁻¹ are difficult to assign in details. The bending vibration of C-H is also found at about 1460, 1395 and 1390 cm⁻¹ [197,225]. The band at 1600 cm⁻¹ could be attributed to the presence of H₂O and the bands at 1300-1000 cm⁻¹ are assigned to C-O vibrations [197].

As shown in Figure 6-17, the real Biodiesel soot B100 exhibits more surface oxygen functional components than Printex U soot in view of much stronger absorption signals, especially for the surface components (such as aromatic groups) appearing at 1600-1400 cm⁻¹. This result would give a better explanation for the XPS result that B100 soot exhibits higher oxygen content and lower carbon content than Printex U. In Figure 6-17a, it can be seen that the IR result of Printex U-500 seems to be same with that of raw Printex U, but an apparent change can be observed for Printex U-600 with an increased absorbance signal. This illustrates that the contents of surface functional groups, for example, aromatic groups (1550, 1515, 1460 and 1420 cm⁻¹), C-H (1460, 1395 and 1390 cm⁻¹) and C=O (1750-1726 cm⁻¹), visibly increase on the surface of Printex U-600. It is also noted that the C=C components of Printex U-600 obviously decrease compared to raw and Printex U-500 soot. The previous XPS results reveal that Printex U-600 shows more apparent changes in oxygen and graphene contents than Printex U-500, relative to raw soot. The IR results here would be a reasonable explanation for this point. Besides, in Figure 6-17b, it can be observed that the raw and activated B100 samples show a similar shape of IR absorbance profiles.

Compared with raw B100, B100-600 exhibits a similar IR result and B100-500 has a slightly decreased IR signal. This indicates that there is no an obvious change in surface oxygen functional species for raw and activated Biodiesel soot.



Figure 6-17. DRIFTS results of Printex U and B100 samples.

6.5 Correlation of structural and surface properties to reactivity

Many authors have analyzed the relationship between soot structure and oxidative reactivity by using XRD, Raman and HRTEM characterizations and found that the reactivity of soot depends on its structural properties, i,e. length scale, amorphous carbon, the degree of graphitization, nanoparticle size and surface morphology [63,152,170,171,208,227]. Wu et al. [100] studied the surface organic components (such as aromatic carboxylate, carboxylic anhydrides and lactones) of soot during soot combustion in the presence of catalysts through DRIFTS tests and summarized that the catalytic reactivity of soot is related to the concentration of surface organic components. Müller et al. [197] investigated the correlation of the noncatalytic reactivity of different soot samples to surface functional groups by DRIFTS measurements and confirmed an important role of the functionalisation on the onset of soot combustion.

Figure 6-7 and Figure 6-8 show that the activated Printex U and Biodiesel soot samples all present an increased particles aggregates size. The previous study has discussed the relationship between particles aggregates size and soot reactivity, it was

found that smaller particles aggregates are more reactive than larger ones [159]. The result in the present work cannot illustrate this point. For example, the activated soot Printex U-600 exhibits the best reactivity in both O_2 and $NO + O_2$, but its mean particles aggregates size is the largest one. This might indicate that smaller soot particles aggregates have been oxidized during the activation. In the case of Biodiesel soot samples, the activated soot shows a decreased low-temperature reactivity (Figure 6-3), this may be ascribed to the loss of smaller particles aggregates.

It was reported that high surface area of soot could promote the oxidative reactivity [224]. The previous BET results reveal that the activated soot samples show higher surface area than raw soot. The increased surface area apparently enhances the reactivity of the activated Printex U soot, however, it cannot that of the activated Biodiesel soot.

Raman spectroscopy is an important method to study the nanostructural features of soot and D1 band FWHM and the relative intensity of D3 band (I_{D3}/I_G) were reported to be the main parameters to evaluate soot structure [170,196]. Thus, Figure 6-18 presents the correlation of the reactivities (T_m) of Printex U and B100 samples with structural features. For Printex U samples, as shown in Figure 6-18, the activated soot samples show similar and higher D1 band FWHM and I_{D3}/I_G ratios, revealing their similar and increased disorder structure. However, the noncatalytic and catalytic reactivities of soot in O₂ follow the order: Printex U-600 > Printex U-500 \approx Printex U and the catalytic reactivity in NO + O_2 follows the order: Printex U-600 > Printex U-500 > Printex U. This result can not be well correlated to Raman parameters. Besides, in previous HRTEM results, it can be observed that the degree of graphitization changes with the order: Printex U-600 < Printex U-500 < Printex U. The content of graphene carbon on the surface of Printex U samples also follows this order (Figure 6-19). The results can well agree with the catalytic reactivity in NO + O₂. On the other hand, Figure 6-19 shows that the order of surface oxygen content of Printex U samples is Printex U-600 (10.8%) > Printex U-500 (9.9%) \approx Printex U (9.7%). The previous DRIFTS results also reveal that Printex U and Printex U-500

have close quantities of surface functional groups and Printex U-600 has an apparent increase in that compared to them. These conclusions are well correlated to the noncatalytic and catalytic reactivities of soot in O_2 .

In the case of B100 soot samples, as shown in Figure 6-18 and Figure 6-19, it can be known that the noncatalytic reactivity in O_2 follows the order: B100 \approx B100-500 <B100-600 and the catalytic reactivities in both O_2 and NO + O_2 follow the order: B100-500 < B100 \approx B100-600. It is also observed in Figure 6-18 that B100-500 shows lower D1 FWHM value than B100 and B100-600, indicating its an increase in graphitic order, which seems to be correlated to the catalytic reactivity. The I_{D3}/I_{G} ratio of B100-500 exhibits a slightly increased value than that of B100 and B100-600, this indicates higher content of amorphous carbon in B100-500 soot. However, that can not agree with the reactivity. In the previous discussion on Raman results, it was mentioned that it might be difficult to analyze the nanostructure of soot by only using Raman. The HRTEM results reveal that the activated soot samples show a higher disorder than raw B100. In Figure 6-19, the XPS results also indicate that the contents of surface graphene carbon and oxygen follow the order: B100 > B100-500 >B100-600. But these results cannot be well correlated to the reactivity of B100 samples. On the other side, it is noted that B100 and B100-600 show similar DRIFT spectra and slightly higher concentration of surface functional groups than B100-500, which is well correlated to their reactivities.



Figure 6-18. Correlation of the noncatalytic and catalytic reactivities of Printex U and B100 with Raman parameters including D1 band FWHM and I_{D3}/I_G .

