

**STUDY ON THE CATALYTIC OXIDATION OF DIESEL
ENGINE SOOT USING IRON OXIDE CATALYSTS**

By
NAVEED JAN



**DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL SCIENCES**

**DEPARTMENT OF ENVIRONMENTAL SCIENCES
UNIVERSITY OF PESHAWAR,
KPK, PAKISTAN
2011**

STUDY ON THE CATALYTIC OXIDATION OF DIESEL ENGINE SOOT USING IRON OXIDE CATALYSTS

By

NAVEED JAN



A dissertation submitted to the University of Peshawar
in partial fulfillment for the degree of

DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL SCIENCES

DEPARTMENT OF ENVIRONMENTAL SCIENCES
UNIVERSITY OF PESHAWAR,
KPK, PAKISTAN
2011

**STUDY ON THE CATALYTIC OXIDATION OF DIESEL
ENGINE SOOT USING IRON OXIDE CATALYSTS**

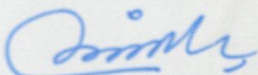
By

NAVEED JAN

A thesis submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Environmental Sciences.

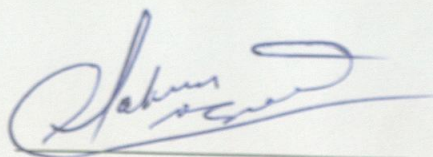
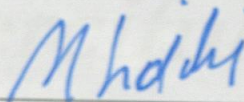
Approved by

Research Supervisor



Dr. Hizbullah Khan
Department of Environmental Science
University Peshawar

External Examiner



Chairperson,
Department of Environmental Science,
University Peshawar

**DEPARTMENT OF ENVIRONMENTAL SCIENCES
UNIVERSITY OF PESHAWAR
KPK, PAKISTAN
2011**

Date 11.9.2012 Controller of Exams, UOP

In the Name of ALLAH
The Most Gracious
The Most Merciful

Remember the two benefits of failure. First, if you do fail, you learn what doesn't work; and second the failure gives you opportunity to try a new approach.



DEDICATION

*Dedicated to my sweet and ever
loving mother, to my wife & to my
kids (Musab Naveed, Mahrukh
Naveed, Manal Naveed)*



Table of Contents

ACKNOWLEDGEMENTS.....	i
ABSTRACT	ii
Chapter – 1	1
INTRODUCTION	1
1.1. General	1
1.2. Aims and Objectives	5
1.3. Theoretical Background	6
1.3.1. Diesel Engine Emissions:	7
1.3.2. Diesel Engine Emissions Legislature:	7
1.3.3. Diesel Emission Treatment Technologies:	8
1.3.4. Oxidation Catalysts:	9
1.3.5. Mechanism of Catalytic Soot Oxidation:	10
1.3.6. Formation, Composition, Structure, & Reaction Scheme of the Soot: ...	11
1.3.7. Kinetic Studies.....	14
1.4. Characterization Techniques	15
1.4.1. Specific Surface Area Measurement (BET Method)	15
1.4.2. Fourier transforms infrared (FTIR) spectroscopy	16
1.4.3. Powder X-Ray Diffraction (PXRD)	17
1.4.4. Scanning Electron Microscopy (SEM).....	17
1.4.5. Thermo-gravimetry (TG).....	18
1.4.6. Temperature-Programmed Techniques	19
1.4.6.1 Temperature-Programmed Oxidation (TPO)	19
1.4.6.2. Temperature-Programmed Desorption (TPD)	20
1.5 Analytical Technique	21
1.5.1 Non-Dispersive Infrared (NDIR) Spectroscopy	21
1.6. Kinetics & mechanism of the non-catalyzed & catalyzed soot oxidation ..	22
Chapter – 2	23
EXPERIMENTAL	23
2.1 Chemicals	23
2.2 Preparation of Soot and Fe_2O_3	23
2.2.1 Preparation of model soot.....	23
2.2.2 Preparation of Fe_2O_3	25
2.3 Characterization of Soot and Fe_2O_3	25
2.3.1 X-ray Diffraction (XRD)	25
2.3.2 BET Surface Area (BSA)	25
2.3.3 Scanning Electron Microscopy (SEM).....	26
2.3.4 Fourier Transform Infra Red Spectroscopy (FTIR)	26

2.3.5	Thermo-gravimetry (TG).....	27
2.3.6	Temperature Programmed Desorption (TPD) studies.....	28
2.4	Catalytic Studies - Temperature Programmed Oxidation (TPO).....	28
2.5	Kinetic Studies	29
Chapter – 3		32
Results and Discussion		32
3.1	Temperature programmed oxidation – Reactivity of soot to oxygen	32
3.2.	FTIR analysis of soot, formation and decomposition of SOCs	51
3.3.	Effect of O ₂ concentration & the catalyst-soot contact on combustion.	66
3.4.	Soot oxidation activity by the combustion temperature.....	72
3.5.	Catalyst performance-Activity	76
3.6.	Morphology of α -Fe ₂ O ₃ & soot particles.....	77
3.7.	Kinetics of the catalytic and non-catalytic soot/O ₂ reaction	92
3.8.	Evaluation of the number of reactive carbon sites in soot/O ₂ reaction.....	96
3.9.	Global kinetic modelling of the catalytic & non-catalytic soot/O ₂ reaction	99
Chapter – 4		1042
Conclusions		1042
Chapter – 5		1044
References		1044

ACKNOWLEDGEMENTS

All praises for Almighty Allah, who created the whole universe and gave us the courage to pursue the scientific knowledge.

Sincere thanks to Dr. Noor Jehan, Chairperson, Department of Environmental Sciences, University of Peshawar, for her motivation and guidance and her generous help in all the aspects.

I wish to express with pleasure my sincere thanks to my supervisor Dr. Hizbullah Khan, Associate Professor, Department of Environmental Sciences, University of Peshawar, for his kind patronization, valuable suggestions and fruitful discussions throughout the course.

I am extremely thankful to Dr. Sven Kureti, Associate Professor, Institute for Technical Chemistry and Polymer Chemistry, University of Karlsruhe (TH), Germany for his many important and valuable suggestions; for his quick, wise and valuable guidance to complete experimental work; for his help and guidance and his daily hour's long fruitful discussion through out my research, which often goes behind the call of the duty, and finally his help, comments, suggestions and constructive criticism during thesis writing.

I am also extremely grateful to my laboratory colleagues especially Dr. Thomas Schroeder, Dr. Florian Schott, Dr. Dirk Reichert and Mr. Steffen Wagloehner at the Institute for Technical Chemistry and Polymer Chemistry, University of Karlsruhe (TH), Germany for their invaluable support and help during this research.

I am grateful to International Seminar, University of Karlsruhe, Germany and German Academic Exchange Service (DAAD) for providing necessary facilities, financial support and guidance. I thank my family for their encouragement and forbearance.

Finally my mother deserves special mention for her unconditional support and prayer. Words fail me to express my appreciation for her life-long love.

Naveed Jan, 2011

ABSTRACT

The wish of all concerned with air pollution is to have a completely unpolluted environment at no cost to anyone. That appears to be impossible, so our logical goal is to have an appropriately clean environment, obtained at an appropriate cost. The main objective of this research was to control the most annoying air pollutant (soot), emitting from fossil fuel combustion sources, through catalysis. To meet the future soot and other pollutants regulations it is necessary to develop such catalyst systems with the help of which an efficient removal of soot will be possible.

In the present work an environmentally friendly; noble metal free oxidation catalyst Fe_2O_3 was search out. For the catalytic soot oxidation first Fe_2O_3 was characterized by surface area measurement, scanning electron microscopy, and powder X-ray diffraction analysis. The synthesized catalyst was tested for the diesel model exhaust gas using temperature programmed oxidation technique. In this research a particular emphasis was given to the catalytic oxidation of soot on iron oxide.

The diesel model soot was prepared by burning a lean $\text{C}_3\text{H}_6/\text{O}_2$ mixture in a diffusion flame and is subsequently collected with a sinter metal filter. The propene soot as well as other carbon samples (graphite, printex, and activated charcoal) were characterized by surface area measurement, scanning electron microscopy, Fourier transform infrared spectroscopy, temperature programmed desorption, thermogravimetry, and powder X-ray diffraction analysis.

The investigation was carried out by using temperature programmed oxidation. The TPO performance in the presence of Fe_2O_3 with 6, 12, 18, and 20 vol.-% O_2 leads to a stronger increase in soot oxidation, than the absence of catalyst.

FTIR spectroscopy was used for the identification of different surface groups on the soot surface. Different types of surface groups were identified including carbonyl, lactone, aldehyde, carboxylic, ether, etc.

Thermo-gravimetric technique was used for the comparison of TPO results from gas flow reactor as well as for the kinetics of soot oxidation. Five different carbon materials (propene soot, printex l, printex u, graphite, and activated charcoal) were used along this thesis. The kinetic of each source were first investigated in TGA

device. The propene soot which was produced in laboratory exhibits the closest structure and composition to the diesel soot. But all soot sources were found to have reasonably similar composition, structure, and thermal behaviour to diesel soot.

XRD and SEM analysis were confirmed the rhombohedrally centred hexagonal structure of hematite (Fe_2O_3).

CHAPTER – 1

INTRODUCTION

1.1. General

Combustion of fossil sources of energy in industry, automobiles and households increase the load of air pollutants on the environment as ever. Huge amounts of pollutants are emitted daily with the effluents evolving from these processes producing solid, liquid and gaseous wastes. Especially, the current environmental pollution produced by diesel exhaust gas is a serious problem, and the situation is getting even worse.

Since the invention of the diesel engine in 1893 its application has become very widely spread over the world. The main reasons for its popularity are the following.

- the combustion efficiency loss is reduced (higher fuel economy).
- the amount of expansion stroke extracted is greater due to the high compression ratio and the operation with the lean-fuel mixtures.
- the pumping work at the partial load is essentially estimated,
low maintenance requirements,
- high durability

The diesel engines are inherently cleaner than the petrol engines and the exhaust temperature is relatively much lower. Due to the high efficiency of diesel engines, the sale of diesel automobiles has been increased significantly since mid 90's (dieselnet.com, 2009). In western Europe, the percentage of diesel passenger cars increased from 14% in 1990 to 32% in 2000 and further to 46% in 2004 (Panorama., 2005). Although diesel fuel is beneficial to reduction of petrol consumption through the higher fuel efficiency, but it contributes to another environmental problem, the diesel soot and nitrogen oxides. The genotoxic effect of diesel exhaust gases or of specific compounds occurring therein, a distinction can be made between *in vitro* and *in vivo* types. *In vitro* studies subject bacteria (the Ames-test) or the mammals or the

extract of the diesel particulates and *in vivo* studies expose live animals (rats, mice, and hamsters) to the diesel exhaust gases.

Winter smog is formed during episodes of quite and cold weather, due to increased burning of fossil fuels for heating or power supply purposes, combined with slow discharge of pollutants in the stagnant atmosphere. Large concentration of particulates and SO_x occur, which cause all kind of respiratory problems, notably to the people with decreased resistance. In a limited number of extreme winter smog episodes, mortality increased statistically.

Diesel soot is hazardous to human health due to its potential mutagenic and carcinogenic activity. Because of the small size of its particles, it can penetrate into the lungs (Oberdoerster., 2004). In addition to a possible effect on the lung cancer, diesel particulates are also suspected of increasing bladder cancer.

Besides having adverse effects on human and animal health, diesel exhaust gases have other undesired properties. Diesel particulate contribute significantly to the soiling of buildings, as the 'blackness' (light absorption properties) of the diesel particulates, which, in environmental studies are often denoted as 'black smoke' is much higher than the blackness of the other fine particles.

In the early seventies, automotive exhaust emission regulations were introduced in both Europe and USA. These first standards applied to the light duty vehicles, a general term for the passenger cars. These standards, expressed in grams of the regulated compound per mile were so lenient that passenger cars can easily fulfil them.

Government legislations for the permissible diesel exhaust emission levels are being tightened because this emission is being linked to the number of respiratory problems. The parliament of the European Union has issued stricter emission standards for diesel engines of heavy duty commercial vehicles.

The use of alternatives for gasoline and diesel fuel has been extensively studied. Motives are multiple, and include the surplus agricultural area of Europe, a recycle of carbon in an attempt to diminish the emission of greenhouse gas CO₂ and a decrease of emission of legislated compounds. Diesel engines can run on the large variety of fuels. Attention has been paid in particular to 'normal' diesel fuels with a modified

composition to 'bio fuels' (vegetable oil and ethanol) and to compressed natural gas (CNG) and methanol. Alternative fuels can be used as pure or mixed with normal diesel fuel.

Many mechanistic models for describing speciation and soot formation in flames are available (Frenklach., 1996). Acetylene and polyaromatic hydrocarbon (PAHs) appear to supply the bulk of the carbon later incorporated into the soot spherules. (Krestinin et al., 2000) postulates that polyynes ($C_{2n}H_2$, $n = 2, 3 \dots$) are the major precursor radicals, partly because their stability increases with temperature. With solid fuels, e.g. coal, soot is formed by the pyrolysis of tarry materials ejected by particles undergoing devolatilisation. The droplets hydrogenate and/or partially oxidise into chains of soot spherules. Most are burned before exiting the flame region, but a significant residual can be found in the flyash of low NO_x burners (Veranth et al., 2000).

Soot from various sources, i.e. from different fuels and combustion conditions tend to be similar in size and composition, which indicates that the same formation processes and growth constraints apply. This has encouraged researchers to produce soot for study in simple laboratory combustors (Lahaye et al., 1996) or to use commercial carbon black as a surrogate (Marcucilli et al., 1994; Neeft et al., 1997).

One of the options to remove soot from the diesel exhaust gases is the use of a filter in combination with catalysts to increase the oxidation activity of the collected soot. Soot can then be oxidized at lower temperature. Soot oxidation catalyst can be applied in three different ways: (i) as a precursor compound, soluble in diesel fuel, (ii) as catalytic compound which are injected upstream of the particulate loaded filter, and (iii) as a catalytic coating on the filter itself. Because of logistic and possible environmental problems related to the first two options, the last option of the catalytic coating is the most desirable way to apply a catalyst for the soot oxidation.

According to the Euro 4 standard, which became effective in October 2005, emission of the particulate matter (PM) from the diesel trucks have to be reduced by 80% compared to Euro 3. Several technical solutions to reduce exhaust gas emission have been suggested. One of the leading technologies involves the use of particulate

traps (Van Satten et al., 2001). The particulate matter is defined by the US Environmental Protection Agency (EPA) as all compounds collected on a preconditioned filter in dilute diesel exhaust gases at a maximum temperature of 52 °C. The wall-flow diesel particulate filter (DPF) attains filtration efficiencies over 90% (for solid matter) under normal operating conditions (Kabin et al., 2004). Though particulate traps show high filtration efficiency, there is need of filter regeneration to prevent filter plugging and back pressure increase. The development of filter with catalyst coverage that combine retention and oxidation of the emitted particulate matter has drawn wide attention (Genc et al., 2005; Fino et al., 2006). Most of the oxidation catalysts used in the international markets are noble metal based (Pt, Pd), which are expensive and due to a low abundance vulnerable to further price increase upon demand. Therefore the search for catalyst, free of noble metals, is of global importance. For the elimination of diesel soot so-called diesel particulate filters (DPFs) are taken into consideration. These technologies are described in detail in a review from Twigg., 2007 and summarized in our publication (Balle et al., 2006).

The most important application of catalytic materials is directly oxidizing the soluble organic fraction (SOF) of the diesel exhaust emissions. In-cylinder diesel particulate matter (PM) control has greatly reduced the PM emission levels in the modern engines. Progress has been especially effective in reducing the soot portion of PM emissions, so the SOF of particulate matter now accounts for a much larger share. Oxidation catalyst can oxidised the large portion of the hydrocarbons present in the soluble organic fraction of PM emissions, as well as gaseous hydrocarbons, carbon monoxide, and odour (Neri et al., 1997).

It has been widely accepted that surface oxygen complexes on carbon act as intermediates during carbon gasification. In case of oxygen gasification, oxygen molecules first dissociatively chemisorbs on carbon active sites to form surface oxygen complexes. Then the complexes decompose as CO₂ and/or CO.

Although the temperature programmed desorption (TPD) technique, which has often used for the characterization of surface complexes, makes it possible to determine the concentration and the thermal stability of the complexes, this technique does not allow the exact identification of the chemical form of the complexes.

Significant efforts have been made to detect the complexes directly with spectroscopic instruments. It has been well known that FTIR spectroscopy is a powerful technique for identifying oxygen functional groups on carbon surfaces (Cerfontain et al., 1986; Zawadzki et al., 1989; Meldrum., 1990).

The pollutants like HC and CO can be converted in the oxygen rich diesel exhaust by using Pt or Pd oxidation catalysts (Zelenka et al., 1996). The mechanism and kinetics of the catalytic oxidation of HC and CO on Pt have been investigated in depth by several groups (Chatterjee et al., 2001; Zerkel et al., 2000; Campell et al., 1980).

1.2. Aims and Objectives

Presently most continuous regenerating systems are based on catalysts, which consist of noble metals (Pt, Pd) or their mixtures with different base metals. These systems are not only expensive but also difficult to apply in the region with high fuel sulphur content. Introduction of a diesel oxidation catalyst technology free of noble metals or with low noble metal content gives additional advantages with respect to cost reduction and system stability. Although significant research has been accomplished internationally to develop noble metal free diesel oxidation catalyst, the results are not satisfactory mainly due to increasing stringent emission legislature.

The first objective of the present work is to clarify the chemical form of the surface oxygen complexes on the soot and to investigate how these surface oxygen complexes detected with FTIR spectroscopy, and then to relate these results from FTIR to the complexes desorbed in TPD.

The second objective of this work is to develop a technology, which allows the efficient search of new catalysts formulations to lower diesel soot oxidation temperature. For this purpose we need such a catalyst, which possess the following characteristics:

- i. It must show low temperature activity, ($T \sim 250\text{ }^{\circ}\text{C}$)
- ii. It must be non-toxic,
- iii. It must be cheap,

- iv. It must be environmentally friendly,
- v. The catalyst must be thermally stable, ($T \sim 1000\text{ }^{\circ}\text{C}$)

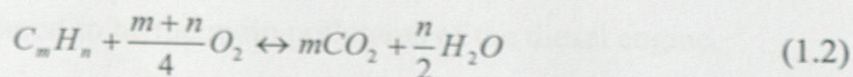
Iron (III) oxide (hematite) is not only a strategic industrial material, but also one of the most used metal oxides with various applications in scientific and industrial fields. Hematite is one of the most frequently used catalysts in chemical industry (Mimura et al., 1998; Chang et al., 1997).

As it is known from the literature that Fe_2O_3 is thermally stable up to $1200\text{ }^{\circ}\text{C}$ (Willey., 1988) and is very good catalyst for soluble organic fraction (SOF) oxidation (Neri et al., 1997); Fe_2O_3 is not toxic and has been used as catalytic component. In the presence of Fe_2O_3 catalyst the soot ignition temperature decreases drastically, while soot is mainly oxidized into CO_2 . Without catalyst, CO is the major product of soot oxidation. A number of reactions can take place, when soot is oxidized catalytically by Fe_2O_3 . Catalytic oxidation of carbon (soot) to the carbon dioxide is the main reaction, in which Fe_2O_3 , or more specifically surface of Fe_2O_3 act as catalyst.



1.3. Theoretical Background

The industrialization of the world is accompanied by a drastic increase in consumption of fossil fuels. The energy stored in fossil fuels is freed mostly by flame combustion, which is the reaction between the carbon containing constituents of the fossil fuel and the oxygen of the air, according to the reaction



Carbon dioxide and water are the main products of this reaction. However, incomplete combustion causes some emissions of unburned hydrocarbons, as well as intermediate oxidation products such as alcohols, aldehydes and carbon monoxide. Thermal cracking reactions takes place in flame results in the formation of hydrogen as well as hydrocarbons that are different from the ones present in fuels itself.

1.3.1. Diesel Engine Emissions:

Diesel engines emission composition varies considerably depending on the fuel, lubricating oil, engine type, and the driving conditions (Kahandawala et al., 2004; Zhu et al., 2005; Tosaka et al., 2000). Diesel emissions are the mixture of gases, vapours, liquid aerosols and substances made of particles. The typical diesel engine exhaust gas consist of carbon (soot), CO, CO₂, NO, N₂O, NO₂, NH₃, SO₂, aliphatic hydrocarbons, polynuclear aromatic hydrocarbons, organic acids, and halogenatic organic compounds.

Components	Concentration	Components	Concentration
CO	100-10000 ppm	Aldehydes	0 mg/mile
HC	50-500 ppm C1	Ammonia	2 mg/mile
NO _x	30-1000 ppm	Cyanide	1 mg/mile
SO _x	Proportional to fuel S content	Benzene	6 mg/mile
PM	200-200 mg/m3	Toluene	2 mg/mile
CO ₂	2-12 vol. %	PAH	0.3 mg/mile

The composition of the diesel particulate matter depends on where and how they are collected. In the tailpipe, where the temperature is high, most of the volatile materials are in the gaseous phase. As the exhaust gas cools down and is diluted by ambient air, nucleation, condensation, and adsorption transform the volatile materials to solid and liquid particulate matter (Kittelson., 1998). Particulate matter and NO_x are considered to be the main pollutants of the diesel engine.