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Figure 6-19. Correlation of the noncatalytic and catalytic reactivities of Printex U and B100 with surface oxygen and graphene contents obtained by XPS.

In fact, it is difficult to correlate structural and surface properties to the reactivity of soot, because the factors that affect soot oxidative reactivity are complex, not only related to the structure and surface property but also to soot oxidation reaction conditions. For example, in the previous isothermal reactions at 350 $\,^{\circ}$ C, under only O₂, the soot oxidation rates of raw and activated Printex U and B100 follow the order: Printex U (0.0082 μ mol_{soot}/s/g_{cat.}) \approx Printex U-500 (0.0082 μ mol_{soot}/s/g_{cat.}) < Printex U-600 (0.0538 μ mol_{soot}/s/g_{cat.}) and B100 (0.0814 μ mol_{soot}/s/g_{cat.}) > B100-500 (0.0243) μ mol_{soot}/s/g_{cat.}) \approx B100-600 (0.0243 μ mol_{soot}/s/g_{cat.}), respectively. However, under NO + O_2 , their oxidation reaction rates all follow the order: raw soot < soot-500 < soot-600. It is also noticed that the isothermal reaction rates under NO + O_2 can be well correlated to HRTEM and XPS results. Moreover, some authors tried to link the nanostructure to soot oxidative reactivity and found there was no an apparent relationship between the reactivity and Raman results [159,228]. In this work, similarly, the Raman results cannot be also well correlated to the reactivity of soot. But some researchers also confirmed that the nanostructure analyzed by Raman is one of the factors that determine the oxidation reactivity of soot [170,196,227]. It was also reported that the reactivity of soot is not only related to the nanostructure but to soot composition [178,179,224], oxygen content [149] and surface functional groups [197]. Thus, the correlation of soot oxidative reactivity should take into account a co-influence of various factors.

Besides, this study gives valuable findings on the changes in the structure, surface and noncatalytic/catalytic reactivity of the activated Printex U model and real Biodiesel soot. In comparison, the two types of soot samples show different features. However, many researchers often use Printex U model to investigate the oxidative reactivity of Diesel soot, this might not be a better route to understand the combustion of real engine soot samples. In actual exhaust gas, higher temperature and oxygen concentration would promote the activation of soot before the exhaust gas going through the DPF. Furthermore, the activation of soot might also occur during soot deposition and DPF regeneration processes. These should be considered in experimental models and studies. This study also gives some useful information on the development and selection of model soot in order to carry out an accurate evaluation of soot oxidation and thus further optimize the DPF regeneration.

6.6 Summary

In the present study, we studied and compared the structure, surface and reactivity of Printex U model and real Biodiesel soot samples through a series of characterizations and TPO measurements. Laser granulometry and BET separately revealed increased particles aggregates size and surface area of the activated soot samples. Raman results confirmed an increased disorder of the activated Printex U soot but could not clearly illustrate the changes in nanostructure of the activated Biodiesel soot. HRTEM showed different morphology of activated soot and different oxidation routes between Printex U and Biodiesel soot. XPS confirmed that the activation of soot increased surface oxygen content and decreased graphene carbon. DRIFTS indicated that the activated Printex U had a visible increase in surface functional groups, while this could not be observed in B100. TPO gave an evidence that the activated Printex U exhibited more apparent promotion on the reactivity than the activated Biodiesel soot. Furthermore, the activated Printex U displayed closer correlation of the reactivity to nanostructure and surface than real Biodiesel soot.

7. Effect of Biodiesel impurities (K, Na, P) on noncatalytic and catalytic activities of soot in model DPF regeneration conditions

7.1 Introduction

Operation of diesel engines as lean burn engines can provide the user with good fuel economy due to their significant advantages in terms of high thermal efficiency and durability. Besides, high air/fuel ratios in their operation effectively reduce the emissions of gas phase hydrocarbons and carbon monoxide. However, severe emission problems relate to particulate matter (PM), in particular, carbon nanoparticles have caused serious environment pollution and human health influences [116,229-232]. Thus, many countries and regions have drawn up more restrictive legislation such as Euro VI emission standard to limit PM emissions [192,233].

In order to comply with the restrictive legislation, many researchers and vehicle manufacturers have been looking for an effective method to reduce PM emissions. They thought that the use of Biodiesel as a renewable fuel can apparently decrease the emissions of carbon particulates and greenhouse gases (GHG) and thereby proposed to replace conventional Diesel by Biodiesel [234,235]. Biodiesel is a synthetic Diesel-like fuel and can be attained from natural sources such as vegetables and animal fats through transesterification of triglycerides [234,236]. In comparison with Diesel, Biodiesel has higher oxygen content, which would decrease the sooting tendency during fuel combustion and thereby soot deposit in the Diesel Particulate Filter (DPF) [149,237-240]. Its combustion also results in the formation of oxygenated soot with more amorphous structure, thus improving soot oxidative reactivity [63,159,241,242].

However, Biodiesel has been characterized to have some inorganic impurities like alkali metals, phosphorus, etc., these impurities would deposit in the whole vehicle exhaust system during the combustion of large amount of Biodiesel [234,243,244].

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Some inorganic elements may interact with the catalysts and soot particles, thereby influencing their physicochemical properties and reactivity. It has been reported that in Diesel Oxidation Catalyst (DOC) and Selective Catalytic Reduction (SCR) systems, the presence of these impurities led to the loss of active sites and deactivation of catalysts [244,245]. It was also found that in DPF, these impurities as ash exist on the monolith wall and also in the soot composition, thereby affecting the passive and active regeneration of DPF [244,246,247].

Many studies have confirmed that the presence of alkali metals in the catalysts has a positive impact on soot oxidation activity [248-254]. It was reported that the K-doped catalysts showed apparently improved catalytic activity during soot oxidation, the researchers thought that the presence of potassium decreased the activation energy of soot oxidation reactions and thereby increased the reactivity [249,250]. Gross et al. [251] studied the soot oxidation activity of ceria catalysts doped by different KNO₃ contents (4-14 wt%) and found a great enhancement of soot oxidation, they thought that high mobility of K improved the contact between soot particulates and catalyst and thus increased the availability of active sites in the catalyst. Aneggi et al. [252] studied the effect of Na, K, Rn and Cs alkali metals on soot oxidation activity of ceria, the result was found that all the elements showed an enhanced activity. Moreover, the intrinsic activity of some alkali metals was also studied through their impregnation on alumina support or directly on carbon black. It was reported that Na, K and Cs have a catalytic impact on carbon oxidation under air and Cs and K even show better reactivity than Pt noble metal [253,254]. However, a few reports illustrate that the presence of phosphorus inhibits soot oxidation activity under O_2 [255-257]. Schobing et al. found that phosphorus has a beneficial effect on C-NO₂ reaction, particularly in presence of water [224]. Thus, the presence of these impurities in Biodiesel would affect the soot reactivity and catalytic activity and thereby the regeneration of DPF. Surprisingly, the impact of inorganic elements on non-catalytic and catalytic reactivities of soot in presence of NO_x (NO and NO₂) in the feed gas is rarely reported in the literature.