1.3.2. Diesel Engine Emissions Legislature:

Diesel emission of PM and NO_x is currently discussed with regards to human health and the environment. The EU commission and the Environmental Protection Agency (EPA) in the United States are highlighting the fine particulate as one of the current priorities for the environmental hygiene in the Europe and the United States respectively. The international community has acknowledged this problem and imposed limits on diesel emission. Progressively, the emission standards are becoming

more and more stringent. European legislation on exhaust emissions has made major progress since its initiation in 1992.

Table 1.1 EU emission standards for diesel passenger cars (g km⁻¹)

	Date	CO	HC+NO _x	NO _x	PM
Euro 1	07/1992	2.72	0.97	-	0.14
Euro 2	01/1996	1.00	0.90	-	0.10
Euro 3	01/2000	0.64	0.56	0.50	0.05
Euro 4	01/2005	0.50	0.30	0.25	0.025
Euro 5	09/2009	0.50	0.23	0.18	0.005
Euro 6	09/2009	0.50	0.17	0.08	0.005

The US Environmental Protection Agency has imposed a tiered system for emissions reduction through 2010. Under the tiered 2 emissions which were finalized in 1999 and to be phased in between 2004 and 2009, the same emission standards apply to all vehicle weight categories when tested on the Federal Test Procedure 75 driving cycle and emissions are measured in g/mile (FTP) (Johnson et al., 1994). There is growing call to standardize the test cycle worldwide.

1.3.3. Diesel Emission Treatment Technologies:

Diesel engines generate fewer greenhouse gas emissions but emit larger amounts of PM and NO_x compared to their gasoline counterparts. During the combustion of diesel fuel, fuel is injected into pre-compressed air forming droplets surrounded by oxygen deficiency, which results in incomplete combustion and thus leads to the solid soot formation. The catalytic after treatment techniques that aims at the combustion of pre-formed PM in the exhaust stream rather than avoiding the formation of PM is the most promising technology. Wall flow ceramic monoliths are the most common type of diesel filter substrate. Many silicon carbide filters are typically extruded in smaller segments and cemented together to form the appropriate filter (Masoudi., 2005).

The diesel oxidation catalyst is an effective device to control CO, HC, poly-aromatic hydrocarbon (PAH), hydrocarbon derivatives, such as aldehydes, and a large part of the constituents of the soluble organic fraction (SOF) of the diesel particulate.

1.3.4. Oxidation Catalysts:

The use of catalyst in soot removal from the particulate traps is logical choice. Catalysts for the oxidation of the carbonaceous materials, e.g. graphite, activated carbon, and coal have been studied for a long time. Catalytic oxidation of soot is in many ways are analogous to these oxidation reactions, in which many catalysts have appeared to be active. The catalytic soot oxidation is thought to be more reactive than graphite and other carbon samples. This could be caused by a less pronounced ordering of crystallites (clustered of stacked layers of graphite basal planes) and a higher impurity concentration resulting in a larger active surface area and in higher reaction rates.

The pursuit of a technique for diesel soot control has prompted a research into the application of catalysts to lower ignition temperatures and so promote combustion (Querini et al., 1999; Neri et al., 2003; Oi-Uchisawa et al., 2003; Kim et al., 2003; Galdeano et al., 2004; Badini et al., 1998; Van Satten et al., 2000; Kureti et al., 2003; Leocadio et al., 2004; Neeft et al., 1996; Setiabudi et al., 2003). Most of the oxidation catalysts used in the international markets is noble metals based which are expensive and due to a low abundance vulnerable to further price increases upon increasing demand (Twigg., 2005). Moreover, precious metals catalyze the formation of sulphate and sulphuric acid. EU, USA and Japan have decided to reduce the sulphur content of diesel fuel. Low sulphur will prevent the deactivation of the catalyst by poisoning from sulphur oxides. (Neeft et al., 1997; Neeft et al., 1998) studied the influence of the catalyst-soot contact on the catalytic activity. Most research groups used model soot (Printex U), a commercially available carbon black which is said to possess almost identical properties as real diesel soot (Tosaka et al., 2000). The continuously generating trap (CRT) was commercialized by Johnson Matthey for trucks and buses. It comprises an oxidation catalyst (Pt) followed by a wall flow monolith (jmcatalysts.com., 2009). The so-called Catalysed Continuously Regenerating Trap

(CCRT) are used in the selected heavy duty diesel application where the duty cycle does not always provide sufficient temperature for the proper function of the CRT (Allansson et al., 2004) while this system functions well in the Europe where ultra low sulphur diesel fuel is widespread, the system may fail in the countries with high sulphur fuel.

The variation in the oxygen concentration can affect the reaction rate. The reaction order in the oxygen concentration was found to vary between 0 and 1 in various studies and the reaction rate is generally taken as sole function of oxygen partial pressure (Khan et al., 1971; Otto et al., 1980; Miyamoto et al., 1990).

1.3.5. Mechanism of Catalytic Soot Oxidation:

The mechanism of soot oxidation is not completely understood. Catalysed reaction mechanism is relatively different from the uncatalysed condition- as the order of reaction, the activation energy and the primary products are changed substantially. The mechanistic nature of the oxidation of soot particulate may involve either of the pathway e.g. activation of carbon atoms within the particulate and/or the catalyst acting as a source of activation of carbon atoms within the particulate or the catalyst acting as a source of activated oxygen which can be regenerated. Two oxidation mechanisms are proposed to occur in the catalyzed carbon oxidation: a redox mechanism and a spill over mechanism. According to van Satten et al., 2000, Amariglio and Duval were the first to suggest that the only metals which can oscillate between two oxidation states can catalyze the oxidation of the graphite sheet. The oxides of metals which readily change valency have been identified by Setzer et al., 1993; as superior catalysts. Cu, Fe, and Co were found to be more active than Ni and Zn. Neeft et al., 1996; found that the oxides of Co_3O_4 , V_2O_5 , Fe_2O_3 , La_2O_3 , MnO_2 and NiO , exhibit high to moderate activities in tight contact but hardly any activity in loose contact. Other oxides such as PbO , Cr_2O_3 , MoO_3 , CuO , and Ag_2O are still active in loose contact. Neri et al., 2003; found that Fe_2O_3 was a good catalyst for soluble organic fraction (SOF) oxidation but that CuO and V_2O_5 were found better for the carbon component. (Querini et al., 1999; Querini et al., 2000) reported that for tight contact, metal oxide catalysts burned soot at lower temperature. Some catalysts can

oxidise graphite without being in contact. Baumgarten et al., 1988; observed increased rate of coke oxidation while there was no direct contact between the catalyst and coke. The catalyst catalyzes the formation of a mobile compound (O_{ads}) which migrates to the coke where it reacts to form CO_2 and/or CO . This mechanism is known as the spillover mechanism, which was proposed by Cooper et al., 1989.

According to Mul et al., 1998; both the spillover and redox mechanism can occur spontaneously. The dominating mechanism depends on the physical contact between the catalyst and soot.

In the case of iron contact with soot relatively very little is known. Mul et al., 1998, found no sign of Fe-OC interaction by using infrared spectroscopy.

1.3.6. Formation, Composition, Structure, & Reaction Scheme of the Soot:

Soot formation occurs in the high temperature, fuel rich reaction zone around the individual fuel droplets, where fuel hydrocarbons are oxidized under substoichiometric oxygen conditions. In this reaction zone the reaction is limited by the oxygen concentration. Oxygen transport occurs by diffusion through the flame front, therefore, this type of reaction zone is called a 'diffusion flame'. Another flame type which occurs in the processes of combustion is the 'premixed flame' the combustion of a premixed amount of fuel and air. Temperatures are higher in premixed flame than the diffusion flame. As studies on the soot formation in the diesel engine cylinders pose practical problems, many studies have been performed under model conditions. Diffusion flames in burners are often studied. Soot formation process in burner, diffusion flames do not fundamentally differ from those in the diesel engine.

The formation of soot is thought to take place via a number of elemental steps: pyrolysis, nucleation, surface growth and coagulation, aggregation, and oxidation. These processes take place on different time scales, ranging from a few microseconds (initial nucleation processes), to some milliseconds (completion of soot formation, oxidation and cooling by cylinder expansion).

Diesel particulates, which are often erroneously referred to as diesel soot, are composed of a number of different constituents. In the combustion chamber the so-called primary soot particles are formed as a result of nucleation and growth. The

specific composition of the diesel soot determines its reactivity in the oxidation reactions. Therefore this composition is one of the starting points considering option to increase the oxidation reactivity of soot.

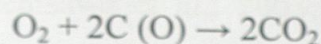
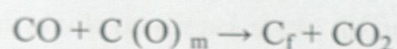
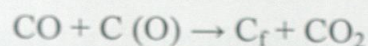
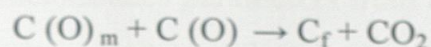
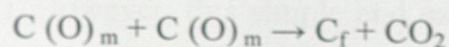
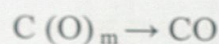
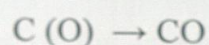
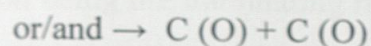
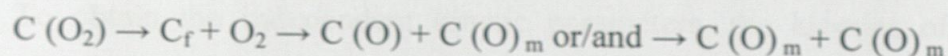
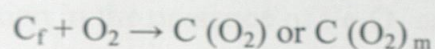
Donnet., 1993; has been discussed the nature of soot. The fundamental unit of the soot agglomerates are the spherules with diameters of 10-50 nm (Walker et al., 1966). As the name implies, most of these particles are almost spherical, but a number of less regular shapes may be found. The surface of the spherules has adhering hydrocarbon material or soluble organic fraction (SOF) and the inorganic material. Ahlostrom et al., 1989 found that on heating diesel soot at a rate of 10 K/min, hydrocarbons were lost in the range of 150-400 °C, with a pronounced peak at 200 °C. Courcot et al., 1997; tested highly impregnated soot and found three distinct hydrocarbon peaks. The spherules are joined together by shared carbon deposition to form loose particles of 0.1-1 µm size. The nitrogen BET area of soot was found to be only 40% of the external surface area calculated for the spherules whose diameter was measured by electron microscopy (Neoh et al., 1984). Though the porosity of these particles may be of the order of 0.95, they cannot be broken down into the individual spherules, even by strong ultrasound treatment (Marcucilli et al., 1994). Viewing of the spherules by electron microscopy reveals laminations with surface steps, which are produced by numerous crystallites in concentric orientation (Donnet., 1993).

A good introduction to carbon oxidation was provided by Marsh et al., 1989. Moulijn et al., 1995; they argue that at gasification temperatures the carbon surface will be relatively simple. They identify three types of carbon-oxygen complex of increasing stability: carboxyl, semiquinone and pyrone groups. Only a fraction of the oxygen-containing complexes take part in the gasification reactions (Kapteijn et al., 1994).

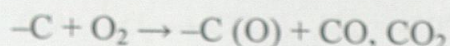
Ahmad et al., 1987; examined thin films of the pyrolytic carbon deposited from a sub-stoichiometric methane flame. From the temperature programmed desorption (TPD) they identified two types of adsorbed oxygen complex, and propose different sites for CO and CO₂ release.

Du et al., 1990; Du et al., 1991; examined the adsorption/oxidation steps of oxygen with a soot produced in a laboratory premixed ethylene flame. This method of preparation ensured that no metal was included. The mean spherules size was 43 nm. By TPD they identified a critical activation energy for desorption, below which the oxygen complex is rapidly desorbed and above which is persistent. This critical value varies exponentially with temperature but only slightly with time.

The reaction scheme proposed by Marsh et al., 1989; involve free carbon sites C_f , chemisorbed localised molecular oxygen $C(O_2)$, chemisorbed mobile molecular oxygen $C(O_2)_m$, chemisorbed localised atoms of oxygen $C(O)$ and chemisorbed mobile atoms of oxygen $C(O)_m$:



De Soete., 1988; found that the oxygen adsorbates occupied only a small fraction (<5%) of the surface sites. This result was confirmed by Ma et al., 1996 for the spherocarb oxidation at low temperatures. They conclude that the carbon surface displays heterogeneity with regards to adsorption processes. The adsorption step results in the release of a molecule of CO or CO_2 for the every molecule of O_2 adsorbed:

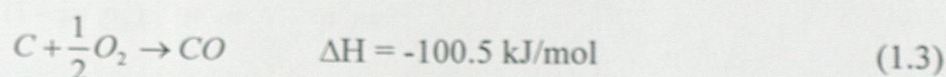


1.3.7. Kinetic Studies

The kinetics of soot oxidation is widely discussed by global approaches, i.e. potential rate laws (Neeft et al., 1997; Jacquot et al., 2002; Stanmore et al., 2001). Numerous studies on nanosized Au catalysts useful for CO oxidation have been published (Bandyopadhyay et al., 2006), which demonstrate that these materials have insufficient thermal stability for the practical application. In addition, some iron-containing oxides also have been reported to be effective in CO oxidation, either as catalyst e.g. LaFeO₃ (Voorhoeve et al., 1976), Fe₂O₃/Cr₂O₃/Al₂O₃ (Fagel et al., 2001), Fe₂O₃/SiO₂ (Randall et al., 1997), or as a support e.g. Au/Fe₂O₃ (Kahlich et al., 1999), Pd/Fe₂O₃ (Schalow et al., 2006). However, very little work has been done on the CO oxidation in the presence of Fe₂O₃ catalyst.

To obtain the independent kinetic parameters, the kinetics of the soot/ O₂ reaction being the dominating reaction in the catalytic as well as non-catalytic soot/ O₂ conversion is examined separately. Thermobalances are widely used for the kinetic studies of the combustion of solids. The good control of temperature and the high sensitivity for measuring the materials weight loss justify thermogravimetric analysis (TGA). However, this simple and useful technique necessitates precautions. Methods to extract kinetics parameters from thermograms obtained during the heating up of the sample are available (Sestek et al., 1971; Satava., 1973). When determining kinetics constants for the combustion of very porous materials with large surface areas, such as carbon black or diesel soot, diffusion of oxygen has been shown to control oxidation (Oi-Uchisawa et al., 2003; Gilot et al., 1993). In some TGA situations, diffusion limitations can be overcome or ameliorated experimentally (Allen et al., 1990; Lisa et al., 1992).

The rate of oxidation is limited by the kinetics, with a slower soot oxidation rate at lower temperatures (Goldenberg et al., 1983).



The soot is oxidized at temperatures of about 600 °C quickly and completely. The thermal oxidation of carbon by oxygen has been widely studied whereas the reaction mechanism was proposed by Moulijn research group (Moulijn et al., 1995; Neeft et al., 1997).

1.4. Characterization Techniques

The synthesised catalysts/soot particles are routinely characterized by several conventional techniques to determine their composition, structure and texture, these include X-ray diffraction (XRD), specific surface area measurement, electron microscopy, thermogrammatry, temperature programmed oxidation (TPO) and temperature programmed desorption (TPD) study. Spectroscopic technique like FTIR has also been proved to be highly valuable in the characterization of the interaction between soot and the catalyst surface.

1.4.1. Specific Surface Area Measurement (BET Method)

To measure BET surface area it is necessary to derive the monolayer capacity n_m^a , defined as the amount of adsorbate required to form a complete monolayer on the surface of unit mass of the adsorbent. The specific surface area a_s (BET) is then obtained from n_m^a by taking a value for the average area a_m , occupied by the adsorbate molecule (i.e. the molecular cross-sectional area) in the filled monolayer. Thus

$$a_s \text{ (BET)} = n_m^a \cdot L \cdot a_m \quad (1.5)$$

where L is the Avogadro constant.

By making certain assumptions, Brunauer, Emmett and Teller (Brunauer et al., 1938), were able to simplify the summation of the amounts adsorbed in all layers and arrive at their first and most useful form of (equation 1.5),

$$\frac{p/p_0}{n^a(1-p/p_0)} = \frac{1}{n_m^a} + \frac{(c-1)p/p_0}{n_m^a c} \quad (1.6)$$

where c is constant. It is evident that the BET equation requires a linear relation between $p/n^a(p_0-p)$ and p/p_0 – or between $p/p/[n^a(1-p/p_0)]$ and p/p_0 . According to (eq.

1.5), the values of n_m^a and c can be obtained from the slope and intercept of the linear BET plot.

Nitrogen (at 77K) is generally considered to be the most suitable adsorbate for the determination of the surface area of nonporous, macroporous, or mesoporous solids. It is usually assumed that the BET nitrogen monolayer is close-packed, giving $a_m(N_2) = 0.162 \text{ nm}^2$ at 77 K.

1.4.2 Fourier transforms infrared (FTIR) spectroscopy

Infrared spectrometers can be divided into three categories: dispersive, multiplex, and non-dispersive. Dispersive instruments use gratings or prisms to achieve wavelength selection and is typically used for qualitative work. Multiplex instruments, or Fourier Transfer Infrared (FTIR) Spectrometers, use a Michelson interferometer to modulate the intensity of the infrared radiation as a function of frequency, and then employ Fourier transform to convert the resulting time dependent spectrum into a standard wavenumber spectrum. FTIR spectroscopy can be used for both qualitative and quantitative work.

It has been well-known that FTIR spectroscopy is a powerful technique for identifying oxygen functional groups on carbon surfaces [88-98]. However FTIR measurement of highly carbonized material has met with difficulty in obtaining a spectrum of good quality, because of the low concentration of surface complexes and the high adsorption co-efficient of carbon (Morterra et al., 1985; Morterra et al., 1985; Morterra et al., 1985; Politou et al., 1990; Flanning et al., 1993).

In the present study spectra were recorded on an ATI Mattson (USA) Galaxy 5020 FTIR spectrometer equipped with a MCT detector. The IR cell made of stainless steel contains a ZnSe window and was connected to a gas-handling system. The spectra were recorded in the range from 800 to 2000 cm^{-1} with an instrument resolution of 4 cm^{-1} . 2000 scans are accumulated to a spectrum resulting in a time resolution of 5 min. The temperature was monitored by a K type thermocouple placed 5 mm underneath the sample surface. The control computer is operated with the software winfirst (year 1994).

1.4.3. Powder X-Ray Diffraction (PXRD)

PXRD is the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).

The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d_{hkl} spacing in the crystal lattice as given in Bragg's equation

$$\lambda = 2 \cdot d_{hkl} \cdot \sin\theta \quad (1.7)$$

The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure. X-ray diffraction crystallites thickness is reported as 1.2 nm by Heywood et al., 1990; and 1.4 nm by Ishiguro et al., 1991.

PXRD patterns were recorded at room temperature on a Siemens D 501 (Germany) employing Ni filtered $\text{CuK}\alpha$ ($\lambda = 0.1543$ nm) radiation operated at 40 kV and 30 mA. A 2θ step size of 0.02° was used with an integration time of 1 s. The samples were measured using a rotation velocity of 120 rpm.

1.4.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is employed for the surface morphology of the catalyst & soot (Courcot et al., 1997; Neoh et al., 1984; Imanari et al., 1981). SEM permits qualitative characterization of the catalyst surface and helps to interpret the phenomena occurring during calcinations and pre-treatment. The most important advantage of electron microscopy is that the effectiveness of preparation method can directly be observed by looking to the metal particles. From SEM the particle size distribution can be obtained. This technique also reveals whether the particles are

evenly distributed or packed up in large aggregates. If the particles are sufficiently large, their shape can be distinguished and their crystal structure is then determined (Imanari et al., 1981).

SEM was performed using JEOL JSM-5910 electron microscope operated at 20 kV with a tungsten filament at the electron source. Energy-dispersive analysis of the emitted X-ray (EDX) was performed, in combination with SEM, using Energy-dispersive X-ray spectrometer Oxford INCA200.

1.4.5. Thermo-gravimetry (TG)

Thermo-analytical techniques are commonly used in research laboratories. Examples of the each technique are thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermo-analytical (TA) techniques have certain advantages and disadvantages in the comparison with the more traditional flow-reactor techniques which are also widely employed. An important advantage of TA techniques is their convenience, as small sample sizes can be used and the analysis is rather fast compare to the flow reactor experiments. The main disadvantage of the TA techniques is that the sample is enclosed in a small crucible. As a result, the gas feed flow around the sample, instead of through the sample as is the case in most flow reactor samples.

Thermo-gravimetry (also known by the acronym "TG"; alternative spellings include thermo-gravimetry and thermo-gravimmetry) is a branch of physical chemistry, materials research, and thermal analysis. It is based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time, and additionally of pressure and gas composition.

Thermo-gravimetry (TG) is a technique for measuring the change in weight of a sample as a function of temperature, whilst the sample is subjected to a controlled temperature programme. Tikhomirov et al., 2006; used a TGA device to study the oxidation of soot by different mixed oxides. A comparison of the effect on the soot oxidation by different nanostructure spined-type oxides was given by Fino et al., 2006. Gilot and co-workers (Gilot et al., 1993; Stanmore et al., 1994; Stanmore et al., 1995; Gilot et al., 1995) studied the interaction between kinetics and mass transfer.

According to them the active layer being less than 1 mm in thickness and the reported rates which do not take account of these effects may be too low.

TG was performed using THERMOWAAGE STA-409, NETZSCH Thermisch Analyse (Germany).

1.4.6. Temperature-Programmed Techniques

In the fields of adsorption and heterogeneous catalysis involving gas-solid interactions and surface reactivities, the techniques of temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) have been developed, which typically involve monitoring surface (or bulk) processes between the solid catalyst and its gaseous environment via continuous analysis of the gas phase composition as the temperature is raised.

1.4.6.1 Temperature-Programmed Oxidation (TPO)

Detailed investigations of carbon oxidation show that molecular O_2 and the O and OH radicals all participate in the soot oxidation (Cavaliere et al., 1994). OH is particularly effective (Lee et al., 1962; Ruth et al., 1998). Roth et al., 1998; showed that hydrogen peroxide has assist soot oxidation at low temperature, due the presence of high concentrations of OH radicals. Setiabudi et al., 2004; noted that each soot sample was completely oxidised during the TPO in O_2 ; for idle and full load the combustion is completed at 800 K, while for Printex-U complete combustion was achieved at 900 K. Printex-U, the flame soot, has been chosen as a soot model, since this model soot has been used to substitute diesel soot in soot- O_2 reaction researches for more than a decade (Jelles et al., 1999). Le Minh et al., 1997; reported on an investigation into CO and CO_2 evolution during TPO of coke deposited on cracking catalysts. Various groups measured coke weight loss during TPO to determine oxidation kinetic parameters, information on coke location, and carbon type on various catalysts (Che et al., 1989; Pieck et al., 1989; Galuszka et al., 1992; Gayubo et al., 1994; Farnandes et al., 1995; Bond et al., 1995).

1.4.6.2. Temperature-Programmed Desorption (TPD)

Temperature programmed desorption (TPD) is the method of observing desorbed molecules from a surface when the surface temperature is increased. Many researchers prefer the name TPD instead of thermal desorption spectroscopy (TDS) because it is not a spectroscopic method. When molecules come in contact with a surface, they adsorb onto it, minimizing their energy by forming a chemical bond with the surface. The binding energy varies with the combination of the adsorbate and surface. If the surface is heated, at one point, the energy transferred to the adsorbed species will cause it to desorb. The temperature at which this happens is known as the desorption temperature. Thus TDS shows information on the binding energy.

Temperature-programmed desorption (TPD) of adsorbed gas from catalysts has become a very common technique for catalyst characterization (Schloten et al., 1985; Menon et al., 1987; Falconer et al., 1983). The information collected from TPD studies are;

- i. The type and amount of the different forms of adsorbed species
- ii. The bond energies between adsorbate and surface, and possibly
- iii. The type of bonding of the adsorbed species on the catalyst surface (Schloten et al., 1985).

However, the determination of the amount of chemisorbed gas is not always very accurate because of various experimental considerations (diffusion, readsorption).

Temperature-programmed desorption of simple bases is a widely used method to assess the total number and strength of acid sites (Sharma et al., 1993; Karge., 1990; Hashinguchi., 1989).

Falconer et al., 1983; have reviewed the applications of temperature-programmed desorption. In a typical TPD experiment, soot or catalyst is contained in a reactor that can be heated at a linear rate. After pre-treatment, the soot or catalyst is saturated with a probe molecule under well defined adsorption conditions. After the excess gas is flushed out of the reactor, the sample is heated in a flowing inert gas stream. A thermocouple inserted in the catalyst measures the temperature and a

detector downstream measures the effluent gas composition. The concentration of the desorbing gas in the effluent gas may be monitored by absorption/titration, thermal conductivity, flame ionization, or mass spectrometry. The desorption rate of the adsorbed gas increases, goes through a maximum, and drops back to zero as the surface is depleted of adsorbate.

The experiment permits the determination of the total amount of gas or vapour that was adsorbed, and of the kinetic parameters of the desorption process, particularly of its activation energy (Falconer et al., 1983; Cvetanovic et al., 1972). Inert gas flow rate, soot or catalyst particle size, soot or catalyst pore size, and soot or catalyst bed depth affect the TPD spectra.

1.5 Analytical Technique

1.5.1 Non-Dispersive Infrared (NDIR) Spectroscopy

Non-dispersive instruments have a much simpler design than both dispersive and multiplex instruments. Non-dispersive instruments have been used for quantitative determination of a variety of gaseous species in the atmosphere by adsorption, emission and reflectance spectroscopy (Simpson., 2004; Skoog et al., 1998; De Castro et al., 1999).

For the quantitative measurement of the CO, and CO₂ concentrations, NDIR spectroscopy is used. With this analysis method the entire IR wavelength spectrum is not used. This technique is based on resonance absorption at the characteristic vibration rotation spectrum bands of non-elemental gases in the middle infrared range between 2 and 12 μm . Because of their bipolar moment, the gas molecules interact with infrared emissions. For selectivity, the receiver is filled with the applicable sample components to establish sensitivity to these components. The absorbance of the pure gas component is measured in a separate pneumatic radiation detector, with which the gas is heated and expands itself proportionally to the radiation intensity. The sample gas is illuminated likewise, expands and irradiated into a balanced container before its entrance the flow and thus the mass of gas is determined. The gases are at the same time quantitatively measured.

CO and CO₂ are monitored by NDIR spectroscopy (Binos 4b.1 from Fisher-Rosemount for CO and CO₂).

1.6. Kinetics & mechanism of the non-catalyzed & catalyzed soot oxidation

Although oxidation reactions of all kinds of carbonaceous materials have been studied to a large extent, relatively little is known about the processes taking place in the non-catalyzed and catalyzed oxidation of carbonaceous materials. For the gasification of the carbonaceous materials with other reactants such as CO₂ or H₂O, much more detail on the kinetics and mechanism have been published for both the non catalytic (Walker et al., 1959; Kapteijn et al., 1986) and the catalytic (Kapteijn et al., 1986; Mckee., 1983; Mckee., 1981; Moulijn et al., 1984) gasification reaction.

Polyvinylpyrrolidone	Water	574954	for 1000000
Carboxylic acid	Water	31233	analyzed
Ammonium Chloride	Water		
Formic acid	Water		
Glucose	Water		

2.2. Preparation of Soot and Fe₂O₃

2.2.1. Preparation of model soot

The model soot is prepared by burning a pulverized 7 oxygen balance in a diffusion burner with the help of a flame and is separated from the exhaust by employing a particulate filter. The diffusion burner is shown in Figure 3.1. The apparatus is described well in the literature (Wells et al., 2000; Ruckenstein, 2003; Klein, 1998). The prepared model composition of 25.8 Mol % C, 1.54 mol % of carbon, 0.7 Mol % (0.3 mol %) of oxygen and 0.5 Mol % (0.5 mol %) of hydrogen (Ruckenstein, 2003) soot containing 1.5 Mol % of Fe₂O₃ is used as a model soot. It is a model soot and not a real soot.

CHAPTER – 2

EXPERIMENTAL

2.1 Chemicals

Various reagents used in this research are listed in table 2.1 along with their specifications. All the reagents used were of high grade purity. Similarly all the gases used in reactions were of required purity.

Table 2.1: List of Reagents

Reagent	Supplier	Catalogue No.	Grade
Polyvinyl alcohol (M=145000 g/mol)	Merck	814894	for synthesis
Iron nitrate	Fluka	31233	analytical
Activated Charcoal	Fluka	-	-
Printex L	Fluka	-	-
Graphite	Fluka	-	-

2.2 Preparation of Soot and Fe_2O_3

2.2.1 Preparation of model soot

The model soot is prepared by burning a propylene / oxygen mixture in a diffusion burner with the help of a flame and is separated from the exhaust by employing a particulate filter. The diffusion burner is shown in figure 2.1. The apparatus is described well in the literature (Balle et al., 2006; Reichert., 2003; Klos., 1998). The generated model soot consists of 98.8 Ma. - % (94.0 mol %) of carbon, 0.7 Ma. - % (0.5 mol %) of oxygen and 0.5 Ma. - % (5.5 mol %) of hydrogen (Reichert., 2003). Soot containing 2.6 Ma. - % adsorbed species is discarded as it consist mostly the adsorbed hydrocarbons.

2.3.2 Preparation of PdO

An aqueous PVA solution (1% w/v) was prepared with the appropriate amount of crosslinking agent (1% w/v) and stirred overnight at room temperature. The solution was then poured into a mold and dried at 60°C for 24 hours. The resulting film was then ground to a fine powder. The powder was then dried at 60°C for 24 hours. The final product was a fine white powder.

2.3.3 Characterization of Surface PdO

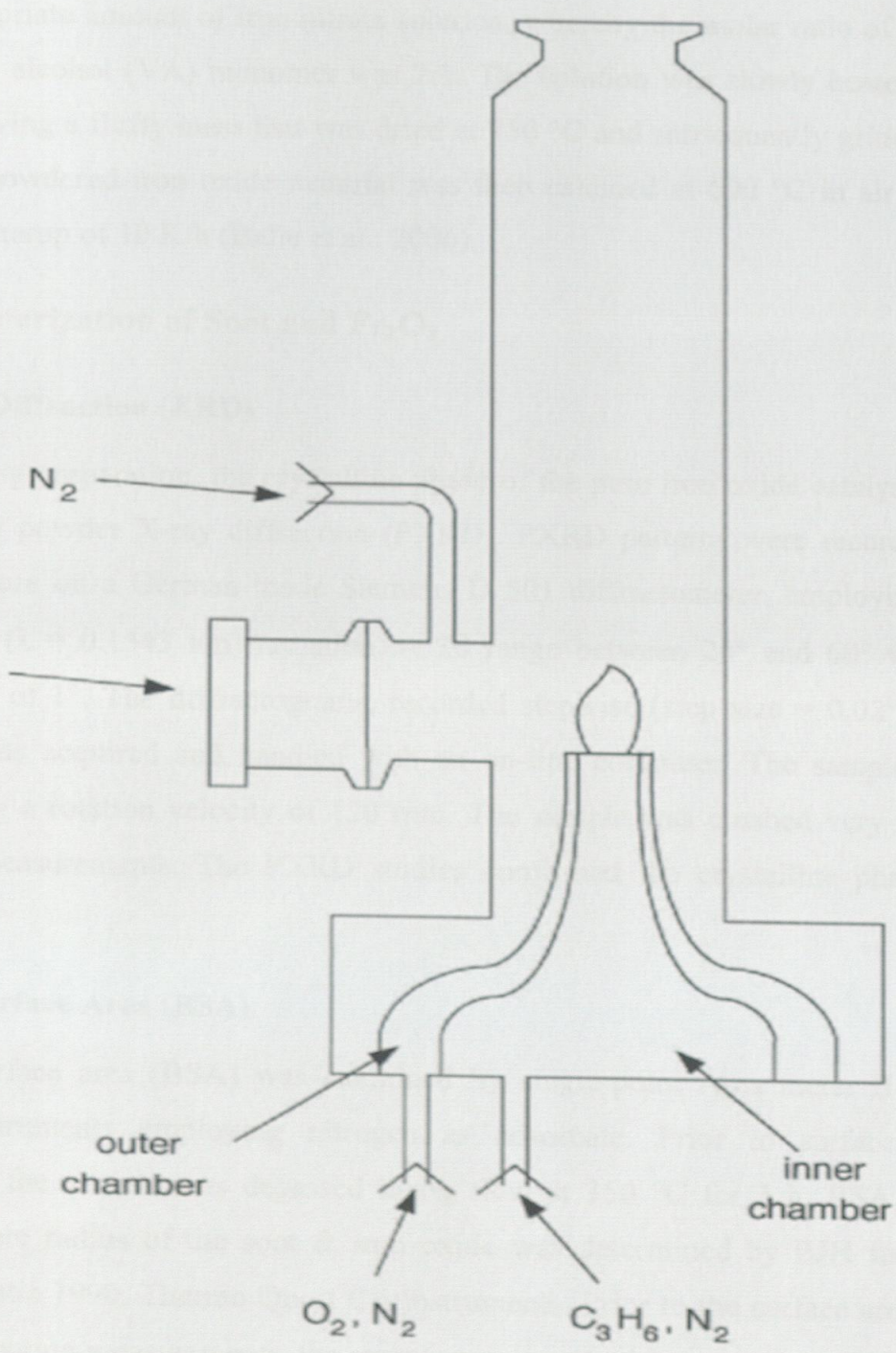
2.3.3.1 X-ray Diffraction (XRD)

Following the preparation of the surface PdO , the sample was characterized by X-ray diffraction (XRD). The XRD pattern was collected using a $\text{Cu K}\alpha$ radiation source. The sample was mounted on a goniometer and the diffraction pattern was recorded. The resulting pattern showed a broad peak at $2\theta \approx 38^\circ$, which is characteristic of the PdO phase.

2.3.3.2 BET Surface Area Analysis

The BET surface area of the surface PdO was determined using nitrogen adsorption-desorption measurements. The sample was degassed at 300°C for 2 hours. The nitrogen adsorption-desorption isotherm was recorded at 77 K. The resulting isotherm showed a hysteresis loop, which is characteristic of mesoporous materials. The BET surface area was calculated to be $150 \text{ m}^2/\text{g}$.

Fig. 2.1 Diagrammatical presentation of Diffusion Burner.



2.2.2 Preparation of Fe_2O_3

An aqueous PVA solution with 9 Ma. % polyvinyl alcohol (PVA) was mixed with the appropriate amount of iron nitrate solution, whereby the molar ratio of metal cation to vinyl alcohol (VA) monomer was 2:1. The solution was slowly heated and evaporated leaving a fluffy mass that was dried at 250 °C and subsequently grinded to powder. The powdered iron oxide material was then calcined at 600 °C in air for 5 hours at a heat ramp of 10 K/h (Balle et al., 2006).

2.3 Characterization of Soot and Fe_2O_3

2.3.1 X-ray Diffraction (XRD)

Following preparation, the crystalline phase of the pure iron oxide catalyst was investigated by powder X-ray diffraction (PXRD). PXRD patterns were recorded at room temperature on a German made Siemens D 501 diffractometer, employing Ni filtered $\text{CuK}\alpha$ ($\lambda = 0.1543$ nm) radiation. A 2θ range between 20° and 60° with a divergence slit of 1°. The diffractograms, recorded stepwise (step size = 0.02°, step time = 1 s) was acquired and handled with an on-line computer. The sample was measured using a rotation velocity of 120 rpm. The sample was crushed very finely prior to the measurements. The PXRD studies confirmed the crystalline phase of haematite.

2.3.2 BET Surface Area (BSA)

BET surface area (BSA) was examined by single-point Area meter II from Stroehlein Instruments employing nitrogen as adsorbate. Prior to surface area measurements, the sample was degassed in N_2 flow at 350 °C for 3 h. BSA, pore volume and pore radius of the soot & iron oxide was determined by BJH formula using Sorptomatic 1990, Thermo Quest CE Instruments. Prior to the surface area and pore size distribution measurements, the sample was degassed in vacuum at 350 °C for 3 h. The BET results of the soot and Fe_2O_3 are summarized in Table 2.2.

Table 2.2: BSA of Fe_2O_3 and different soot samples

Sample	BSA ($\text{m}^2 \text{g}^{-1}$)
Fe_2O_3	25
Propene soot	90
Printex L	152
Printex U	90
Graphite	4

2.3.3 Scanning Electron Microscopy (SEM)

Iron oxide sample was ground in a mortar and coated on a metal disc using double stick tape. Scanning electron microscopy was performed using JEOL JSM-5910 electron microscope operated at 20 kV with a tungsten filament at the electron source.

Energy-dispersive analysis of the emitted X-ray (EDX) was performed, in combination with SEM, using Energy-dispersive X-ray spectrometer Oxford INCA200.

2.3.4 Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR is one of the most widely used tools for the characterization of surface groups. In fact, at face value, it would appear to be the ideal solution to providing quick, inexpensive soot analysis. It is based on the fundamental principles of molecular spectroscopy.

IR studies are made to investigate the interaction between the catalyst and soot surface. The investigations are performed by using soot and other model soot samples with prominent reflectance (phthalic acid, 9-phenol-2,3,7-trihydroxy-6-fluorone, anthracene) and are conducted in the absence as well as in the presence of the catalyst. The catalytic mixtures are prepared when Fe_2O_3 is blended with soot in the weight ratio of 27. the blended procedure is accurately performed by grinding the solids in a mortar that results in tight contact.

The spectra were recorded on an ATI Mattson Galaxy 5020 FTIR spectrometer equipped with a MCT detector. The IR cell made of stainless steel contains a KBr window and was connected to a gas-handling system. The spectra were recorded in the range from 800 to 4000 cm^{-1} with an instrument resolution of 4 cm^{-1} . 2000 scans are accumulated to a spectrum resulting in a time resolution of 5 min. The temperature was monitored by a K type thermocouple placed 5 mm underneath the sample surface. During the measurements IR cell was purged with nitrogen to avoid diffusion of air into the system.

2.3.5 Thermo-gravimetry (TG)

A sample of material (ranging from 60 to 200 mg) is placed on an arm of a recording microbalance, also called thermo-balance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile (most commonly), or in the rate-controlled mode, where the pre-programmed value of the weight changes imposes the temperature change in the way necessary to achieve and maintain the desired weight-change rate. The most common temperature profiles are: jumping to isotherm and holding there for a specified time (soak); temperature ramping at constant rate (linear heating or cooling); and combination of ramp and soak segments.

Unanalyzed and catalyzed soot oxidation in a dynamic gas atmosphere (500 cm^3/min) of synthetic air was followed thermo-gravimetrically, THERMOWAAGE STA-409, NETZSCH Thermisch Analyse (Germany) equipped with on-line work station for data acquisition and handling. The TG (and DTG) curve were recorded while heating the various carbon samples and reaction mixture of catalyst and soot up to different temperature ranging from 700 to 1100 $^{\circ}\text{C}$, at variable heating rate ($\Delta T/\Delta t = 1.5$ and 10 K/min). The fact that the chosen heating rates are rather high is to accomplish conditions relevant to combustion.

The reaction mixture was prepared by grinding in an agate mortar for one minute and the mixture (at 2:1 molar ratio) of catalyst and various carbon samples (Propene Soot, Printex L from Degussa Germany, Graphite, and Activated Charcoal). The resulting mixtures were then examined.

2.3.6 Temperature Programmed Desorption (TPD) studies

Temperature programmed desorption (TPD) of soot was carried out for the estimation of CO & CO₂. In TPD the same laboratory bench was used as for catalytic investigations. 0.120 grams (10 mmol) of soot is pre-treated in nitrogen flow at 150 °C for 15 min. The sample was cooled down to room temperature in N₂. The TPD was started using N₂ as carrier gas at a total flow of 500 ml min⁻¹. The material was heated to 1000 °C at the rate of 1.5 K min⁻¹, whereby reactor effluents were continuously monitored.

CO and CO₂ are monitored by NDIR spectroscopy (Binos 4b.1 from Fisher-Rosemount).

2.4 Catalytic Studies - Temperature Programmed Oxidation (TPO)

With the help of temperature programmed oxidation (TPO) the activity of the catalyst is investigated, during which the gas concentration (O₂) is varied. This makes statements for the catalytic activity or activity of pure carbon black.

For most experiments, as described below, the pure soot and the mixture of soot and catalyst are used. In the case of the catalyst / soot mixture, Fe₂O₃ and soot are mixed in the molar ratio of 2:1, with a pressure of 40 MPa and then milled to a particle size from 125 to 250 microns granules. In each study a granulated mixture of 3.31 g is used that corresponds to 3.19 grams (20 mmol Fe₂O₃) and 0.120 grams (10 mmol soot). For reference purposes pure soot as well as pure granules are also prepared, which the soot sample was diluted with 500 mg crushed quartz wool to avoid hot spots during oxidation. The investigation was carried out by using temperature programmed oxidation (TPO). In all these experiments the same laboratory bench is used that including a reactor of quartz glass tube (i.d. 8 mm) in which the sample is fixed with quartz wool. Soot and soot/ Fe₂O₃ mixture was placed in reactor and then heated in the flow of nitrogen (500 cm³/min) at 150 °C. The reactive gas mixture is switched on and the temperature increases linearly with a rate of 90 K / hour to 650 °C. The total volume of gas flow is 500 cm³/min, while the gas is composed of 6.0, 12.0 & 18.0 vol. -% oxygen in nitrogen. Preliminary studies show that the gas in the empty reactor under the experimental conditions do not change

significantly. The pipes of the bench are made of stainless steel and are heated to 150 °C. The inlet and the outlet temperature of the feed was monitor by a K type thermocouple fitted directly in the front and behind the sample. For simplicity, the inlet temperature is exclusively noted throughout the work in all measurements a small difference of inlet and outlet temperature (<10 K) is observed only, even at maximum oxidation rates. During the examination the total gas flow is kept at 500 cm³/min (STP). The gas flow was controlled by independent gas controllers (MKS Instruments).

A better contact between the soot and catalyst surface, reduced soot particle size, and a higher density of the soot are factors that might also contribute to higher soot oxidation rates. Although the initial particle size does not influence the soot oxidation temperature, care must be taken that the initial particles are not too large in order to be sure that the one minute of milling at the intermediate speed mill speed is sufficient. The use of initial (catalyst-soot mixture) particles 125 to 250 microns and mill time of about one minute can be regarded as a good compromise.

The experimental work consisted of Thermo-gravimetric analysis (TGA), Temperature programmed oxidation (TPO in a flow reactor), and Fourier transform infrared (FTIR) spectroscopic techniques. The purpose of the TG analysis experiments was to determine the fraction of the volatile material present in the soot sample, the reactivity of the soot samples to O₂. In the flow reactor experiments (TPO) the reactivity of the soot samples to the oxygen were explored. The FTIR experiments were performed to analyse the soot oxidation intermediates.

2.5 Kinetic Studies

Thermo-gravimetric analysis (TGA) is a popular method to measure reaction rates in heterogeneous kinetics. Soot is placed in a crucible inside an oven and the mass and temperature of the solid are measured as a function of time. The temperature can be controlled to perform temperature ramp experiments. A quantity of known amount in mg was put in the crucible. The oven was run under synthetic air flow of 500 ml/min. It is more convenient to calculate a specific reaction rate related to a known extensive parameter.