Many studies reported that MnO_x -CeO₂ mixed oxides, as a relatively cheap candidate for soot oxidation, have excellent oxygen storage and redox ability and thus show a high promotion in soot oxidation activity [100,105,118]. Moreover, MnO_x -CeO₂ mixed oxides can not only oxidize NO to NO₂ and storage NO_x at lower temperatures but also release a large amount of active oxygen species during soot combustion [105,119].

The aim of the present work is to study the impact of the presence of Biodiesel impurities on the DPF non-catalytic and catalytic regeneration under model DPF regeneration conditions. A real soot B7, which generated from the combustion of 7% Biodiesel-diesel blends, was used in this work. The soot was doped by 0.5-2 wt% of inorganic elements (Na, K, P) to obtain the impurity-deposited soot samples. In order to evaluate the influence of Na, K and P elements on catalytic oxidation activity of soot, MnO_x-CeO₂ catalyst was prepared through a co-precipitation method and used in the reactivity measurement.

7.2 Materials preparation

7.2.1 Soot samples preparation

Real Biodiesel soot sample was provided by Volvo Group Truck Technology. An engine bench (8L Diesel engine) equipped with a Euro VI post-treatment system containing DOC and DPF was used for soot production. The real soot sample was obtained through the combustion of fuels blend with 7 vol% of methyl ester from rapeseed oil and 93 vol% of standard Euro VI fuel (EN 590). The obtained real soot sample was labeled as B7.

Soot doping was performed through a saturated impregnation method, the real soot sample B7 was impregnated by an aqueous solution of NaNO₃, KNO₃ or NH₄H₂PO₄. Then the final samples with 0.5 wt%, 1.0 wt% and 2.0 wt% inorganic elements were dried at 120 \degree for a day and calcined in a muffle furnace at 350 \degree for 2 h. The

undoped soot was also calcined at the same temperature for 2 h and used for a reference. It was noted 350B7.

7.2.2 Catalyst preparation

MnO_x-CeO₂ mixed oxides (Mn/Ce = 1/4 (mol/mol)) were prepared through a co-precipitation method. Ce(NO₃)₃ 6H₂O (solid, 95% pure) and Mn(NO₃)₂ (liquid, 50 wt.%) as the precursors were firstly dissolved in deionized water, then adding the dispersants PVA (*polyvinyl alcohol*) and PEG (*polyethylene glycol*) into the mixed solution. Finally, the mixture solution was mixed with the precipitant (pH > 9.0) consisting of NH₃·H₂O and (NH₄)₂CO₃ (chemical reagents, Beijing). The obtained precipitates were filtered and dried by a spraying apparatus, then calcined in static air at 500 °C for 3 h in a muffle furnace.

7.3 Reactivity tests by TPOs

7.3.1 Soot oxidation under noncatalytic regeneration conditions

7.3.1.1 Soot-TPOs in 9% b.v. O₂/Ar + 5% H₂O



Figure 7-1. TPO profiles of the doped B7 soot samples under 9% b.v. $O_2/Ar + 5\% H_2O$. (a) K/Na-doped samples; (b) P-doped samples.

Figure 7-1 shows the TPO profiles of the B7 soot samples doped by K, Na and P with

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different concentrations under 9% b.v. $O_2/Ar + 5\%$ H₂O. It was found that the oxidative reactivity of B7 soot is apparently influenced by the presence of K, Na and P. As shown in Figure 7-1a, the ignition of K/Na-doped samples takes place at lower temperatures compared to that of the undoped soot. The temperatures of the maximum soot oxidation rate visibly shift towards lower values after K and Na doping. With the doping amount of K and Na increasing from 0.5% to 2%, the oxidative reactivity of B7 trends to a better result. The promoting role of alkali metals on carbon oxidation by O₂ was also confirmed in the literature [224,253,254]. However, an opposite behavior of phosphorus can be seen in Figure 7-1b, it illustrates that the presence of P impurity in soot inhibits the oxidative reactivity and the deposit of higher content of P leads to a worse reactivity. This result is similar to the previous studies [224,256,257]. The following Figure 7-3 shows the temperatures at 5% or 50% conversion of different soot samples, it was found under the same conditions, the reactivity follows the order: 1% Na/B7 > 1% K/B7 > 350B7 > 1% P/B7.

7.3.1.2 Soot-TPOs in 400 ppm NO₂ + 9% b.v. O₂/Ar + 5% H₂O



Figure 7-2. TPO profiles of the doped soot samples under 400 ppm $NO_2 + 9\%$ b.v. $O_2/Ar + 5\%$ H_2O .

Figure 7-2 shows the TPO profiles of the doped soot samples under 400 ppm NO₂ + 9% b.v. O₂/Ar + 5% H₂O. The results seem to be similar with Figure 7-1. It was also found that the presence of Na and K promotes the soot oxidation and 1% of element concentration exhibits higher promotion than the 0.5%. However, for 0.5% K/B7

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sample, the ignition of soot occurs at higher temperature compared with that of undoped soot. In Figure 7-3a, it is also observed that 1% K/B7 sample shows higher $T_{5\%}$ value than 350B7. It may be explained that partial NO₂ was stored in K/B7 in the form of nitrate and/or nitrite under 5% H₂O, thus decreasing C-NO₂ oxidation reaction at low temperatures. On the other hand, for the P-doped samples, it can be observed in Figure 7-2 that 0.5% P/B7 sample seems to exhibit a slightly increased reactivity compared to 350B7. It was also noted in Figure 7-3a that 1% P/B7 has a lower $T_{5\%}$ (358 °C) than 350B7 (372 °C). The results reveal that the presence of P also enhances the reactivity of soot under $NO_2 + O_2 + H_2O$, which was confirmed in Schobing's work [224]. But the peak temperature (T_m) of 1% P/B7 visibly moves to higher value relative to that of 350B7, their $T_{50\%}$ values also present the same result (Figure 7-3b). This indicates that P element inhibits high-temperature reactivity of soot. Figure 7-3 illustrates the impact of different inorganic elements on soot oxidation reactivity in the presence of NO₂. $T_{5\%}$ and $T_{50\%}$ are as follows: 1% K/B7 > 350B7 > 1% P/B7 > 1% Na/B7 and 1% P/B7 > 350B7 > 1% K/B7 > 1% Na/B7, respectively.



Figure 7-3. Temperature at which 5% of conversion $(T_{5\%})$ (a) and 50% of conversion $(T_{50\%})$ (b) of the 1 wt% doped soot samples.

In addition, it can be seen in Figure 7-3a that the presence of NO_2 apparently decreases the $T_{5\%}$ values of soot samples, revealing the promoting role of NO_2 on soot oxidation at lower temperatures. While, as shown in Figure 7-3b, the promotion of NO_2 becomes weak at higher temperatures ($T_{50\%}$), this is because thermal

decomposition of NO₂ occurs and thereby decreases C-NO₂ or C-NO₂-O₂ reactions.

7.3.2 Soot oxidation under catalytic regeneration conditions

7.3.2.1 Soot-TPOs in 9% b.v. O₂/Ar + 5% H₂O



Figure 7-4. TPO profiles of the doped soot samples with catalyst under 9% b.v. $O_2/Ar + 5\% H_2O$. (a) K/Na-doped samples; (b) P-doped samples.

The catalytic reactivity of the doped soot samples under 9% b.v. $O_2/Ar + 5\%$ H₂O was evaluated through TPO and the results were presented in Figure 7-4. The TPO profiles seem to be similar with those in absence of catalyst (Figure 7-1). It was found in Figure 7-4a that the presence of Na and K visibly enhances the catalytic reactivity of B7 soot in view of the TPO profiles shifting towards lower temperatures. While Figure 7-4b shows that the presence of P inhibits soot catalytic oxidation. The reactivity of the soot samples doped by K, Na and P with different concentrations follows the order: 2% K/B7 > 1% K/B7 > 0.5% K/B7 > 350B7, 2% Na/B7 > 1% Na/B7 > 0.5% Na/B7 > 350B7 and 350B7 > 0.5% P/B7 > 1% P/B7 > 2% P/B7, respectively. Figure 7-7 also illustrates the order of the reactivity (T_{5%} and T_{50%}) of K/Na/P-doped samples is as follows: 1% Na/B7 > 1% K/B7 > 350B7 > 1% P. These results are similar with the previous noncatalytic reactivity under O₂.

In comparison with the previous C-O₂ reaction results in Figure 7-3, the presence of catalyst visibly decreases the $T_{5\%}$ values of the undoped and doped samples from

412-542 °C to 382-492 °C. While there is no an apparent difference in $T_{50\%}$ between with and without catalyst. This indicates that the presence of catalyst effectively promotes the ignition of soot.





Figure 7-5. TPO profiles of the doped soot samples with catalyst under 400 ppm NO + 9% b.v. $O_2/Ar + 5\% H_2O$. (a) Na-doped samples; (b) K-doped samples; (c) P-doped samples.

Figure 7-5 presents the TPO profiles of the doped soot samples with catalyst under 400 ppm NO + 9% b.v. $O_2/Ar + 5\%$ H₂O. It was found that the soot oxidation reactions of all samples take place within a wider temperature window (200-700 °C) and the ignition of soot samples apparently shifts to lower temperatures compared to the results in O₂. Especially in Figure 7-5a and b, it can be seen that all the TPO profiles move towards lower temperatures, which shows a strong promoting role of NO on soot catalytic oxidation, this has been confirmed in the previous studies [105,119,159]. However, in Figure 7-5c, the presence of phosphorus does not make

the peak temperature (T_m) obviously shift towards lower temperatures after adding NO into reaction gas. This indicates that the presence of P weakens the promotion of NO on high-temperature activity.

Figures 7-5a and b show that the presence of Na and K promotes the NO-assisted catalytic oxidation activity of soot except for 0.5% K-doped sample exhibiting a similar reactivity with undoped sample. Higher content of Na or K in soot leads to an increased reactivity. On the contrary, Figure 7-5c reveals that the presence of P apparently inhibits the catalytic reactivity of soot. As same as shown in Figure 7-4b, the deposit of more phosphorus in soot results in a larger decrease in the reactivity. In Figure 7-7, it was found that $T_{5\%}$ and $T_{50\%}$ under NO + O_2 + H_2O separately follow the order: 1% K/B7 > 1% Na/B7 > 1% P/B7 > 350B7 and 1% Na/B7 > 1% K/B7 > 350B7 > 1% P/B7. It is noted that during the ignition of soot, K-doped sample shows higher oxidative reactivity than Na-doped one and P-doped sample also exhibits a promoted reactivity. This is different with the result in O_2 . It illustrates that the impact of inorganic impurities on soot catalytic oxidation also depends on the composition of reaction gas.

7.3.2.3 Soot-TPOs in 400 ppm NO₂ + 9% b.v. O₂/Ar + 5% H₂O



Figure 7-6. TPO profiles of the doped soot samples with catalyst under 400 ppm $NO_2 + 9\%$ b.v. $O_2/Ar + 5\% H_2O$.

The catalytic reactivity of the doped soot samples was also evaluated by TPO under

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400 ppm NO₂ + 9% b.v.O₂/Ar + 5% H₂O and the results are shown in Figure 7-6. The TPO profiles seem to be similar with those under NO + O₂ + H₂O. The promotion of Na and K and the inhibition of P on soot oxidation are also observed here, but the promoting role of 0.5% K is not apparent. As shown in Figure 7-7, T_{5%} and T_{50%} values of the doped samples under NO₂ + O₂ + H₂O follow the order: 1% K/B7 \approx 1% Na/B7 > 1% P/B7 > 350B7 and 1% Na/B7 > 1% K/B7 > 350B7 > 1% P/B7, respectively. The result also reveals the promoting role of P on soot ignition.



Figure 7-7. Temperature at which 5% of conversion $(T_{5\%})$ (a) and 50% of conversion $(T_{50\%})$ (b) of the 1 wt% doped soot samples.