The conversion rate is commonly used (Equation 2.1). It is the rate of conversion 'X' defined by the Equation 2.2, with $m_{c,0}$ representing the initial mass of carbon.

$$r = \frac{dX}{dt} [1/s] \quad 2.1$$

$$X = (m_{c,0} - m_c) / m_{c,0} \quad 2.2$$

For the kinetic studies the same material used as was prepared for TPO studies. Preliminary tests demonstrate that pressing and granulating does not affect the activity of the mixture, where as the initial grinding is found to be crucial step in preparation. Tight contact mode is generally considered to be less representative for the soot deposited in particulate filters, but it is suitable for the intended basic examinations as reproducible conditions are simply provided. For reference purposes pure soot granules are also made. They are prepared in the same way as described for the catalytic mixture.

Non-isothermally measured kinetic parameters, namely, reaction activation energy (E_A), order (n), frequency factor (A), and rate constant (k), for the weight loss process monitoring the soot deep oxidation ($C_{(s)} \rightarrow CO_{2(g)} \uparrow$), were determined by the means of mathematical calculation.

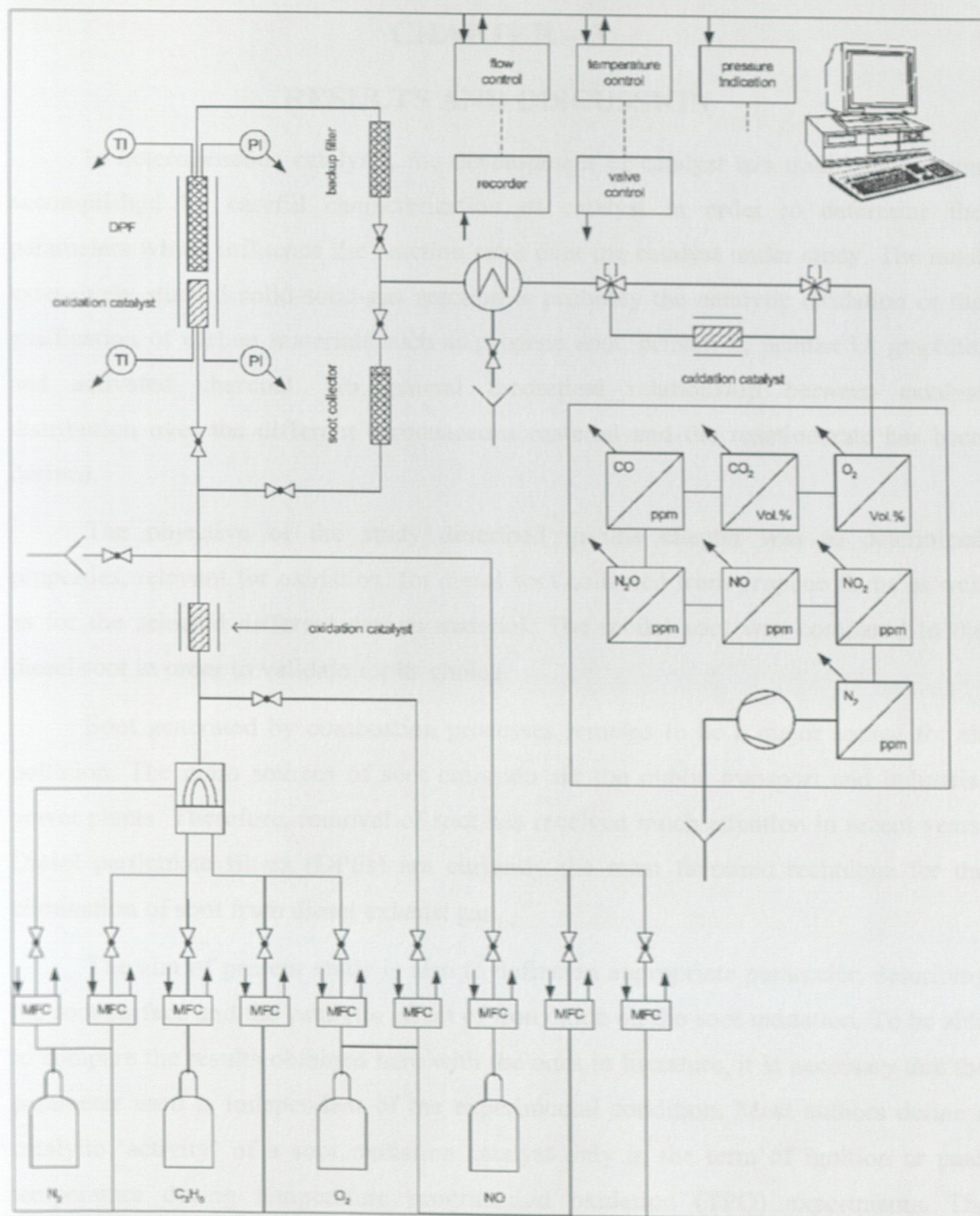


Fig. 2.2: Schematic representation of the TPO/TPD laboratory bench-scale installation (Balle et al., 2006).

CHAPTER – 3

RESULTS AND DISCUSSION

In heterogeneous catalysis, the development of catalyst has traditionally been accomplished by careful characterization of catalyst in order to determine the parameters which influence the reaction rates over the catalyst under study. The most extensively studied solid-solid-gas reaction is probably the catalytic oxidation or the gasification of carbon materials such as propene soot, printex L, printex U, graphite, and activated charcoal. No general theoretical relationship between catalyst distribution over the different carbonaceous material and the reaction rate has been derived.

The objective of the study described in this chapter was to determine properties, relevant for oxidation, for diesel soot collected from propene flame as well as for the selected different carbon material. The model soot was compared to the diesel soot in order to validate for its choice.

Soot generated by combustion processes remains to be a major source for air pollution. The main sources of soot emission are the public transport and industrial power plants. Therefore, removal of soot has received much attention in recent years. Diesel particulate filters (DPFs) are currently the most favoured technique for the elimination of soot from diesel exhaust gas.

The aim of present study is also to define an appropriate parameter, describing the soot surface and the catalytic effect of iron oxide on the soot oxidation. To be able to compare the results obtained here with the ones in literature, it is necessary that the parameter used is independent of the experimental condition. Most authors define a catalytic 'activity' of a soot oxidation catalyst only in the term of ignition or peak temperature during temperature programmed oxidation (TPO) experiments. The temperature of the peak depends however on the experimental conditions used.

3.1 Temperature programmed oxidation – Reactivity of soot to oxygen

Depending on the engine operation modes, a complex mixture of partially burned and unburned fuel and of lubricating oils is normally bounded to the particles

emitted from diesel engine. The compounds are normally of high and intermediate molecular weight compounds, known as soluble organic fraction (SOF). Compared to the primary soot particle, which is mainly composed of elemental carbon, these adsorbed hydrocarbon compounds are easier to oxidise. In order to measure the oxidation of soot with and without catalyst, temperature programmed oxidation technique was used with different oxygen concentration (6%, 12%, 18%). In diesel soot oxidation, catalyst play a synergistic role wherein it catalyses oxidation of the hydrocarbons that constituents of the soluble organic fraction adsorbed on the soot. The reaction being exothermic in nature generates heat that assists the catalytic oxidation of the soot. TPO data of the soot as well as Fe_2O_3 /soot mixture that are obtained with different gas composition are summarized in table 3.1.

Table 3.1: represent the total molar amount of CO and CO_2 formed in TPO as well as corresponding temperature T ($^{\circ}\text{C}$). TPO experiments are performed with and without Fe_2O_3 catalyst under the reaction conditions of $m(\text{soot}) = 0.12 \text{ g}$ (10 mmol C), $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$.

	n(CO) (mmol)	n(CO_2) (mmol)	T_m ($^{\circ}\text{C}$)
Fe_2O_3/propene soot			
6 vol. % O_2	0.000	10.000	420
12 vol. % O_2	0.023	9.977	416
18 vol. % O_2	0.008	9.992	411
Propene soot			
6 vol. % O_2	---	---	---
12 vol. % O_2	5.027	4.973	565
18 vol. % O_2	5.319	4.837	550

The laboratory results on carbon oxidation activity of iron oxide catalyst are presented in Figure 3.1. The catalyst appears to get activated immediately after 200°C . However, significant oxidation of the carbon material is observed beyond the 300°C . The peak corresponding to the maximum activity is around 416°C . The exothermic

carbon oxidation reaction is expected to propagate the reaction rate after it achieves significant activity. This activity could be considered reasonably well, in view of the very low surface area of the catalyst used. There was a very low CO concentration of about 5 ppm. The sudden drop in CO₂ generation is because of the consumption of the carbon material in the reaction mixture. Therefore, this does not indicate the lowering of activity and rather confirms the complete oxidation of carbon. The catalyst show unaffected structure up to about 1000 °C even after prolonged exposure (Stachowiak et al., 2005). Such a thermal stability is sufficient, even considering the failure-mode scenarios like soot oxidation after excessive accumulation, generation of the high localized temperature due to delayed soot oxidation, etc.

Fig. 3.2 represents the TPO of the non-catalysed soot oxidation. In the presence of oxygen soot oxidation increases as it is clear from the figure. The non-catalytic combustion temperature of the soot depends on the contents of adsorbed hydrocarbons, and experimental conditions, but generally exceeds 500 °C.

This effect is beneficial for C-NO₂ based reactions filter regeneration because 5-15% O₂ is always present in the exhaust gas. The TPO profile of the catalyzed soot oxidation are significantly shifted to lower temperature, e.g. the temperature at maximum CO₂ concentration (T_m) is decrease from 550 to 420 °C. In the presence of catalyst, CO formed only in trace amount. The maximum concentration of CO upto 0.32 vol. % is found in absence of catalyst. TPO data in Fig. 3.2 represents the excellent catalytic activity for the soot oxidation as a result there is no CO at 250 °C. The peak oxidation temperature corresponding to maximum activity is around 416 °C. The exothermic carbon oxidation is expected to propagate the reaction rate after it achieves significant activity. The initial slope of CO₂ plots increases which is the sign of the C/O₂ reaction that is simultaneous and influenced similarly by the contact conditions between catalyst and carbon. This could be considered as excellent catalytic activity, in view of the very low surface area of the catalyst used. There is practically no CO generation, which is sometimes present as a product of incomplete combustion. The sudden drop of CO₂ generation is because of consumption of the carbon material in the reaction mixture. Therefore, this does not indicate the lowering of activity and rather confirm the complete oxidation of soot. The expected O₂ uptakes are based on

the supposition (i) that only CO_2 is formed, and (ii) that 100% of sample is oxidized. The results showed a lower O_2 uptake in the absence of the catalyst than in its presence; the agreement with the expectation in this case was excellent we conclude some CO was formed, but that the Fe_2O_3 catalyst succeeded in oxidising it to CO_2 .

Fig. 3.3 and 3.4 show the TPO of the catalysed soot oxidation with 12 and 18 % oxygen. As it is clear from these figures that as the vol. % of O_2 is increases the catalytic combustion of the carbon occurs at lower and lower temperature. So this is not surprising at all since oxygen is obviously expected to have a direct promoting effect on the carbon combustion. It also quite interesting to note that at 6.0, 12.0, and 18.0 vol.% , the shoulder of the broad peak remain unaffected with the different percentage of oxygen. The temperature for the respective shoulder is 280 °C. It is clear from these figures that the concentrations of CO_2 and CO yielding complexes increasing with the gasification time.

Surface oxygen complexes increase the rate of catalyzed soot oxidation. For Fe_2O_3 catalyst, the reaction rate is increased over the whole conversion range. CO_2/CO ratios also increase in the presence of surface oxygen complexes, an effect that is very large for Fe_2O_3 catalyst.

It is clear from Fig. 3.5 that heat ramp also play a key rule in catalytic soot oxidation. When the ramp is increased from 1.5 to 10 K/min, the peak became sharp and the broadness of the peak disappears.

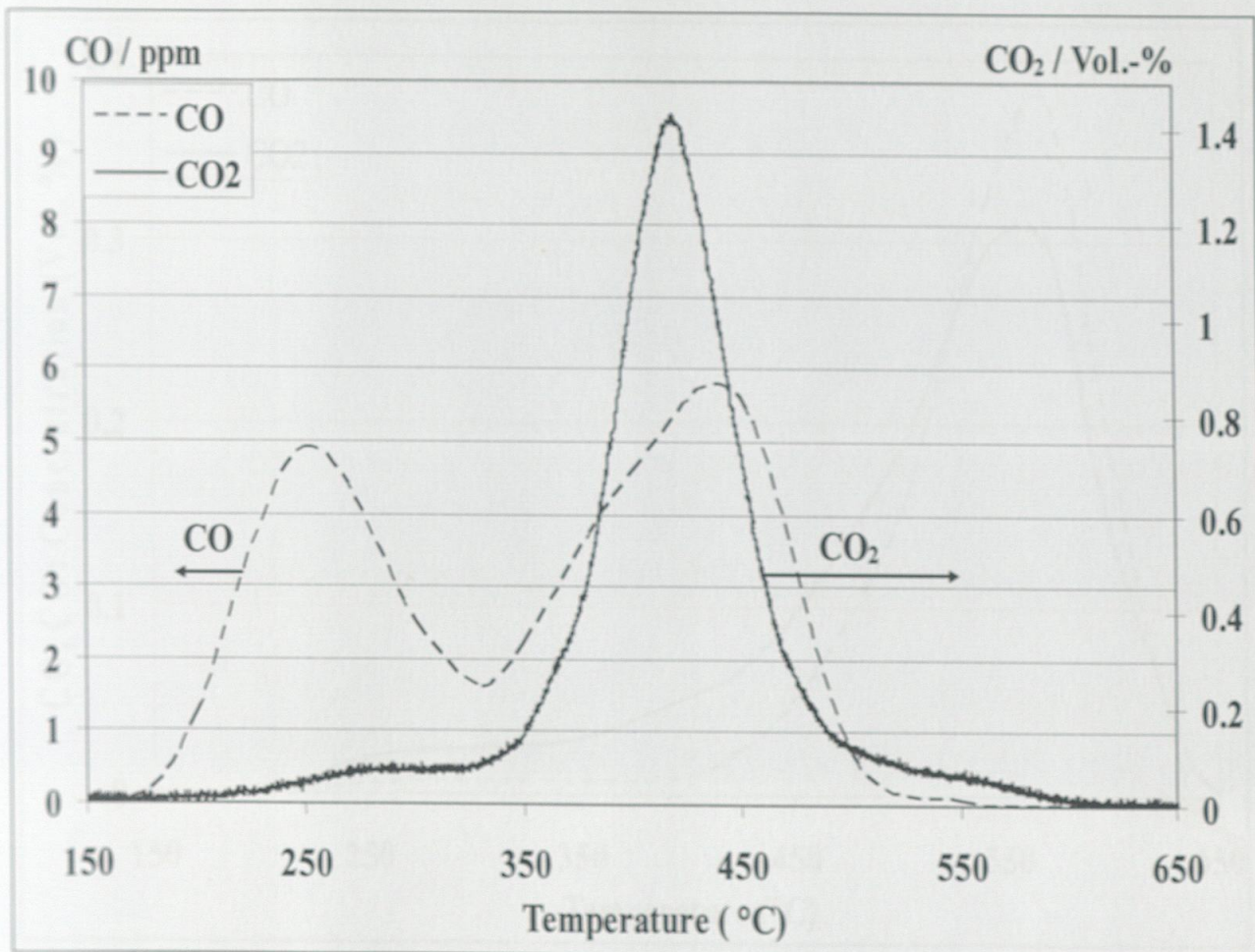


Figure 3.1

TPO pattern of the Fe_2O_3 / propene soot. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19$ g (20 mmol), $m(\text{C}) = 0.12$ g (10 mmol), $c(\text{O}_2) = 6.0$ vol. %, N_2 balance, $F = 500$ cm^3/min (STP), $\Delta T/\Delta t = 1.5$ K/min, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

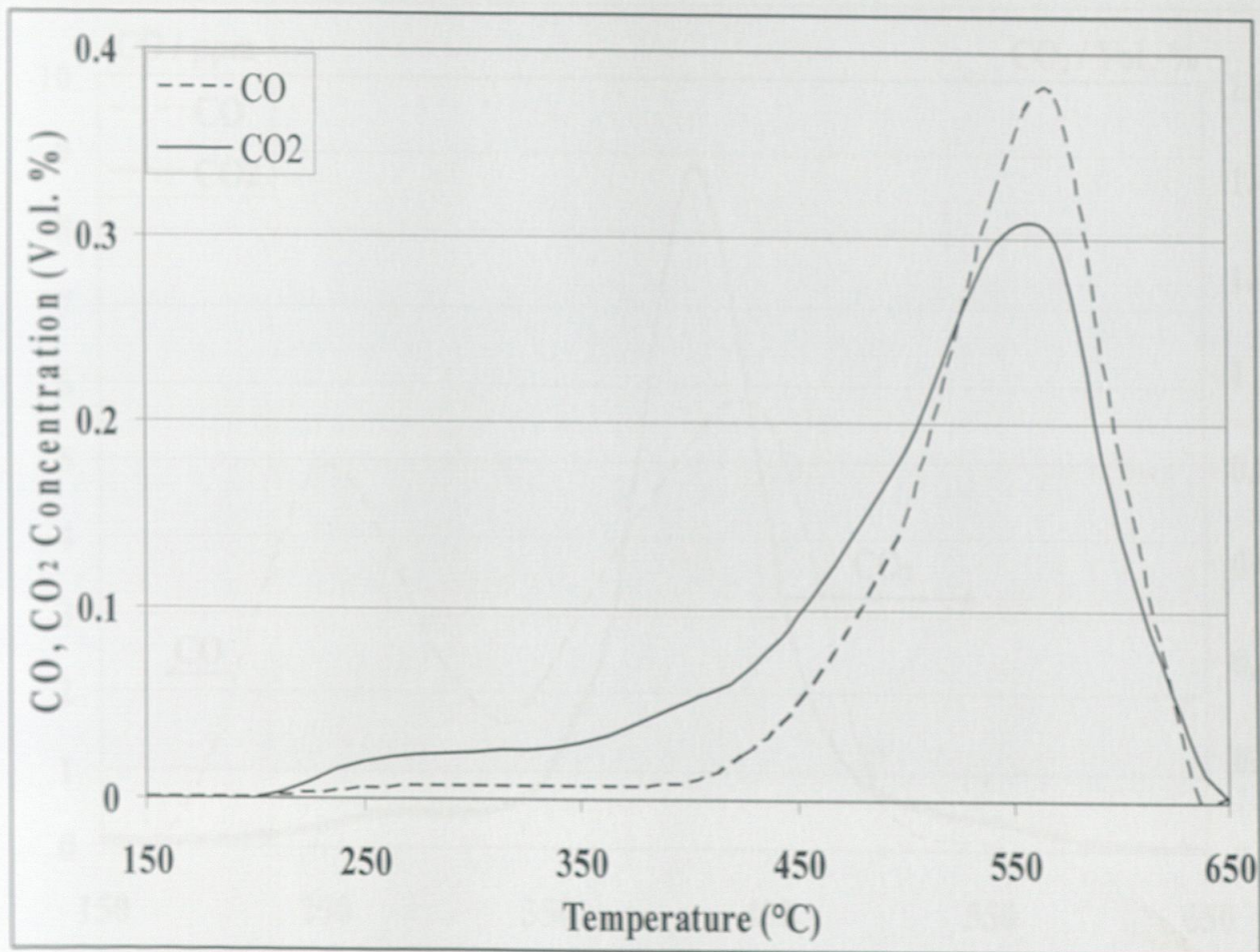


Figure 3.2

TPO pattern of the propene soot. Reaction conditions: $m(C) = 0.12$ g (10 mmol), $c(O_2) = 6.0$ vol. %, N_2 balance, $F = 500$ cm³/min (STP), $\Delta T/\Delta t = 1.5$ K/min, soot used of 125-250 μm .