Figure 7-7 presents $T_{5\%}$ and $T_{50\%}$ values of soot conversion profiles under different reaction gases. By comparison, the presence of NO_x (NO and NO₂) visibly enhances the catalytic reactivity of soot. In the previous study [105], the authors compared the promoting role of NO and NO₂ during soot oxidation over Pt/MnO_x-CeO₂ catalyst and found that NO more highly promotes soot oxidation activity than NO₂. In Figure 7-7, 1% K/B7 sample shows lower $T_{5\%}$ under NO, but the $T_{50\%}$ values under NO and NO2 are very close. A similar $T_{5\%}$ under NO_x is seen in 350B7 and 1% Na/B7 samples, while their $T_{50\%}$ values are lower under NO than that under NO₂. These may be attributed to higher promotion of NO. However, $T_{5\%}$ and $T_{50\%}$ of the P-doped sample all present a higher value under NO than that under NO₂, indicating higher promotion of NO₂.

7.4 Physicochemical properties

7.4.1 Raman analysis



Figure 7-8. Analysis of the Raman spectra and curve fits of 350B7 sample.

Sample	$FWHM_{D1}/cm^{-1}$	FWHM _G /cm ⁻¹	$I_{\rm D1}/I_{\rm G}$	$I_{\rm D3}/I_{\rm G}$	$A_{\rm D3}/A_{\rm G}$
350B7	134	65	1.03	0.91	0.42
0.5% K/B7	131	64	1.06	0.89	0.45
1% K/B7	133	67	1.03	0.92	0.49
0.5% Na/B7	131	64	1.04	0.94	0.57
1% Na/B7	134	72	1.02	0.95	0.68
0.5% P/B7	125	67	1.03	0.93	0.44
1% P/B7	128	67	1.04	0.91	0.33

Table 7-1. Raman results of soot samples.

Figure 7-8 as an example shows the Raman spectra of 350B7 sample, and the Raman results of other samples are not shown here because their Raman curves are similar. It can be observed that there are two overlapping peaks, which appear at around 1350 cm⁻¹ (D peak) and 1580 cm⁻¹ (G peak), respectively [63,171,259]. The D peak, which includes D1, D2, D3 and D4 bands, is generally associated with the defective structure of carbon and the G peak should be assigned to highly ordered graphitic structure. It was reported that D1 band at around 1350 cm⁻¹ is related to the disordered graphitic lattice and D3 band at around 1500 cm⁻¹ can provide some information about chemical structure of graphite-like and amorphous carbon, thus D1 FWHM (full width at half maximum) and relative intensity of D3 are considered to be important

parameters to analyze carbon structure [170,259]. It was also reported that the FWHM of G and D bands and the relative intensity of D band (I_D/I_G) can be correlated to the degree of graphitization of carbonaceous materials [214-219]. The authors thought that higher order of carbon would be characterized by lower FWHM and I_D/I_G values. Some researchers thought that the structural defects in graphene layers are also related to the ratios between D and G band areas (A_D/A_G) [170].

Table 7-1 shows the Raman results of different soot samples. In the case of K-doped samples. It can be noted that 0.5% K/B7 and 1% K/B7 samples show similar FWHM values of D1 and G bands as well as I_{D1}/I_G and I_{D3}/I_G compared to 350B7 sample. This illustrates that the degree of graphitization of the doped soot is not apparently affected by K. But it is also observed that the A_{D3}/A_G of 1% K/B7 exhibits a visible increase from 0.42 to 0.49, which indicates that the addition of K into soot increases the structural defects. In case of Na-doped samples, they show similar D1 FWHM and I_{D1}/I_{G} values with 350B7 sample, revealing a similar structure of the disordered graphitic lattice in carbon. It is also seen that 0.5% Na/B7 shows a very close G FWHM value but 1% Na/B7 an obvious increase from 65 to 72 cm⁻¹ compared with 350 B7, this indicates that the doping of 1% Na into B7 soot decreases the degree of graphitization. Furthermore, the Na-doped samples show higher I_{D3}/I_G and A_{D3}/A_G values than 350 B7, this reveals that the introduction of Na apparently increases the amount of defective sites and amorphous carbon. The 1% Na-doped sample displays more apparent result than 0.5% Na-doped sample. In comparison with K-doped samples, the addition of Na exhibits a higher promotion on increasing structural defects of carbon in view of higher I_{D3}/I_G and A_{D3}/A_G values.

For the P-doped samples, it can be noted that there is no an apparent change in G band FWHM, I_{D1}/I_G and I_{D3}/I_G values compared to 350B7 sample. However, their D1 band FWHM values decrease visibly, this may indicate an increased order in graphitic lattice. The 1% P-doped sample shows an apparent decrease in A_{D3}/A_G from 0.42 to 0.33, which illustrates the decrease of structural defects in graphene layers. While the A_{D3}/A_G of 0.5% P-doped sample has no obvious change. In short, the Raman reuslts

indicate that the introduction of P into soot causes a decreased trend of structural defects in carbonaceous materials.

In the previous reactivity results, K- and Na-doped soot samples all show an improved reactivity under both noncatalytic and catalytic conditions. This should be attributed to their increased structural defects. The presence of Na in soot exhibits larger promotion on the reactivity than that of K, this is because Na-doped soot presents more structural defects than K-doped soot. However, P-doped samples show a decreased reactivity compared to 350B7, which should be related to the decreased trend of their structural defects.

7.4.2 BET analysis

Table 7-2. specific surface area (S_{BET}), microporous pore volume (V_{micro}) and mesoporous pore volume (V_{meso}) of doped B7 soot samples.