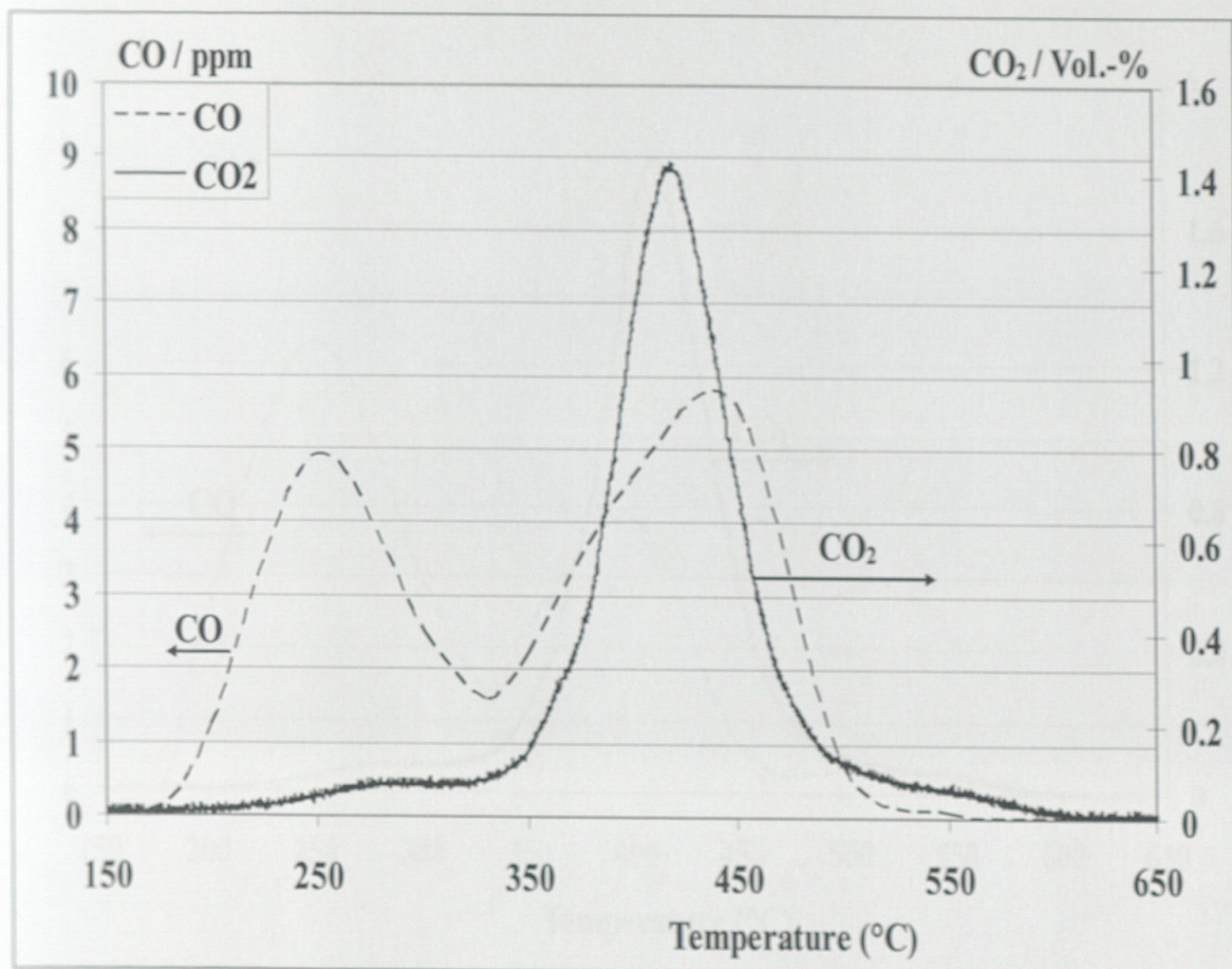


Figure 3.3

TPO pattern of the Fe₂O₃/propene soot. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 12.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, Fe₂O₃/soot used of 125-250 μm .

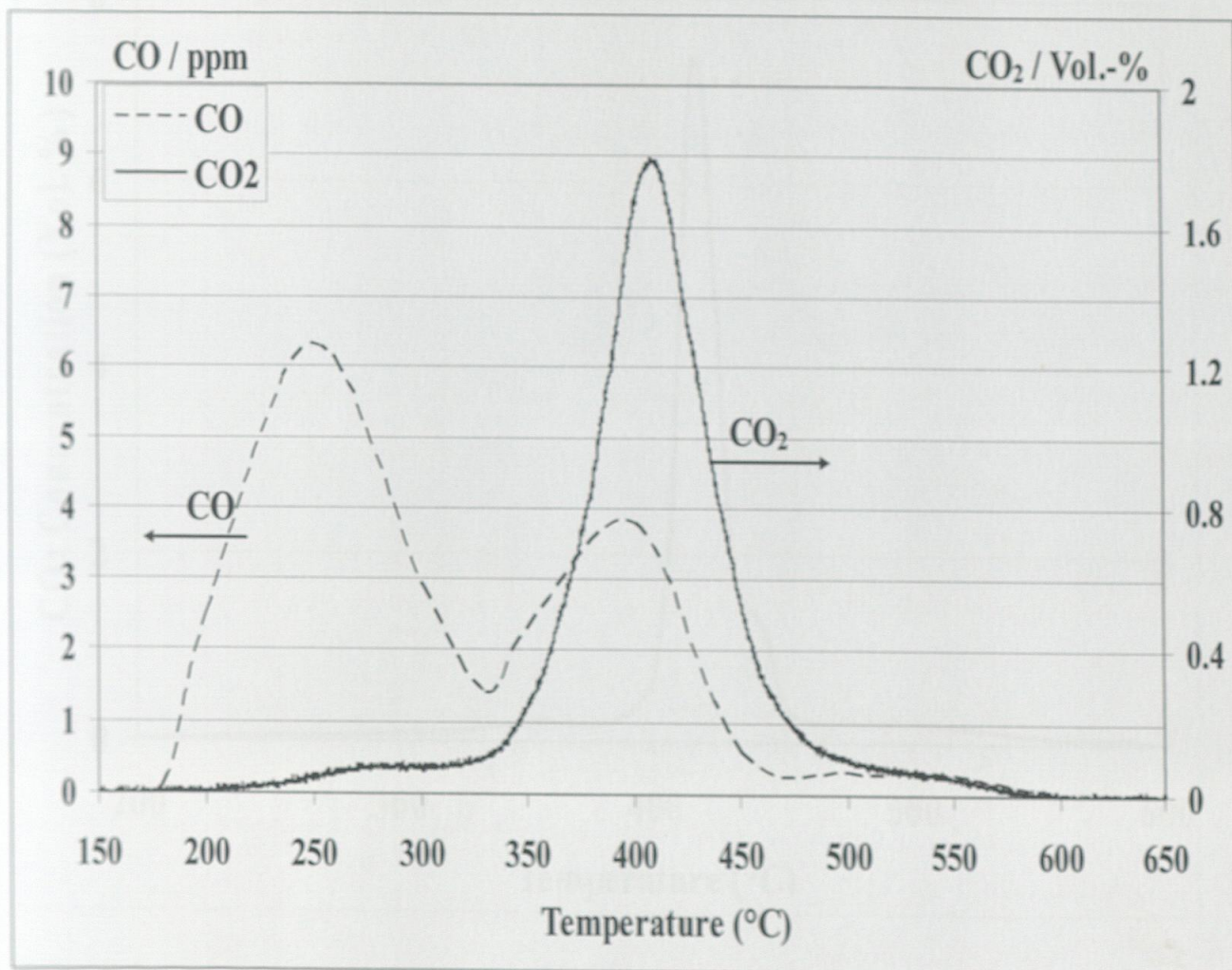


Figure 3.4

TPO pattern of the Fe_2O_3 / propene soot. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19$ g (20 mmol), $m(\text{C}) = 0.12$ g (10 mmol), $c(\text{O}_2) = 18.0$ vol. %, N_2 balance, $F = 500$ cm^3/min (STP), $\Delta T/\Delta t = 1.5$ K/min, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

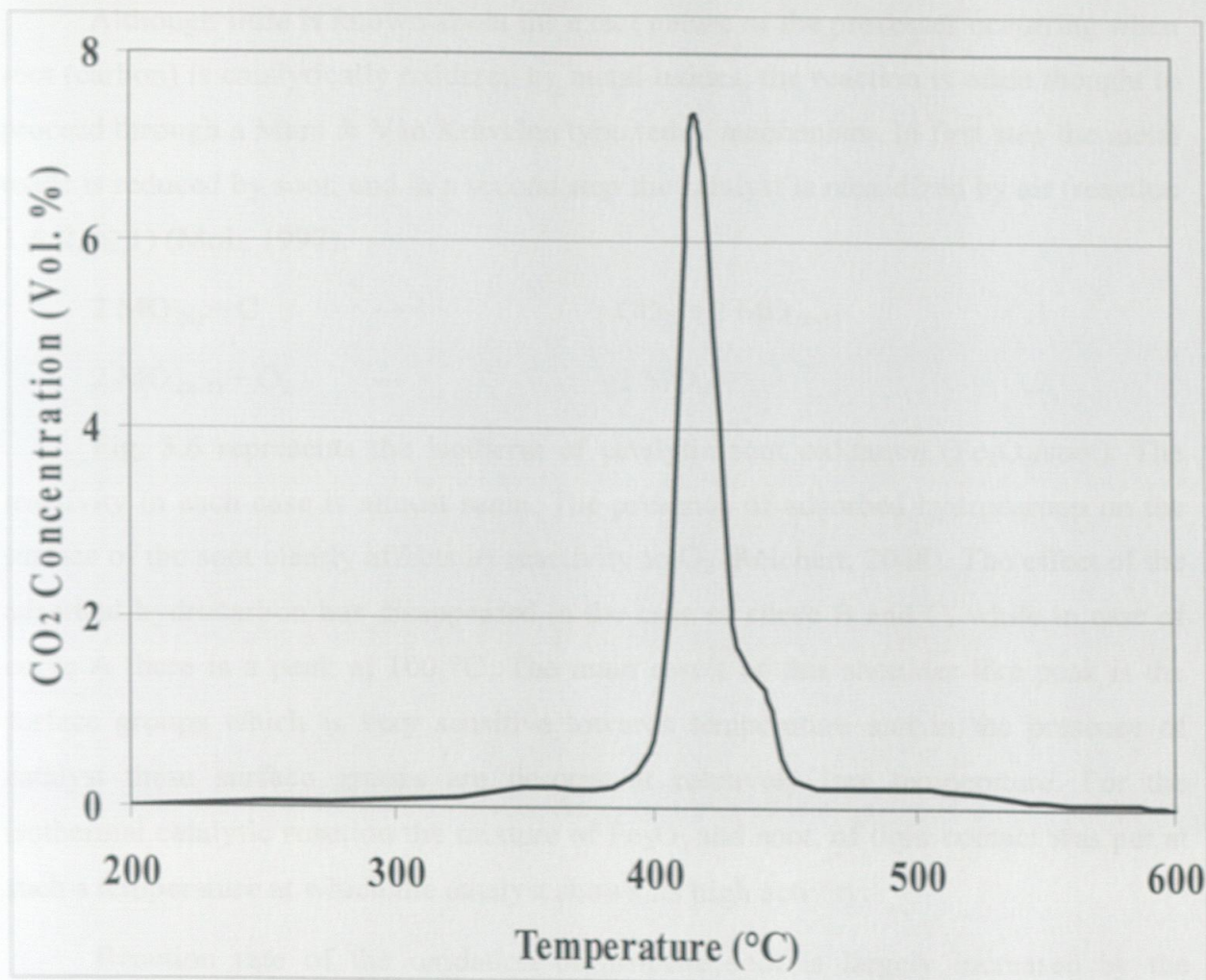


Figure 3.5

TPO pattern of the Fe_2O_3 / propene soot. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19$ g (20 mmol), $m(\text{C}) = 0.12$ g (10 mmol), $c(\text{O}_2) = 18.0$ vol. %, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 10 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

Although little is known about the exact nature of the processes occurring when soot (carbon) is catalytically oxidized by metal oxides, the reaction is often thought to proceed through a Mars & Van Krevelen type redox mechanism. In first step the metal oxide is reduced by soot, and in a second step the catalyst is reoxidized by air (reaction 1 & 2, $n \geq 1$) (Mol., 1997).

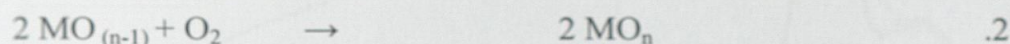
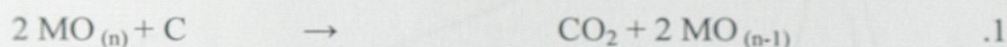


Fig. 3.6 represents the isotherm of catalytic soot oxidation ($\text{Fe}_2\text{O}_3/\text{soot}$). The reactivity in each case is almost same. The presence of adsorbed hydrocarbon on the surface of the soot clearly affects its reactivity to O_2 (Reichert, 2008). The effect of the adsorbed hydrocarbon has disappeared in the case of curve B and C, while in case of curve A there is a peak at 100 °C. The main result of this shoulder like peak is the surface groups which is very sensitive towards temperature and in the presence of catalyst these surface groups are desorbs at relatively low temperature. For the isothermal catalytic reaction the mixture of Fe_2O_3 and soot, of tight contact was put at such a temperature at which the catalyst shows its high activity.

Reaction rate of the oxidation of propene soot is largely increased by the addition of Fe_2O_3 catalyst is the most active metal oxide catalyst in the present study, increasing the reaction rate under isothermal conditions (400 °C) in 6.0 vol. % O_2 in N_2 . These results apply to an optimized contact between the powder form catalyst and soot.

In Fig. 3.7 the oxygen content of the soot is deduced from the TPD pattern that indicate the desorption of CO (9.2 mg/g_{soot}) and CO_2 (3.3 mg/g_{soot}). From these findings, it is reasonable to postulate that the evolution of CO_2 in TPD comes mainly from the decomposition of the lactone and/or acid anhydride. It is generally accepted that the CO desorption in TPD originates from the decomposition of the carboxyl and/or ether type complexes.

From Fig. 3.8, the content of H is determined by TPO, in which the hydrogen is deduced in the form H_2O (43 mg/g_{soot}).

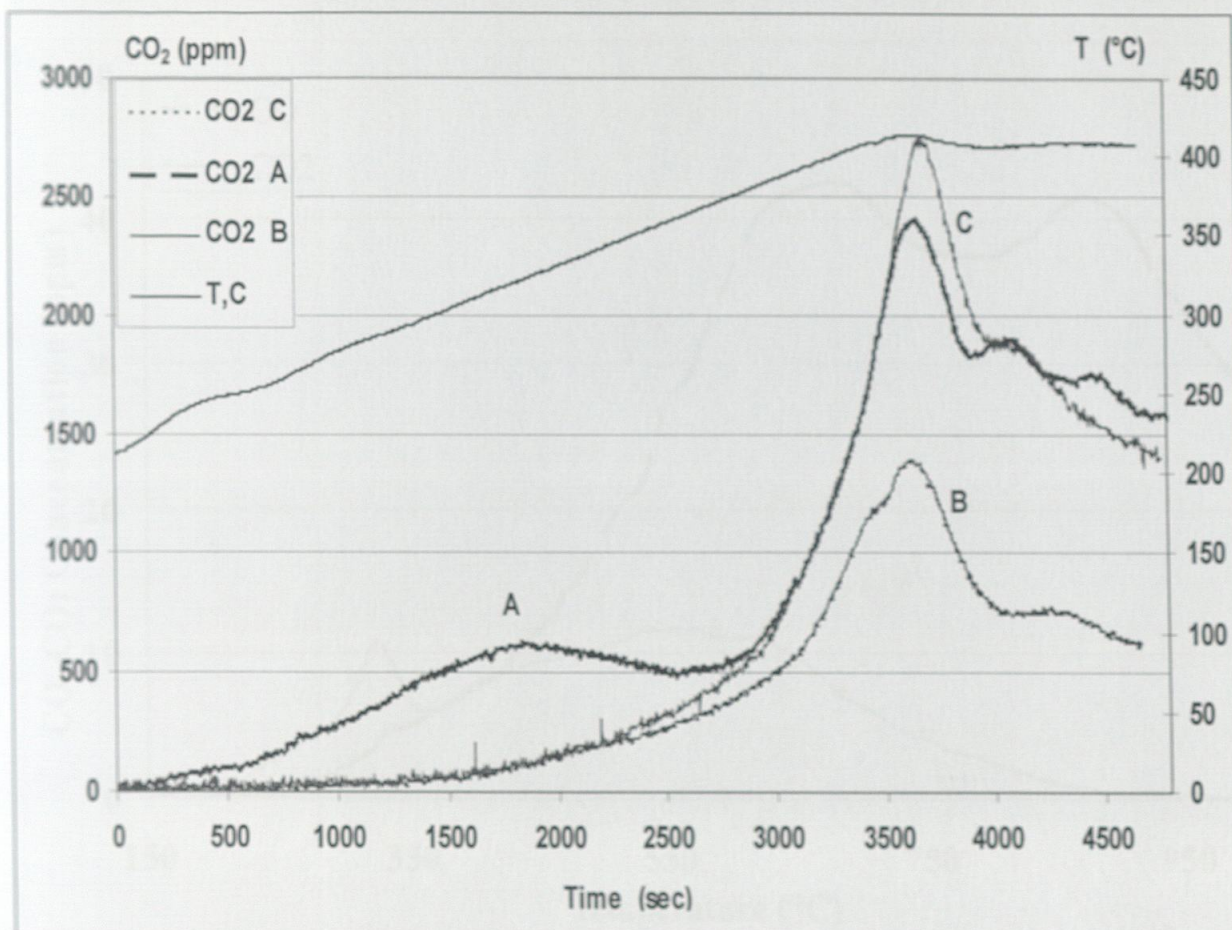


Figure 3.6

Isotherm of the catalytic propene soot oxidation. Inlet temperature (—) = 200 to 420 °C, and concentration of CO₂, (— —) = 3.314 g of Fe₂O₃/soot (A), (·····) = 2.389 g of Fe₂O₃/soot (B), (·····) = 2.010 g of Fe₂O₃/soot (C). Reaction condition: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 6.0 \text{ vol. \%}$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, Fe₂O₃/soot used of 125-250 μm , ($n(\text{Fe}_2\text{O}_3)/n(\text{C}) = 2$).

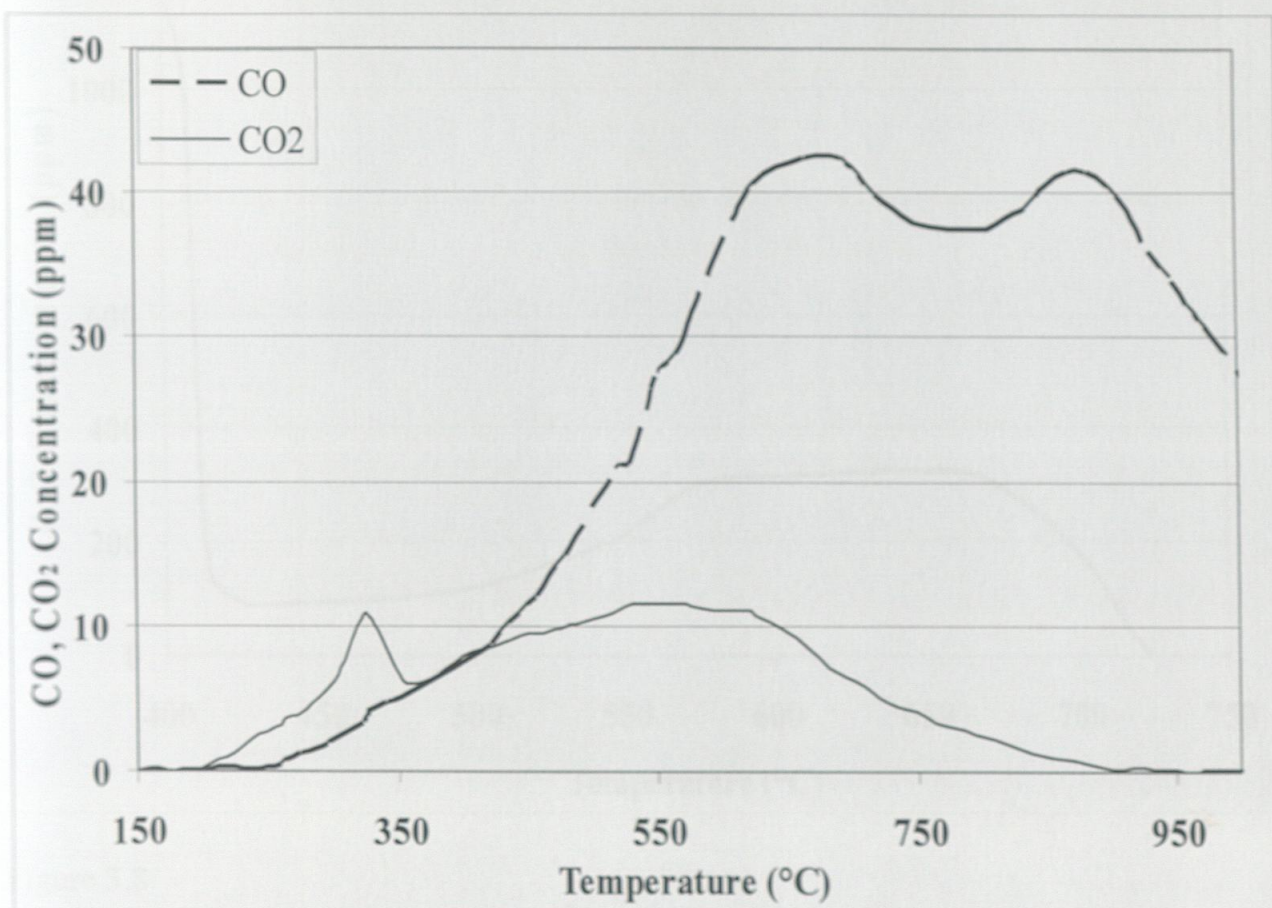


Figure 3.7

Formation of CO (— —) and CO₂ (—) in TPD of propene soot. Reaction conditions: $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), N_2 flow = $500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, soot used of 125-250 μm .