Sample	$S_{\rm BET}$ (m ² /g)	Microporous S_{BET} (m ² /g)	Mesoporous S_{BET} (m ² /g)	$V_{ m micro}$ (cm ³ /g)	$V_{\rm meso}$ (cm ³ /g)
350B7	345	358	259	6.6×10^{-3}	1.63
0.5% K/B7	198	202	135	1.4×10^{-2}	0.34
1% K/B7	337	354	249	1.7×10^{-2}	0.64
0.5% Na/B7	286	323	188	1.7×10^{-2}	0.49
1% Na/B7	238	262	108	8.4×10^{-2}	0.17
0.5% P/B7	289	308	206	8.0×10^{-2}	0.54
1% P/B7	237	282	105	9.4×10^{-2}	0.16

The values of surface area (S_{BET}), micropore surface area, mesopore surface area, micropore volume (V_{micro}) and mesopore volume (V_{meso}) are listed in Table 7-2. Impregnation of B7 soot by K, Na and P significantly decreases the surface area and mesopore volume but increases micropore volume. This should be attributed to physical blocking of surface sites in pores. It can be noted that the addition of 0.5% K into soot leads to a sharp decrease in surface area but that of 1% K a slight decrease compared to 350B7 sample. It was reported that the impregnation of soot with alkali metals would result in a modification of the bulk carbonaceous structure through the Chapter VII. Effect of Biodiesel impurities (K, Na, P) on noncatalytic and catalytic activities of soot in model DPF regeneration conditions

insertion of the metals in the structure and thereby increase BET surface area and micropore volume [224]. This role of alkali metals might exist in the 1% K-doped soot sample, as a result, it shows much higher surface area than 0.5% K-doped soot sample. On the other side, for Na- and P-doped samples, their surface areas apparently decrease with the increase of the doping amount (from 0.5% to 1%).

However, the surface area and pore volume cannot be well correlated to the reactivity of the doped soot samples. For example, the introduction of Na and K greatly promotes the reactivity, but the doped samples present a decreased surface area. The result might illustrate that the reactivity of the doped soot samples do not depend on their surface area.



7.4.3 HRTEM analysis

Figure 7-9. HRTEM images of different soot samples.

The morphology of different soot samples (including 350B7, 1% K/B7, 1% Na/B7 and 1% P/B7) was characterized through HRTEM, and the results are shown in Figure

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7-9. All samples show highly ordered graphitic carbon layers and disordered amorphous structure. The crystalline layers in graphitic carbon exhibit strongly bent ribbons and long chainlike agglomerates. In the case of 350B7 sample, it can be observed that it shows visible crystalline layers and high structural order. In the case of the doped soot samples, the Na- and P-doped samples exhibit less crystalline layers and more disordered carbon or amorphous carbon than the other samples. The morphology of K-doped sample seems to be similar with that of the undoped 350B7 sample.

The observation on HRTEM images can not well agree with the results of Raman and reactivity. For example, it is confirmed that P-doped sample exhibits less disordered carbon and structural defects through Raman spectroscopy and thus a poorer reactivity, but HRTEM image shows that it has higher disorder. This may be difficult to correctly evaluate the nanostructure of soot by HRTEM images because the measurement of TEM may be limited by the heterogeneity of soot materials. The results of HRTEM also illustrate that the reactivities of the doped soot samples cannot depend on their morphology features.

7.4.4 XPS analysis



Figure 7-10. XP spectra of C1s, O1s of 350B7 soot sample.



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Figure 7-11. XP spectra of C1s, O1s, Na1s of 1% Na/B7 soot sample.



Figure 7-12. XP spectra of C1s, O1s, P2p of 1% P/B7 soot sample.

	1	ě	-			1 1
Sample	С	0	O _(CO)	S	Na	Р
350B7	86.3	13.6	10.9	0.2	/	/
1% Na/B7	84.1	14.3	13.4	0.3	1.2	/
1% P/B7	85.2	14.1	10.6	0.2	/	0.5

Table 7-3. Elemental composition of the soot samples in wt% determined by XP Spectroscopy.

Figure 7-10, Figure 7-11 and Figure 7-12 present the results of XP spectra of 350B7, 1% Na/B7 and 1% P/B7, respectively. It can be clearly observed in C1s XPS that the undoped and doped soot samples mainly consist of graphene, aliphatic carbon and molecular carbon (R-OH, C-O-C, -COOH, -C(O)-O-C, -C=O, etc.) [255,256]. The O1s XPS reveal that the detected oxygen mainly originates from carbon-oxygen complexes (CO). The XP spectrum of the S2p (BE = 168.63 eV and 166.30 eV) [260,261], which is not shown here due to lower sulfur content, also illustrates the presence of sulfur in B7 soot. In 1% Na/B7 sample (Figure 7-11), the O1s XP spectrum detected the presence of S in the form of SO_x at 531.55 eV, which may be attributed to the formation of Na₂SO_x (x = 3 or 4) [224]. The XP spectrum of Na1s shows that Na was only detected in the form of sulfate/sulfonate at 1071.36 eV [224]. In the case of 1% P/B7 (Figure 7-12), Phosphorous was detected in the form of phosphate at 133.71 eV [255,256]. Thus, the single (O-P) and double bindings (O=P) were also detected in the O1s XP spectra (O-P: 531.45 eV; O=P: 532.85 eV) [255].

Table 7-3 lists the elemental composition of the soot samples in wt% determined by XP Spectroscopy. It can be seen that the doped samples (1% Na/B7 and 1% P/B7) exhibit higher oxygen content than 350B7 sample, this may be due to the formation of sulfate and phosphate species. But 1% Na/B7 sample shows the highest oxygen content in (CO) form, which may be ascribed to the formation of more surface (CO) species. Higher sulfur content of 1% Na/B7 soot is likely attributed to the formation of Na₂SO_x decreasing the loss of sulfur during calcination step. Table 7-3 also illustrates that the content of Na in Na-doped sample (1.2%) is higher than the theoretical content (1%). The lower content of P may result from partial P entering

into the bulk structure of carbon and forming C-O-PO₃ or (CO)₃-P species [224].

The previous TPO results reveal the Na-doped soot sample shows higher noncatalytic and catalytic reactivity under both O_2 and $NO_x + O_2$ than 350B7 and P-doped soot sample. The XPS results confirm that 1% Na/B7 shows higher oxygen content (14.3%), especially that in (CO) form (13.4%), than 350B7 and 1% P/B7. This might be one of factors that promote soot oxidation reactivity. Besides, the P-doped sample shows a similar oxygen content with 350B7 sample, however, this cannot explain an obvious inhibition of P on soot oxidation reactivity. The result also illustrates that the oxygen content on the carbon surface is not only one factor that depends on the reactivity of soot. The previous Raman results reveal that 1% P/B7 exhibits an increase in structural order and thus a decreased reactivity, this indicates that the reactivity of soot is also related to the structure.

On the other side, other factors may also determine the reactivity of soot. For example, the presence of K or Na in soot could play a role of catalyst to decrease the activation energy of soot oxidation, thus improving the reactivity [250,253,254]. Moreover, K also promotes the contact between catalyst and soot due to its high mobility and thereby the catalytic reactivity [251].

7.5 summary

A real Biodiesel soot was impregnated by Na, K and P through a saturated impregnation method. The research mainly focuses on the impact of Biodiesel impurities on the noncatalytic and catalytic reactivity of soot under model DPF regeneration conditions. TPO measurements confirmed that the introduction of Na and K enhanced the noncatalytic and catalytic reactivity of soot under both O₂ and NO_x + O₂ and Na-doped sample showed better results. The presence of P in soot inhibited the the noncatalytic and catalytic reactivity in view of the increased $T_{50\%}$ value, but it promoted the ignition of soot under NO_x + O₂ mixture. The characterizations revealed that the soot doped with Na and K exhibited increased

structural defects and P led to a decrease in disordered structure. They also indicated that the reactivity of the doped soot is related not only to surface oxygen content and structure but also to the other factors such as the catalytic role of Na and K. HRTEM and BET results revealed that the reactivity of the doped soot samples could not be well correlated to their morphology and surface area.

8. Conclusions

In the chapter 4, the experiment studied the role of NO adsorption/desorption on soot oxidation activity of MnO_x -CeO₂ catalyst under NO + O₂ mixture. The physical-chemical properties of the NO-adsorbed MnO_x -CeO₂ catalyst were characterized through DRIFTS, XPS, Raman spectroscopy, TPD with IR and MS, Soot-TPR coupled to MS. The catalytic activity of the catalyst was evaluated by TPO and isothermal reaction. DRIFTS results confirmed that NO_x were stored in the forms of nitrites, nitrates, nitro compounds and N₂O₄. XPS and Raman results revealed that NO adsorption on the surface of the catalyst led to the change in the surface Ce/Mn states and the increase of oxygen vacancies, respectively. TPD experiments indicated that the decomposition of nitrates would lead to the production of a large amount of NO and super-oxides (Ce-O₂⁻). TPR confirmed a key role of oxygen in NO-assisted soot oxidation reactions. The activity measurement also revealed that the adsorption/desorption of NO promoted the low-temperature soot oxidation activity. This promotion is related to the increase of oxygen vacancies and the desorption of active oxygen from surface nitrate decomposition.

The work presented in chapter 5 aims to investigate and compare the non-catalytic of and catalytic reactivities real and model soot samples through temperature-programmed oxidation (TPO). Such reactivity was furthermore correlated with soot structural properties, determined by laser granulometry, XRD, Raman and HRTEM. Biodiesel soot samples were obtained through the combustion of different fuels in a real Diesel engine, whereas model soot samples were produced in a laminar burner. TPO evidenced that the soot generated with 100% Biodiesel (methyl ester) was more reactive than real soot generated with 7% Biodiesel (7% methyl ester). The model soot from the diesel surrogate (Aref) containing 7% oxygenate additive $(C_{11}H_{22}O_2)$ exhibited higher reactivity than the model soot containing 30% additive, whereas the model soot (Degussa Printex U) showed the poorest reactivity of this series. The presence of NO₂ more apparently promoted the non-catalytic reaction of real soot. In the presence of the MnO_x -CeO₂ catalyst, soot reactivity depended both on

reactant gas composition and on soot-catalyst contact, following the order: $NO + O_2 > NO_2 + O_2 > O_2$ and tight > pressure > loose, respectively.

In the chapter 6, the experiment focused on the structure, surface and reactivity of the activated Printex U model and real Biodiesel soot samples through BET, Raman, HRTEM, XPS, DRIFTS and temperature-programmed oxidation (TPO). TPO evidenced that the activated Printex U soot was more reactive than the activated Biodiesel soot (B7 and B100) generated from a real Diesel engine under both O_2 and NO + O_2 mixture. BET displayed an increased surface area and a decreased pore size of activated soot. Raman and HRTEM revealed that the activated soot showed an increased disorder. The morphology features also confirmed different combustion processes of Printex U and B100. XPS illustrated that the activation decreased surface graphene carbon and increased oxygen content. DRIFTS indicated that the activation did not increase the concentration of surface functional groups of B100 but increased that of Printex U. It was proved that the reactivity of activated Printex U samples is more dependent on structural and surface properties compared with that of the activated Biodiesel soot samples.

These studies in chapters 5 and 6 provided valuable findings on the soot oxidation rate and the parameters influencing it, which could contribute to develop accurate soot models that are required for robust regeneration strategies. The use of 100% biofuel induces significantly lower soot deposits in DPF that being correctly estimated (adapted biofuel soot models) might reduce the need of active regenerations and therefore the fuel consumption and the catalyst ageing. Therefore, the understanding of how the fuel type and engine operation affects the particle morphology and its reactivity are crucial for optimizing the DPF regeneration strategy. For the development of new coating formulations, the selection of model soot to be used in synthetic gas benches shall be taken with care, as it was shown in that study the risk of having different behaviors for example for the carbon-black Printex U often reported in literature. The catalyst evaluation studies shall therefore take into account the use of burner and real engine soot samples as well as realistic operating conditions in terms of gas composition and soot/catalyst contact in order to perform an accurate benchmark.

The experiments in chapter 7 mainly studied the impact of Biodiesel impurities on the noncatalytic and catalytic reactivity of soot under model DPF regeneration conditions. A real Biodiesel soot was impregnated by Na, K and P through a saturated impregnation method. TPO measurements confirmed that the introduction of Na and K enhanced the noncatalytic and catalytic reactivity of soot under both O_2 and $NO_x + O_2$ and Na-doped sample showed better results. The presence of P in soot inhibited the the noncatalytic and catalytic reactivity in view of the increased $T_{50\%}$ value, but it promoted the ignition of soot under $NO_x + O_2$ mixture. The characterizations revealed that the soot doped with Na and K exhibited increased structural defects and P led to a decrease in disordered structure. They also indicated that the reactivity of the doped soot could be related not only to surface oxygen content and structure but also to the other factors such as the catalytic role of Na and K as well as the soot-catalyst contact.