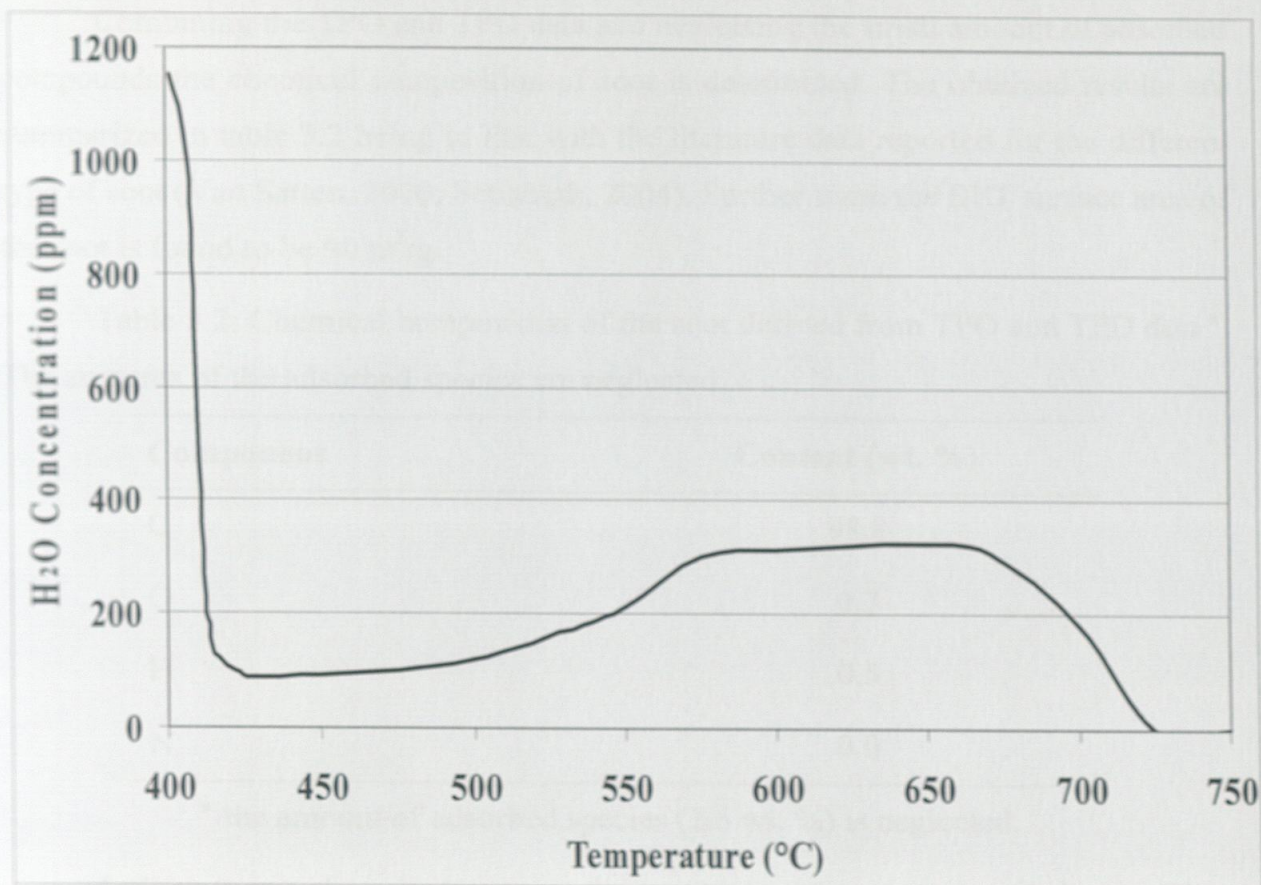


Figure 3.8

Formation of H₂O (—) in TPO of soot. Reaction conditions: $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 6.0 \text{ vol. \%}$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, soot used of 125-250 μm .

Combining the TPO and TPD data and neglecting the small amount of adsorbed compounds the chemical composition of soot is determined. The obtained results are summarized in table 3.2 being in line with the literature data reported for the different type of soot (Van Satten, 2000; Setiabudi, 2004). Further more the BET surface area of the soot is found to be 90 m²/g.

Table 3.2: Chemical composition of the soot derived from TPO and TPD data*. The amounts of the adsorbed species are neglected.

Component	Content (wt. %)
C	98.8
O	0.7
H	0.5
N	0.0

* the amount of adsorbed species (2.6 wt. %) is neglected.

In literature carbon, hydrogen, and nitrogen contents were reported to be 70 to 93.4 wt. %, 0.4 to 5 wt. %, and 0.3 to 1 wt. % respectively (Lies et al., 1984; Lies et al., 1988; Murphy et al., 1981). Ahlstrom et al., 1989; found a remarkable a low carbon content of 54 wt. %.

Fig. 3.9 represents the TPD pattern of fresh soot with 20 mmol amount instead of 10 mmol. As it is clear from the figure that by doubling the amount of soot results in the increase of CO concentration two folds, while a three fold increase in the concentration of CO₂ was also observed. The experiments were performed in the same reaction conditions that were used for 10mmol soot.

Fig. 3.10 and 3.11 shows the TPD of the fresh soot that was preliminary exposed to 6.0 vol. % oxygen at 100 °C and 300 °C, respectively. The soot which is exposed to 6.0 vol. % oxygen at 100 °C adsorbed less amount of oxygen as compare to the exposure at 300 °C. As a result at 700 °C, the maximum CO concentration is 70 ppm for oxygen exposure at 100 °C, while at 300 °C exposure it is 100 ppm. The maximum CO₂ concentration at 600 °C is 15 ppm and 25 ppm respectively. It is clear

from these results that as the temperature increase the O_2 adsorption on the soot surface also increases.

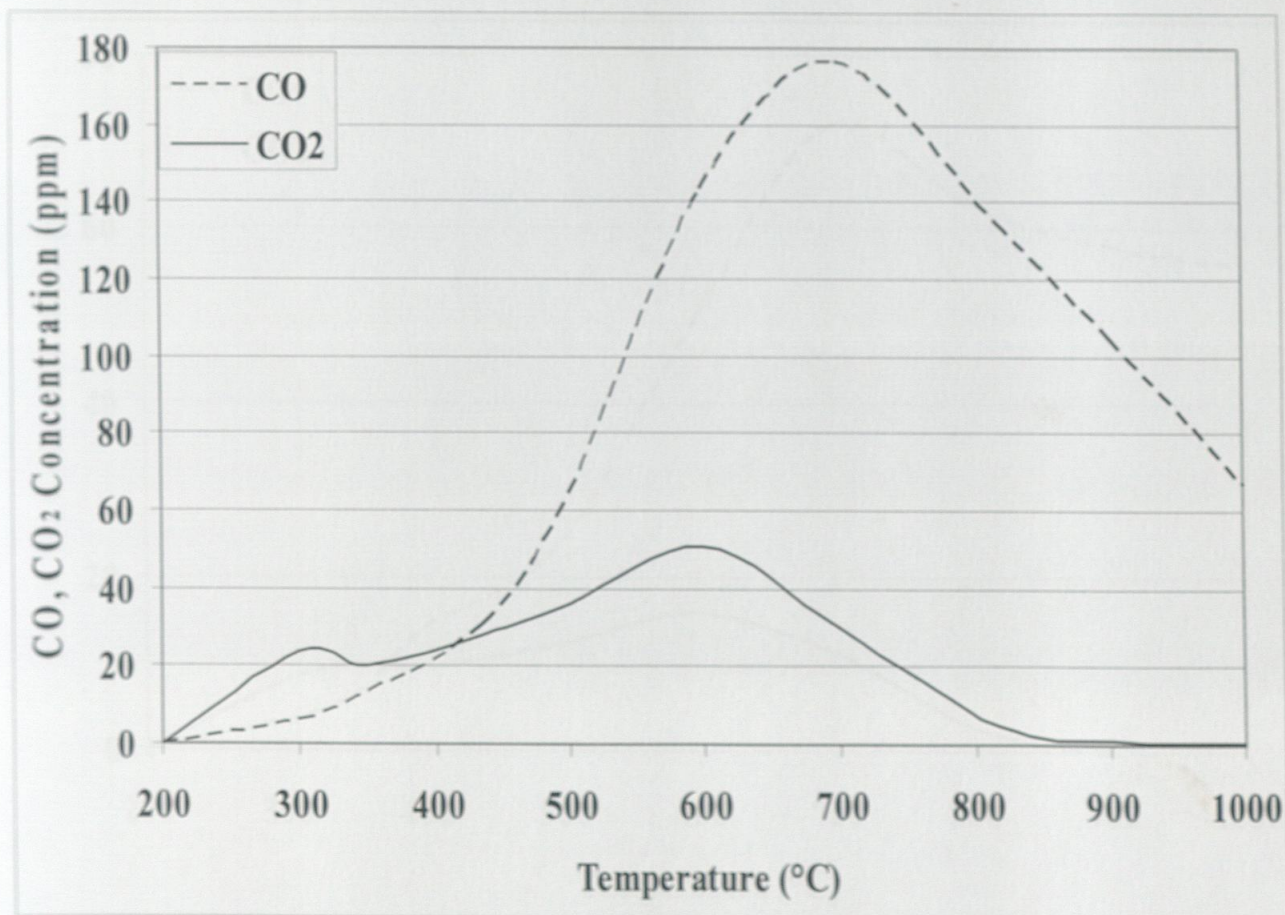


Figure 3.9

Formation of CO (---) and CO₂ (—) in TPD of soot. Reaction conditions: $m(C) = 0.24$ g (20 mmol), N_2 flow = 500 cm³/min (STP), $\Delta T/\Delta t = 1.5$ K/min, soot used of 125-250 μ m.

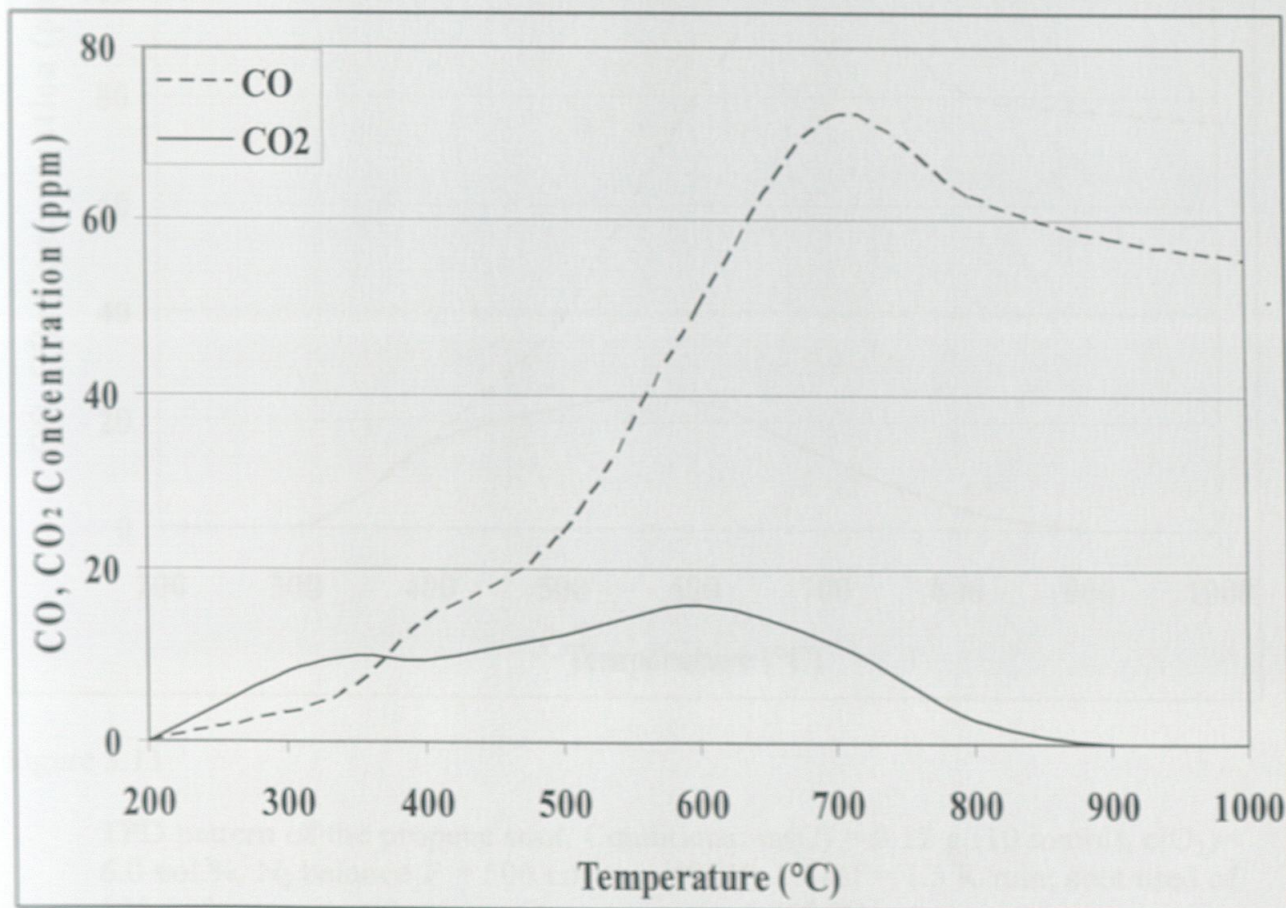


Figure 3.10

TPD pattern of the propene soot. Conditions: $m(C) = 0.12$ g (10 mmol), $c(O_2) = 6.0$ vol.%, N_2 balance, $F = 500$ cm³/min (STP), $\Delta T/\Delta t = 1.5$ K/min; soot used of 125-250 μ m and preliminary O_2 exposure is at 100 °C.

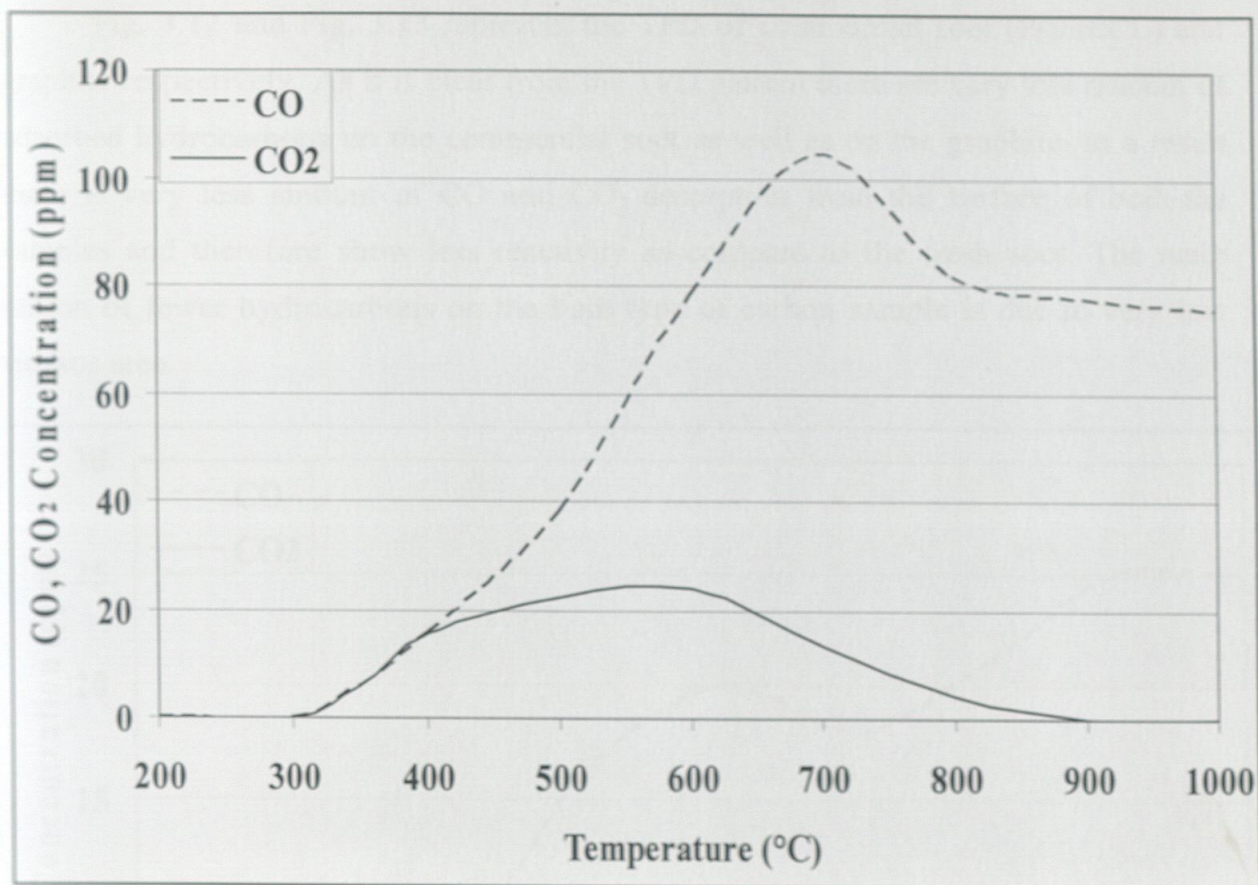


Figure 3.11

TPD pattern of the propene soot. Conditions: $m(C) = 0.12$ g (10 mmol), $c(O_2) = 6.0$ vol.%, N_2 balance, $F = 500$ cm³/min (STP), $\Delta T/\Delta t = 1.5$ K/min; soot used of 125-250 μ m and preliminary O_2 exposure is at 300 °C.

Fig. 3.12 and Fig. 3.13 represent the TPD of commercial soot (Printex L) and graphite respectively. As it is clear from the TPD pattern there are very less amount of adsorbed hydrocarbons on the commercial soot as well as on the graphite, as a result there is very less amount of CO and CO₂ desorption from the surface of both the samples and therefore show less reactivity as compare to the fresh soot. The main reason of fewer hydrocarbons on the both type of carbon sample is due to very low surface area.

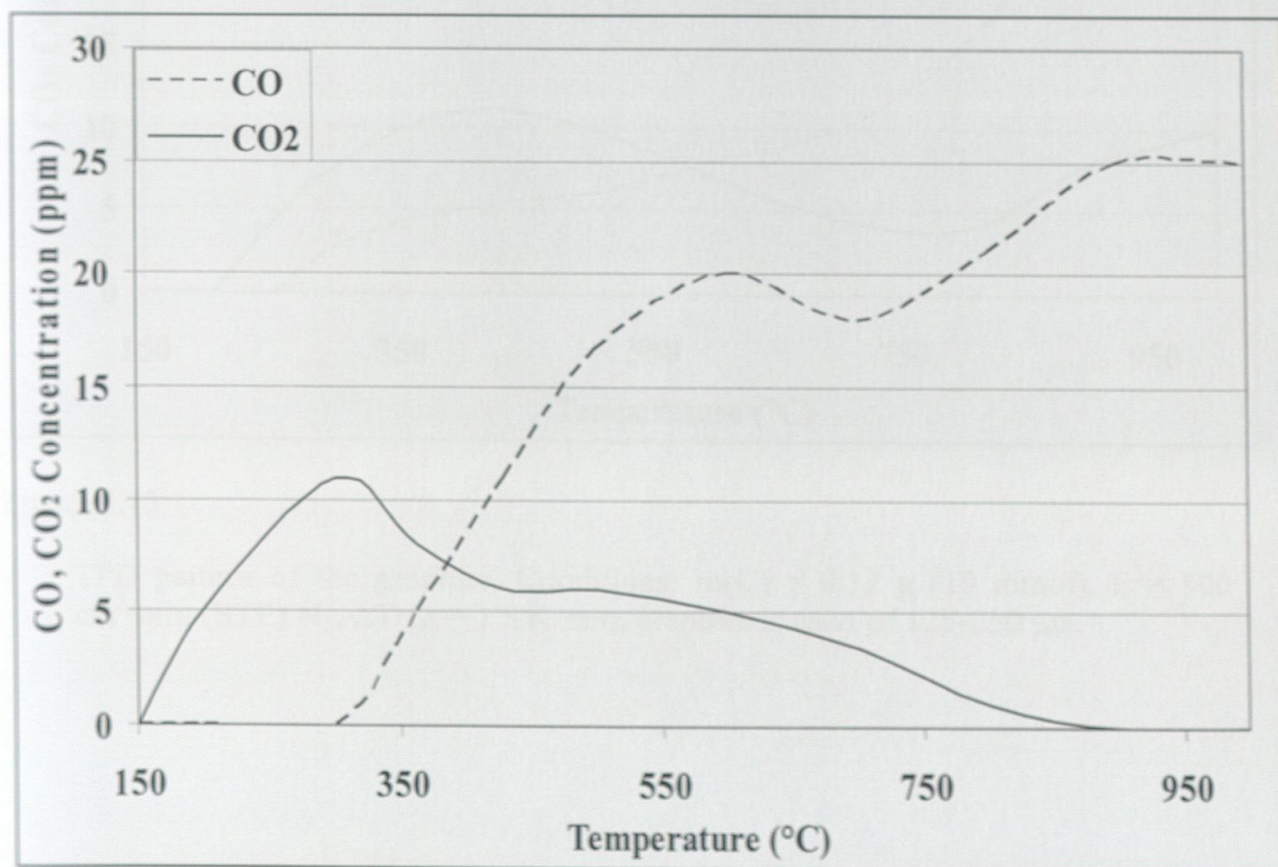


Figure 3.12

TPD pattern of the commercial soot Printex L. Conditions: $m(C) = 0.12$ g (10 mmol), $F = 500$ cm³/min (STP) N₂, $\Delta T/\Delta t = 1.5$ K/min, commercial soot is used of 125-250 μ m.

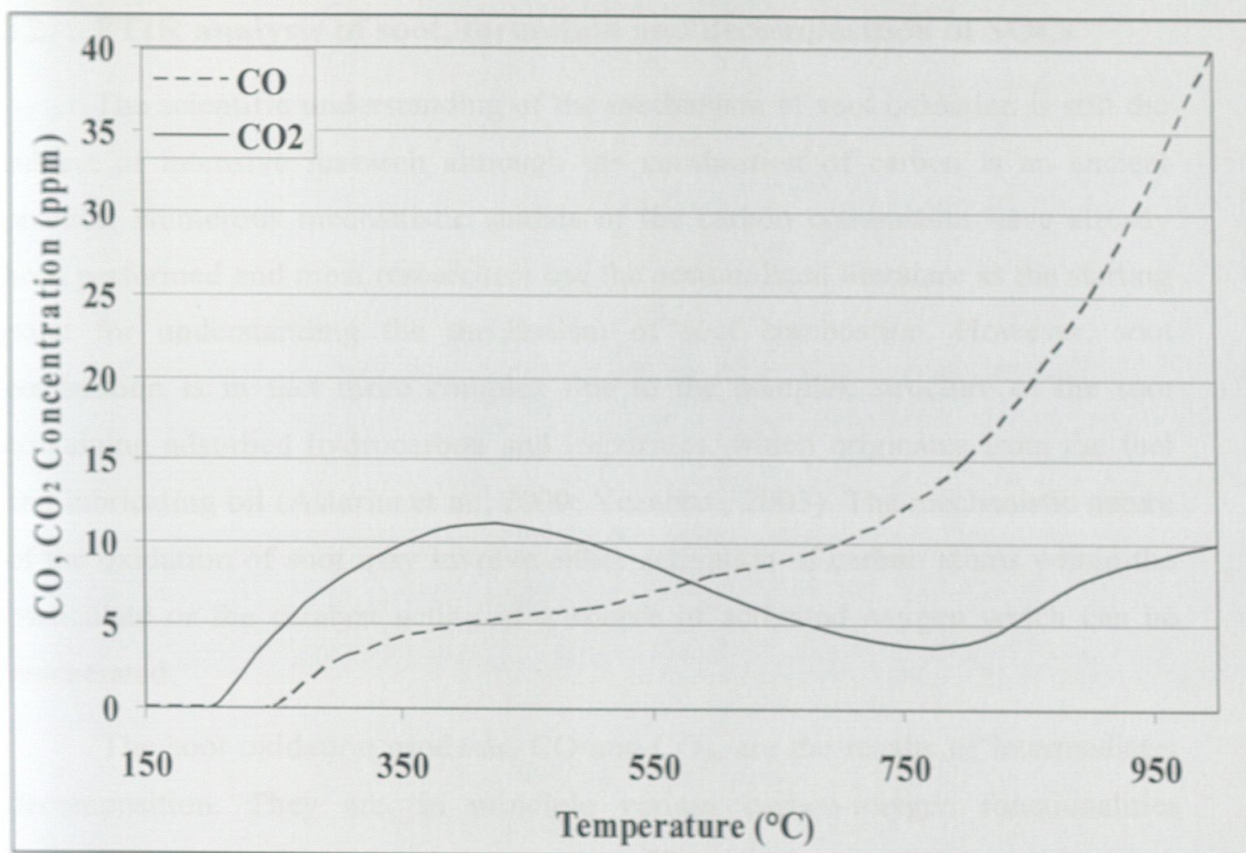


Figure 3.13

TPD pattern of the graphite. Conditions: $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $F = 500 \text{ cm}^3/\text{min}$ (STP) N_2 , $\Delta T/\Delta t = 1.5 \text{ K/min}$, graphite is used of 125-250 μm .

3.2. FTIR analysis of soot, formation and decomposition of SOCs

The scientific understanding of the mechanism of soot oxidation is still the subject of intensive research although the combustion of carbon is an ancient practice. Numerous mechanistic studies of the carbon combustion have already been performed and most researchers use the accumulated literature as the starting point for understanding the mechanism of soot combustion. However, soot combustion is in fact more complex due to the complex structure of the soot containing adsorbed hydrocarbon and impurities, which originates from the fuel and lubricating oil (Astarita et al., 2000; Yezerets., 2003). The mechanistic nature of the oxidation of soot may involve either activation of carbon atoms within the particulate or the catalyst acting as a source of activated oxygen which can be regenerated.

The soot oxidation products, CO and CO₂, are the results of intermediates decomposition. They are, in principle various carbon-oxygen functionalities formed on the surface of carbon particles. Here the intermediates are named as soluble organic fractions (SOFs). Upon heating, SOFs decompose by releasing CO and/or CO₂. The fact that many functional groups give bands in close ranges explains the appearance of the broad bands. Therefore it is not possible to specify the functional groups individually.

The TPD technique, which has been often used to characterize surface complexes, does not allow the exact identification of the chemical form of the complexes. In order to clarify the chemical form, spectroscopic technique such as Fourier transform infrared (FTIR) spectroscopy has been utilized by many researchers.

Fig. 3.14 represents the spectra of the propene soot without pressing & propene soot pressed at 40 MPa. From the figure it is clear that both the pressed and unpressed soot contain the three broad peaks with a shoulder that indicates the carbon-oxygen complexes with moderately high intensities. It has to be noted that these broad peaks composed of many carbon oxygen functionalities of high intensities, which is already present at the surface of propene soot. The reason for

the comparison between the press and non press soot is actually to see the surface groups in both the cases. As it is clear from the figure, both types have the same results and there is no pronounce effect of pressing at high pressure on the soot surface. Further more the FTIR spectra were taken for the commercial soot (Printex-L from Degussa) and the graphite which is shown in fig. 3.15 and 3.16. In both the spectra's the regions of the different surface complex are quite clear. In each case the peak at 1770 cm^{-1} are assigned to C=O stretching in lactone and /or acid anhydride. According to the literature (Socrates, 1980), the distinction between the former and later groups depends on whether the peak in this range appears as a singlet around 1750 cm^{-1} or doublets with one falling between 1750 and 1790 cm^{-1} and the other between 1830 and 1880 cm^{-1} .



Figure 3.14

FTIR spectra of soot (Printex-L and Degussa) and graphite. The top trace is for soot (Printex-L) and the bottom trace is for soot (Degussa). The x-axis is wavenumber in cm^{-1} and the y-axis is transmittance.

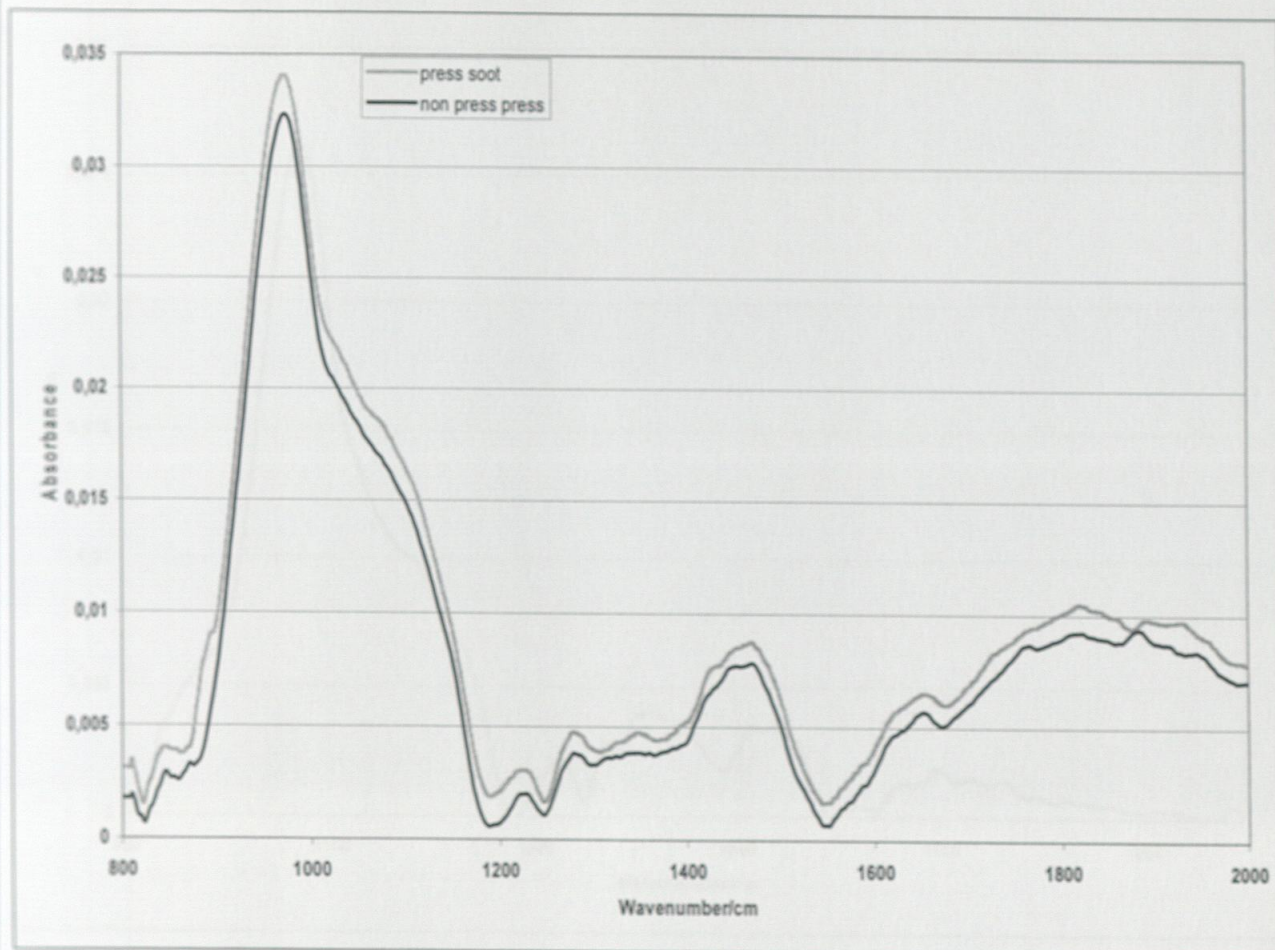


Figure 3.14

FTIR spectrum of the fresh soot (-) and fresh soot pressed to pellet with 40 MPa (—); data are recorded at 100 °C temperature under N₂ flow (500 cm³/min).

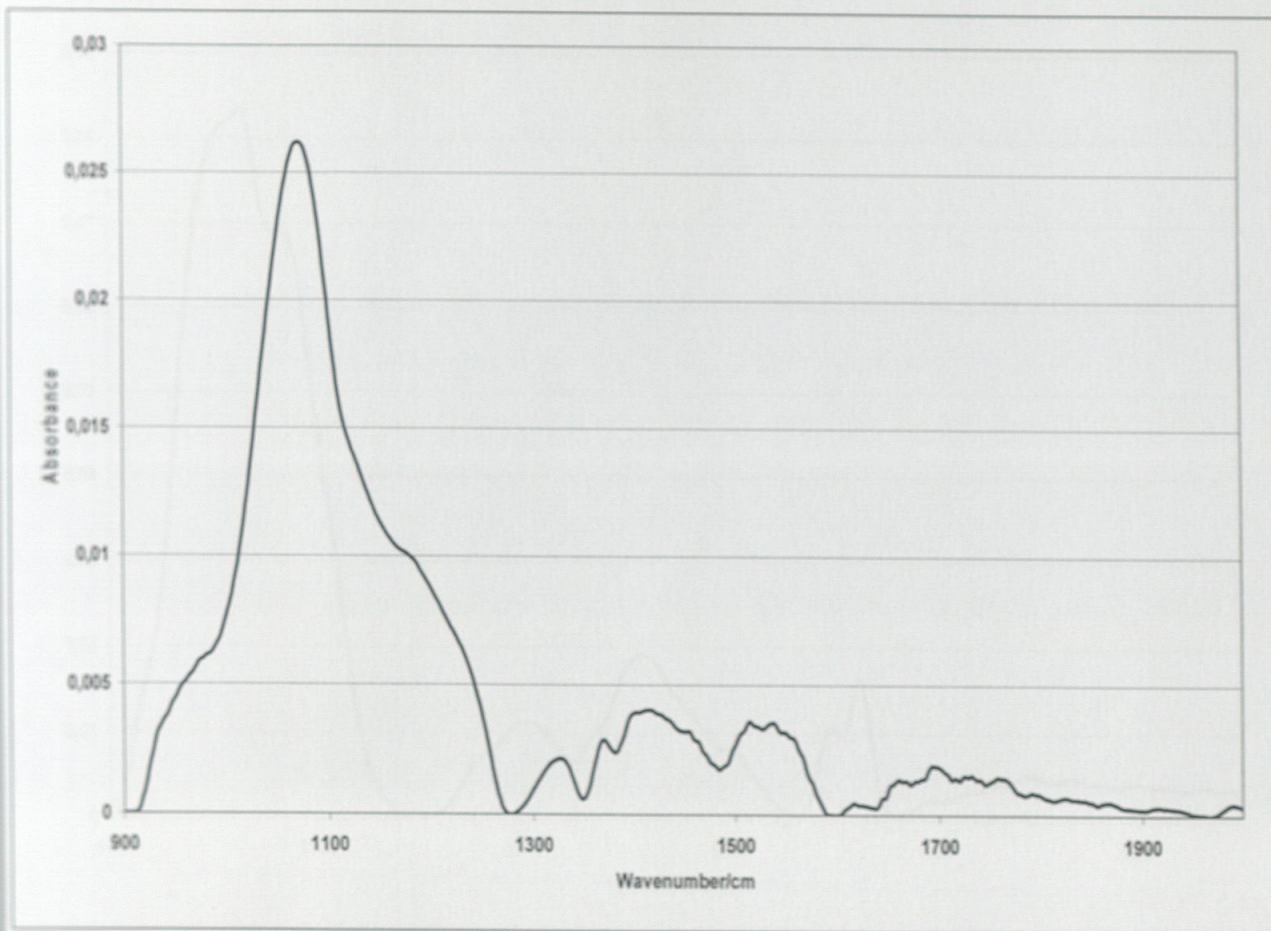


Figure 3.15

FTIR spectra of the Printex L; data are recorded at 100 °C temperature under N₂ flow (500 cm³/min).

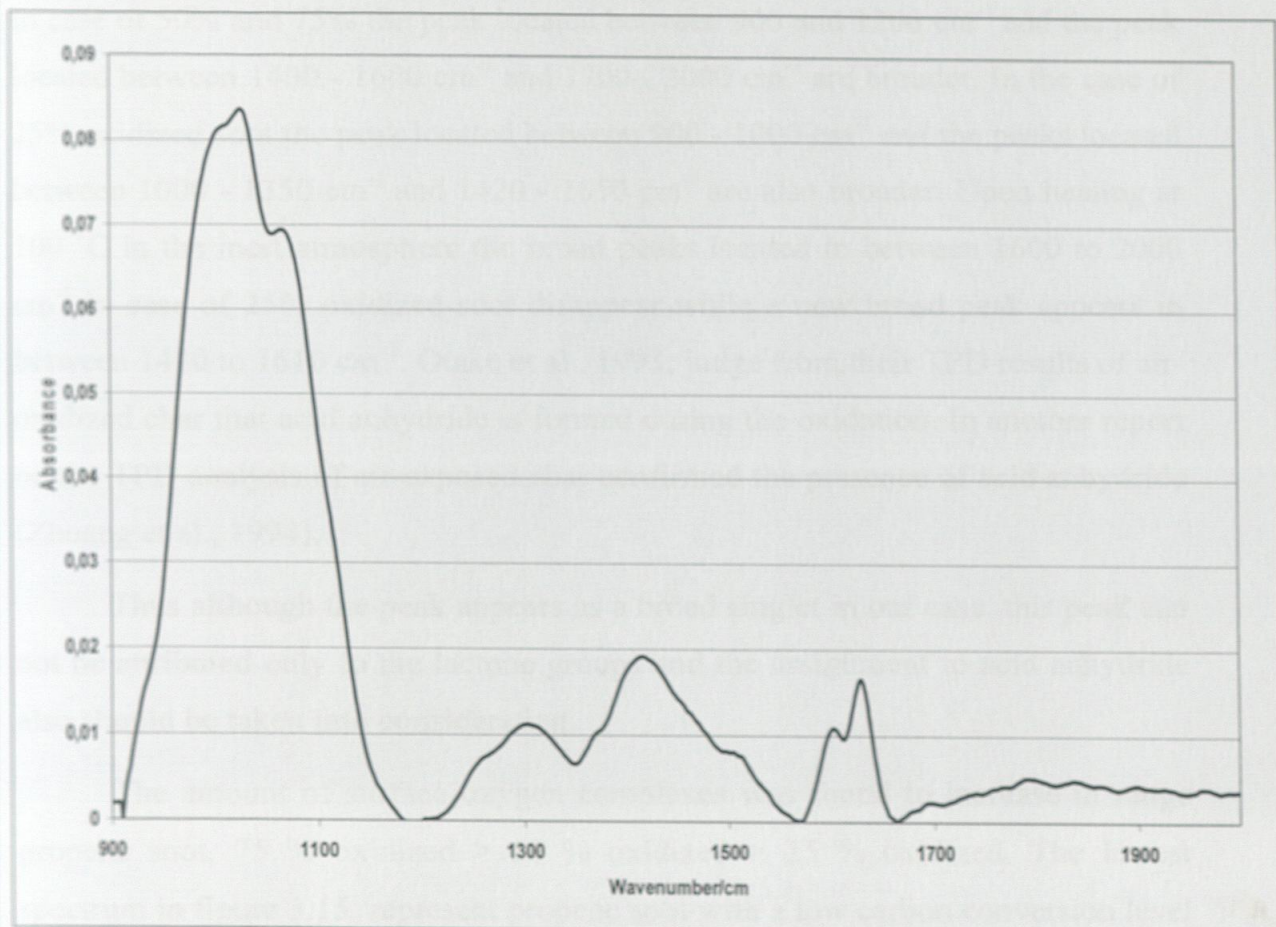


Figure 3.16

FTIR spectra of the Graphite; data are recorded at 100 °C temperature under N_2 flow ($500 \text{ cm}^3/\text{min}$).

Figure 3.17 represents the spectra of oxidized soot at different percentage. In case of 50% and 75% the peak located between 900 and 1200 cm^{-1} and the peak located between 1400 - 1600 cm^{-1} and 1700 - 2000 cm^{-1} are broader. In the case of 25% oxidized soot the peak located between 900 - 1000 cm^{-1} and the peaks located between 1000 - 1350 cm^{-1} and 1420 - 1650 cm^{-1} are also broader. Upon heating at 100 °C in the inert atmosphere the broad peaks located in between 1600 to 2000 cm^{-1} in case of 25% oxidized soot disappear while a new broad peak appears in between 1430 to 1610 cm^{-1} . Otake et al., 1993; judge from their TPD results of air-oxidized char that acid anhydride is formed during the oxidation. In another report on the TPD analysis of air-exposed char confirmed the presence of acid anhydride (Zhuang et al., 1994).

Thus although the peak appears as a broad singlet in our case, this peak can not be attributed only to the lactone groups and the assignment to acid anhydride also should be taken into consideration.

The amount of surface oxygen complexes was found to increase in range propene soot, 75 % oxidized > 50 % oxidized > 25 % oxidized. The lowest spectrum in figure 3.15, represent propene soot with a low carbon conversion level of a 25 % oxidized.

The peak at 1610 cm^{-1} is a characteristic peak for carbon materials (Morterra et al., 1982; Akhtar et al., 1985; Friedel et al., 1967). The assignment of this peak is however still a matter of argument, whether it can be assigned to polyaromatic C=C stretching vibration or to carbonyl groups which are highly conjugated to with the polyaromatic matrix, such as quinones. The aromatic ring stretching modes are known to be enhanced when carbonyl groups are conjugated with the aromatic system. The peak at 1610 cm^{-1} can be regarded as a measure of the amount of such carbonyl. The broad peak at 1200 cm^{-1} can be attributed to the C-O stretching band. It may be composed of two parts, one from ether type complexes and the other from lactone and/or acid anhydride.

On the basis of above discussion, the following reaction scheme of carbon gasification with O_2 , can be obtained.

$C_f + O_2 \rightarrow \text{carbonyl, ether (+CO)}$	.1
$C_f + O_2 \rightarrow \text{lactone, acid anhydride}$	.2
$C_f + \text{carbonyl, ether} + O_2 \rightarrow CO_2 + CO \text{ or carbonyl, ether}$	.3
$C_f + \text{carbonyl, ether} + O_2 \rightarrow \text{lactone, acid anhydride}$	.4
$\text{lactone, acid anhydride} \rightarrow CO_2 (+CO) + 2C_f$	.5
$\text{Carbonyl, ether} \rightarrow CO + C_f$	.6



Figure 3.17

FTIR spectra of the 25% 1- and 20% 1- and 25% 2-oxidized polybutadiene films are shown at 100 °C. The curves were taken at the same time.