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Annexes

Annex. 1 Abbreviations and symbols

Abbreviations	Explanations
DPF	Diesel Particulate Filter
SOF	Soluble Organic Fraction
PM	Particulate Matter
SOCs	Surface Oxygenated Complexes
PVA	Polyvinyl alcohol
PEG	Polyethylene glycol
BET	Brunauer-Emmett-Teller
XRD	X-Ray Diffraction
TPR	Temperature-Programmed Reduction
TPD	Temperature-Programmed Desorption
MS	Mass Spectrometer
IR	Infrared-Ray
TGA	Thermal Gravimetric Analysis
HRTEM	High-Resolution Transmission Electron Microscopy
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectra
XPS	X-ray Photoelectron Spectra
TPO	Temperature-Program-Oxidation
DOC	Diesel Oxidation Catalyst
SCR	Selective Catalytic Reduction
GHSV	Gas Hourly Space Velocity
Raman	Raman Spectroscopy
FWHM	Full Width at Half Maximum
CRT	Continuously Regeneration Trap
CCRT	Catalyzed Continuously Regeneration Trap

Table Annexes 1-1. List of abbreviations and explanations.

Symbols	Explanations
-C(O)	Carbon-Oxygen Complexes
O*	Active Oxygen
$-O_2^-$	Super-Oxygen Species
D	Thickness of Crystallites
L	Crystalline Length
<i>K</i> , <i>K</i> ′	Shape Factors in XRD
eta_{002},eta_{100}	Full Widths at Half Maximum of 100 and 002 Bands in XRD
m/z	Proton Number/Charge Number Ratio
f(x)	Carbon Fringe Length Distribution
μ	Mean Value of Fringe Lengths
σ	Standard Deviation
σ^2	Variance
B.E.	Binding Energies
$T_{ m i}$	Ignition Temperature
$T_{ m m}$	Temperature of Maximal Soot Oxidation Rate
$T_{5\%}$	Temperatures at which 5% of Soot Conversion
$T_{50\%}$	Temperatures at which 50% of Soot Conversion
$X_{\rm CO}$	Molar Fractions of CO in ppmv
$X_{\rm CO2}$	Molar Fractions of CO ₂ in ppmv
$V_{ m M}$	Molar Volume
m _{soot,ini.}	Initial Quality of Soot
m _{cat.}	Initial Quality of Catalyst
$S_{\rm CO2}$	Selectivity of CO ₂
CM	MnO _x -CeO ₂
CM-NO	NO-adsorbed MnO _x -CeO ₂
Ce^{3+} - \Box	Oxygen Vacancy
$A_{ m OV}$	Area of O-Vacancy
$A_{ m F2g}$	Area of F_{2g} Band
M1, M2, M3	Model Soot
R1, R2	Real Engine Soot
$I_{\rm D}/I_{\rm G}$	I_D/I_G Ratio
B7	The Soot From the Burning of 7% Biodiesel-Diesel Blends
B100	The Soot From the Burning of 100% Biodiesel
$S_{ m BET}$	Specific Surface Area
R	Mean Pore Size
$V_{ m p}$	Pore Volume
350B7	B7 Soot Calcined at 350
1% K/B7	1 wt% K doped into B7 Soot
1% Na/B7	1 wt% Na doped into B7 Soot
1% P/B7	1 wt% P doped into B7 Soot

Table Annexes 1-2. List of symbols and explanations

Abstract

Diesel has been widely applied in the vehicle field due to its high efficiency, durability and low costs. However, the high emissions of particulate matter (PM) from Diesel exhaust gas have led to severe environmental pollution and human health threat. DPF aftertreatment system that combines the catalytic reactions is considered to be an efficient solution to meet the restrictive emission standards. MnO_x -CeO₂ mixed oxides have high redox ability and oxygen storage capacity, thus they as promising catalysts have been widely studied and employed in soot oxidation reactions. In the present research, it was found that NO adsorption/desorption on MnO_x-CeO₂ catalyst promoted the low-temperature reactivity of soot due to the changes in the surface Ce/Mn states and an increase of oxygen vacancies. Moreover, the active oxygen species generated from nitrates decomposition played an important role during the promoted soot oxidation. It was revealed that non-catalytic and catalytic reactivities of real Biodiesel and model soot samples were furthermore correlated with soot structural properties. In the presence of the MnO_x-CeO₂ catalyst, soot reactivity also depended both on reactant gas composition and on soot-catalyst contact. Besides, the activation of soot under O₂ showed a positive role on its structural and surface properties and thereby enhanced its reactivity. In the end, a real Biodiesel soot was impregnated by Na, K or P, reactivity results evidenced that alkali metals Na and K exhibited a positive effect on soot oxidation but phosphorus showed an inhibition under both O_2 and $NO_x + O_2$.

Keywords: Biodiesel soot, Model soot, Catalytic reactivity, Nanostructure; MnO_x-CeO₂

R ésum é

Le diesel a ét é largement utilis é dans le secteur automobile en raison de son efficacit é dev é, de sa durabilité et de ses faibles coûts. Cependant, les émissions de particules provenant des gaz d'échappement diesel ont entra î é une grave pollution de l'environnement et une menace pour la sant é humaine. Le système de post-traitement «filtre à particules » en combinant des réactions catalytiques est aujourd'hui consid ér é comme une solution efficace pour respecter les normes. Les mat ériaux de type oxydes mixtes MnO_x -CeO₂ ont une capacit é r édox et une capacit é de stockage d'oxygène élevée. Ils ont été largement étudiés et utilisés comme catalyseurs prometteurs dans les réactions d'oxydation des suies. Dans cette étude, il a été constat é que l'adsorption/d ésorption de NO sur le catalyseur MnO_x-CeO₂ favorisait la r éactivit é à basse temp érature de la suie en raison des modifications des états Ce/Mn en surface et d'une augmentation des lacunes d'oxygène. De plus, les espèces d'oxygène actif générées par la décomposition des nitrates jouent un rôle important lors de l'oxydation favoris é de la suie. Nous avons montr é que les r éactivit és non catalytiques et catalytiques de biodiesel r él et d'échantillons de suie mod des étaient en outre corr d ées aux propri ét és structurelles de la suie. En pr ésence de MnO_x -CeO₂, la réactivité de la suie dépend aussi bien de la composition du gaz réactif que du contact catalyseur/suie. En outre, l'activation de la suie sous O₂ joue un r ôle positif sur ses propriétés structurelles et de surface et améliore ainsi sa réactivité. Finalement, une véritable suie de biodiesel a été imprégnée par Na, K ou P, les résultats de r éactivit é ont montr é que les m étaux alcalins, Na et K, avaient un effet positif sur l'oxydation de la suie, mais que le phosphore présentait lui une inhibition.

Mots cl és: Suie de biodiesel, Suie mod de, R éactivit é catalytique, Nanostructure; MnO_x-CeO₂.