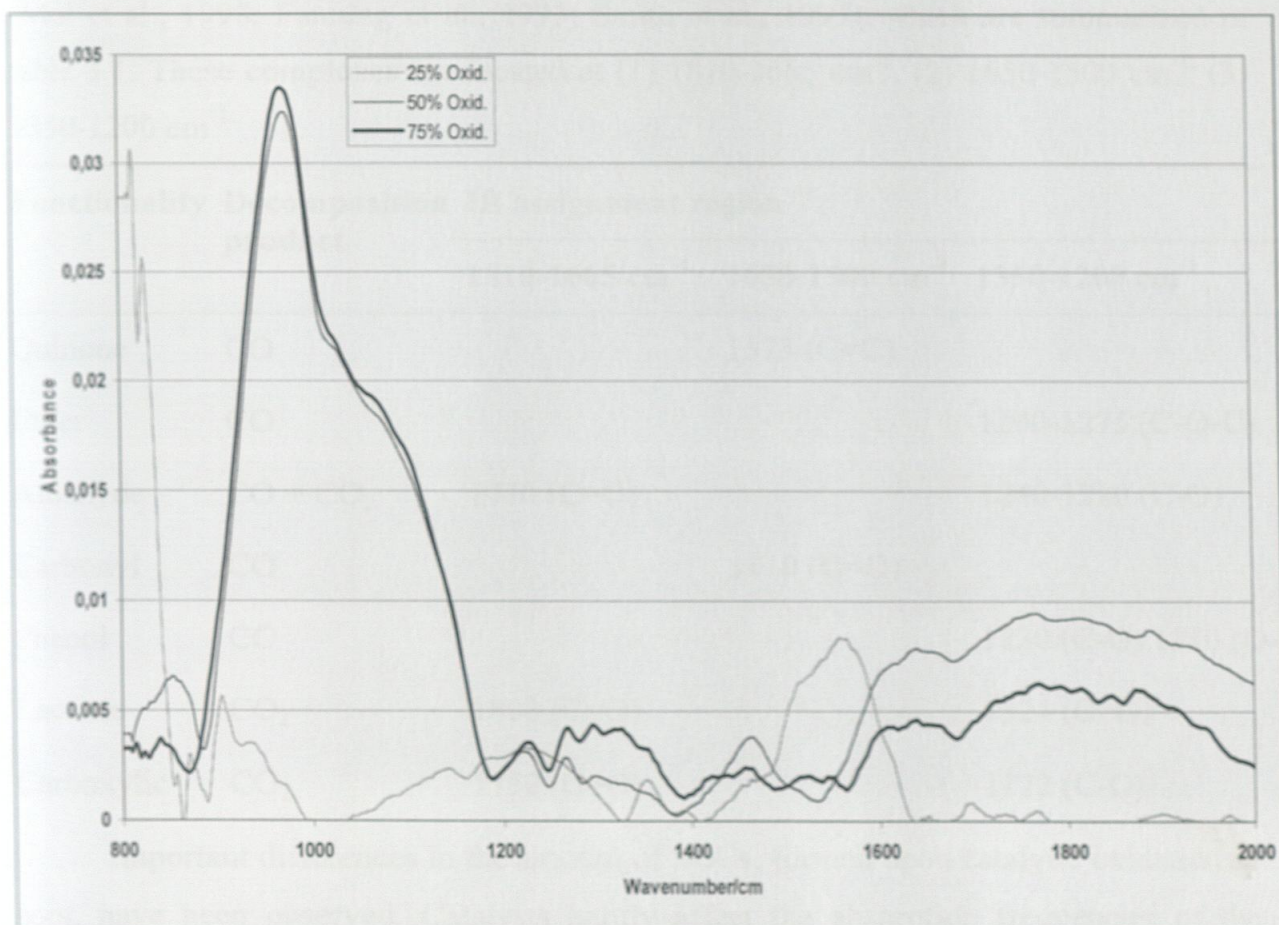


Figure 3.17

FTIR spectrum of the 25 % (·····), 50 % (---) and 75 % (—) oxidised propene soot; data are recorded at 100 °C temperature under N₂ flow (500 cm³/min).

The typical wave numbers of carbon-oxygen complexes are taken from literature (Mol et al., 1998; Fanning et al., 1993; Smith et al., 1995), which are summarized in table 3.1. These complexes are located at (1) 1810-1665 cm^{-1} , (2) 1650-1500 cm^{-1} , (3) 1350-1200 cm^{-1} .

Functionality	Decomposition product	IR assignment region		
		1810-1665 cm^{-1}	1650-1500 cm^{-1}	1350-1200 cm^{-1}
Quinone	CO		1573 (C=C)	
Ether	CO			1200-1275 (C-O-C)
Aldehyde	CO + CO ₂	1770 (C=O)		1240-1280 (C-O)
Carbonyl	CO		1610 (C=O)	
Phenol	CO			1230 (C-O) 1310 (O-H)
Lactone	CO ₂	1808 (C=O)		1324 (C=O)
Carboxylic	CO ₂	1752 (C=O)		1172 (C-O)

Important differences in the amount of SOCs, formed upon catalytic oxidation of soot, have been observed. Catalysts hardly affect the absorption frequencies of the SOCs: indications for metal oxide/soot interaction such as M-O-C bonds (M for the transition metal) have not been found. Thus, from IR examinations we derive an absent or at least a very weak interaction between the surface groups of soot and Fe₂O₃ catalyst. In principle, such an interaction might occur between Lewis acid Fe³⁺ sites of the catalyst and free electron pairs of the surface oxygen groups of the soot. This could lead to a decrease in the binding energy of neighbouring (C-C) bonds and thus to an enhancement of the attack of O₂ as proposed by quantum-mechanical calculation from Huang et al., 1999. However, our IR data do not support this model of catalytic oxidation activation. On the other hand the physical contact between soot and catalyst most likely results in van der waals interaction thus having no impact on the neighbouring (C-C) bond strength and leading to oxygen migration on the soot away from the contact point.

The IR spectra of the propene soot and fresh mixture of Fe_2O_3 /propene soot are depicted in figure 3.18. For comparison, the corresponding IR spectrum of pure soot sample is shown by the bold dotted line. These spectra were obtained by pasting the individual soot samples and Fe_2O_3 /soot mixture on potassium bromide window, which was prepared by pressing KBr. Pure soot shows a broad absorption around 1800 cm^{-1} , then a peak at 1600 cm^{-1} and a very broad absorption between 900 and 1400 cm^{-1} . These regions are the characteristic of absorption by the C=O bond in substituted aldehydes and ketones and other carbon-oxygen bonds (Akhtar et al., 1985; Akhtar et al., 1985; Herzberg 1945). The breaths of these spectral features suggest IR absorption by similar functional groups (e.g. C=O or HC=O) in molecular structures with the different local bonding environments. As it is clear from the figure that by addition of catalyst to soot a clear shift of peaks is taking place. In case of Fe_2O_3 /soot mixture the peak is shifted from 1600 to 1500 cm^{-1} , while the peak at 1000 cm^{-1} is shifted toward 900 cm^{-1} with high intensity. The observation is in line with results from Mul et al., 1998.

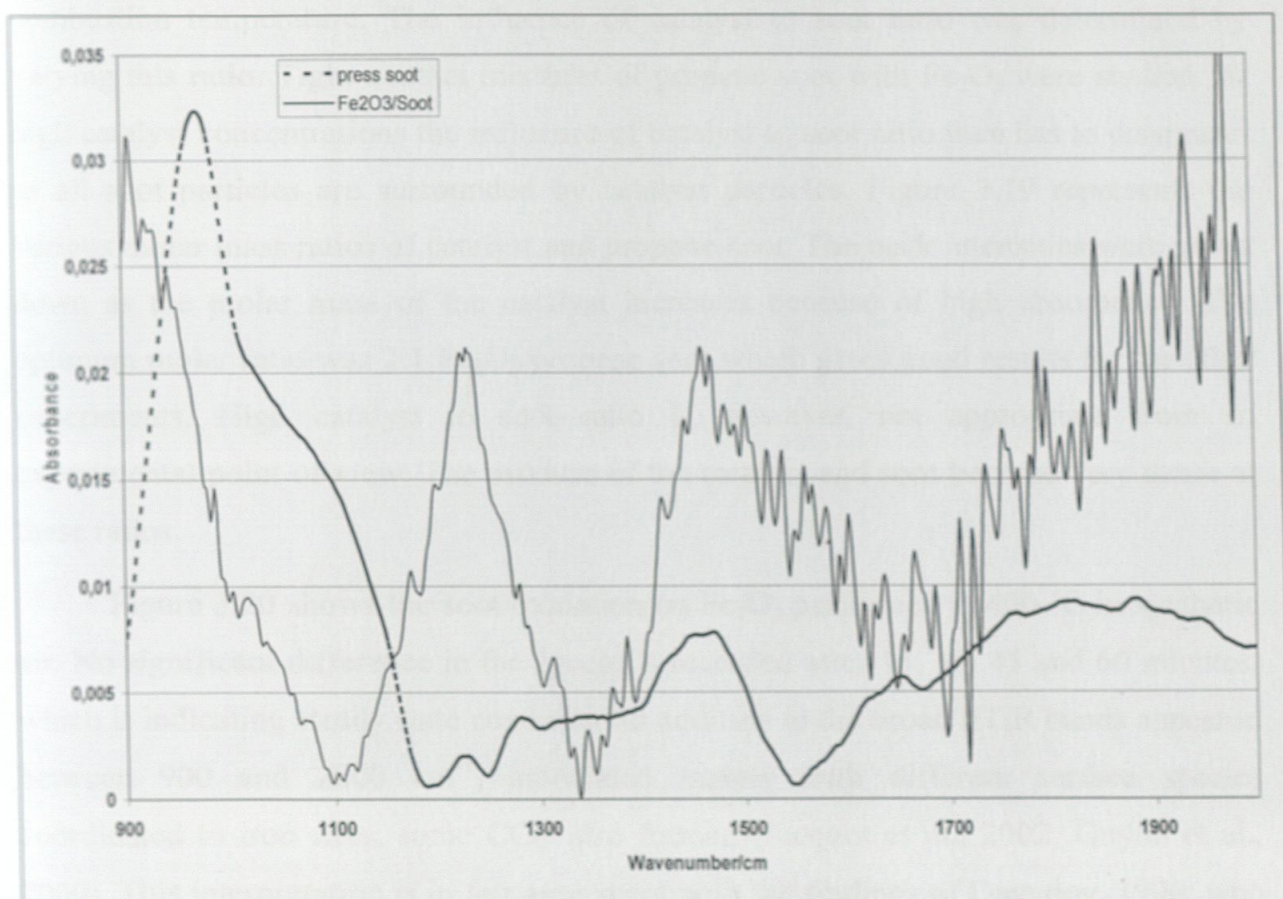


Figure 3.18

FTIR spectrum of the pure soot (---) and Fe₂O₃/soot mixture (—); data are recorded at room temperature under N₂ flow (500 cm³/min) ($n(\text{Fe}_2\text{O}_3)/n(\text{C})=2$).

The ratio between the soot and catalyst strongly influences the propene soot combustion temperature. The influence of catalyst to soot ratio was determined by varying this ratio. Tight contact mixtures of propene soot with Fe_2O_3 were studied. At high catalyst concentrations the influence of catalyst to soot ratio then has to disappear, as all soot particles are surrounded by catalyst particles. Figure 3.19 represents the various molar mass ratios of catalyst and propene soot. The peak intensities were going down as the molar mass of the catalyst increases because of high absorbance. The optimum molar ratio was 2:1 Fe_2O_3 /propene soot which gives good results for the other experiments. High catalyst to soot ratio is, however, not appropriate from an experimental point of view. The mixture of the catalyst and soot become very dense at these ratios.

Figure 3.20 shows the soot oxidation on Fe_2O_3 performed at 400 °C in synthetic air. No significant difference in the spectra's recorded after 15, 30, 45 and 60 minutes, which is indicating steady state condition. In addition to the broad FTIR bands appeared between 900 and 2000 cm^{-1} , associated mainly with different surface species coordinated to iron sites; some CO_2^- also formed (Jacquot et al., 2002; Guyon et al., 2000). This interpretation is in fair agreement with the findings of Davydov, 1990; who also noted the exclusive formation of coordinated carbonate on Fe_2O_3 . The FTIR spectra of Fe_2O_3 /soot mixture suggesting strongly the conversion of soot to CO_2 .

Fig. 3.21 represents the Fe_2O_3 /printex mixture, which was exposed to air at 400 °C. The bold line represents the spectra in nitrogen flow. As the sample is exposed to air, the peak intensities are increases with the time and the maximum peak intensity was recorded after one hour which is clear from the figure.

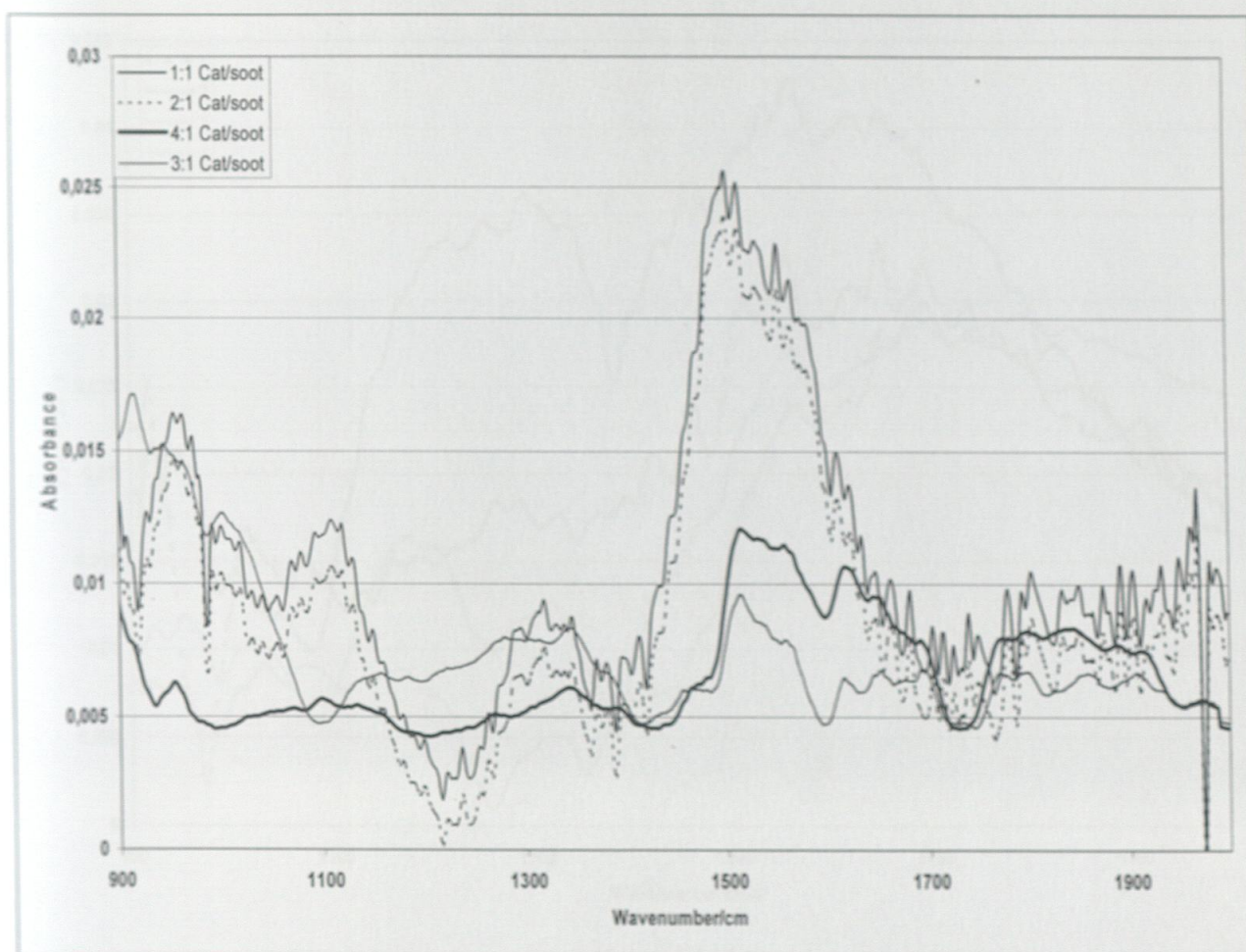


Figure 3.19

FTIR spectra of the various Fe_2O_3 /soot molar ratio, (—) = 1:1, (---) = 2:1, (·····) = 3:1, (—) = 4:1; data are recorded at 100 °C temperature under N_2 flow (500 cm^3/min).



Figure 3.20

FTIR spectra of the Fe_2O_3 /soot mixture exposed to air. (---) = subsequent treatment in air at 400 °C after 15 min, (—) = after 30 min, (·····) = after 45 min, (—) = after 60 min; data are recorded at 400 °C temperature under air flow ($500 \text{ cm}^3/\text{min}$) ($n(\text{Fe}_2\text{O}_3)/n(\text{C}) = 2$).

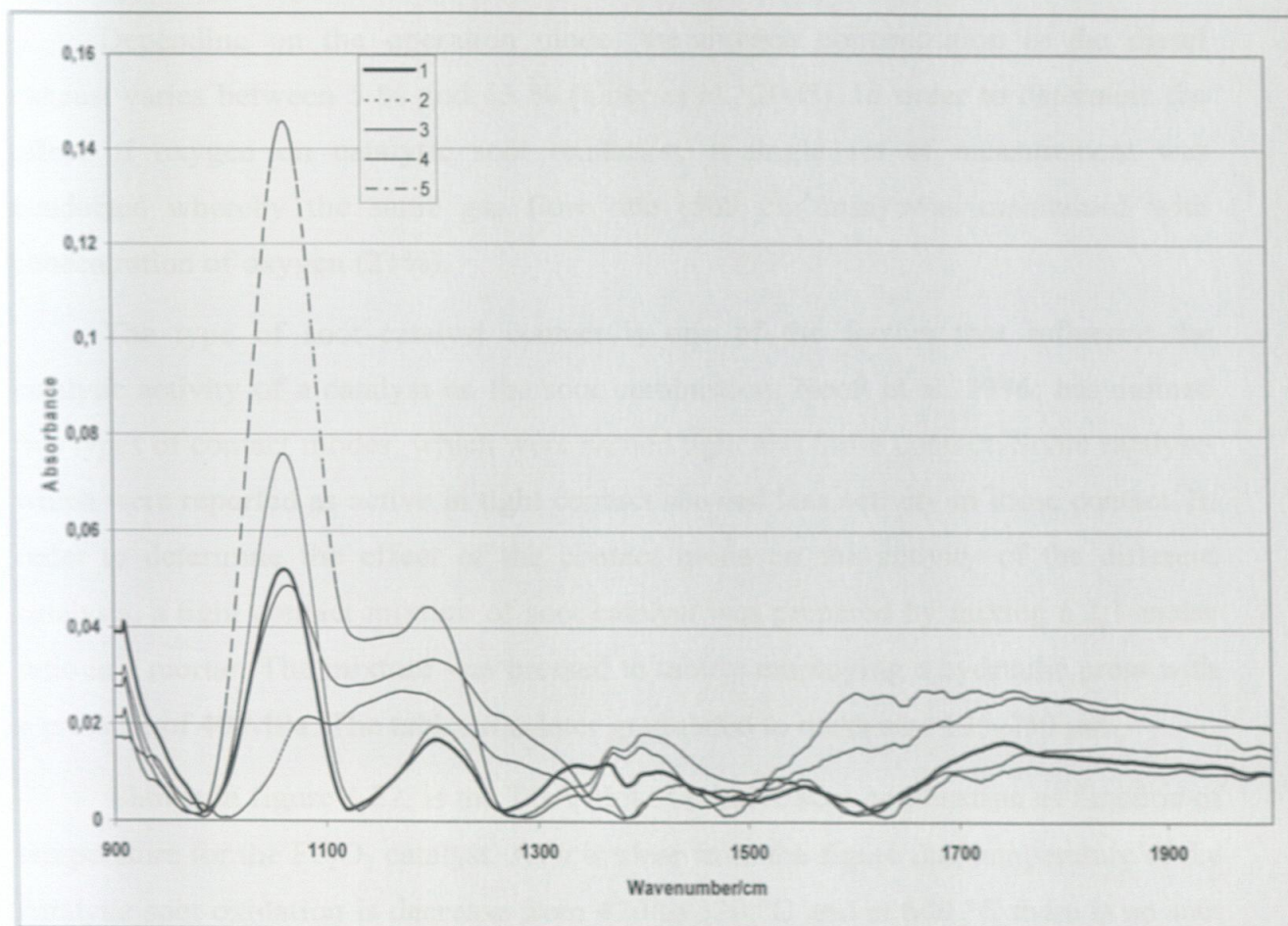


Figure 3.21

FTIR spectra of the Fe_2O_3 /printex mixture exposed to air at 400°C . (—) = N_2 flow ($500\text{ cm}^3/\text{min}$), (·····) = subsequent treatment in air at 400°C after 15 min, (—) = after 30 min, (---) = after 45 min, (—·—) = after 60 min; data are recorded at 400°C temperature under air flow ($500\text{ cm}^3/\text{min}$) ($n(\text{Fe}_2\text{O}_3)/n(\text{C})=2$).

3.3. Effect of O₂ concentration & the catalyst-soot contact on combustion.

Depending on the operation mode, the oxygen concentration in the diesel exhaust varies between 5 % and 15 % (Uner et al., 2005). In order to determine the effect of oxygen on catalytic soot oxidation, a single set of measurement was conducted whereby the same gas flow rate (500 cm³/min) was maintained with concentration of oxygen (21%).

The type of soot-catalyst contact is one of the factors that influence the catalytic activity of a catalyst on the soot combustion. Neeft et al. 1996; has defined two types of contact modes, which were named tight and loose contact. Some catalysts which were reported as active in tight contact showed less activity in loose contact. In order to determine the effect of the contact mode on the activity of the different catalysts, a tight contact mixture of soot/catalyst was prepared by mixing a 2:1 molar ratio in a mortar. The mixture was pressed to tablets employing a hydraulic press with a pressure of 40 MPa. The tablet was later granulated to mesh size 125-250 μ m.

Shown in figure 3.22, is the TGA plot of relative soot combustion as function of temperature for the Fe₂O₃ catalyst. As it is clear from the figure that temperature of the catalytic soot oxidation is decrease from 420 to 320 °C and at 600 °C there is no soot particle present. The activity of the catalyst is defined by the combustion temperature, which is the temperature of the TGA curve where 50% (T₅₀) of the soot is oxidized. In these figure of the combustion experiments, the sharp mass loss are attributed to the thermal runaway reactions (ignition).

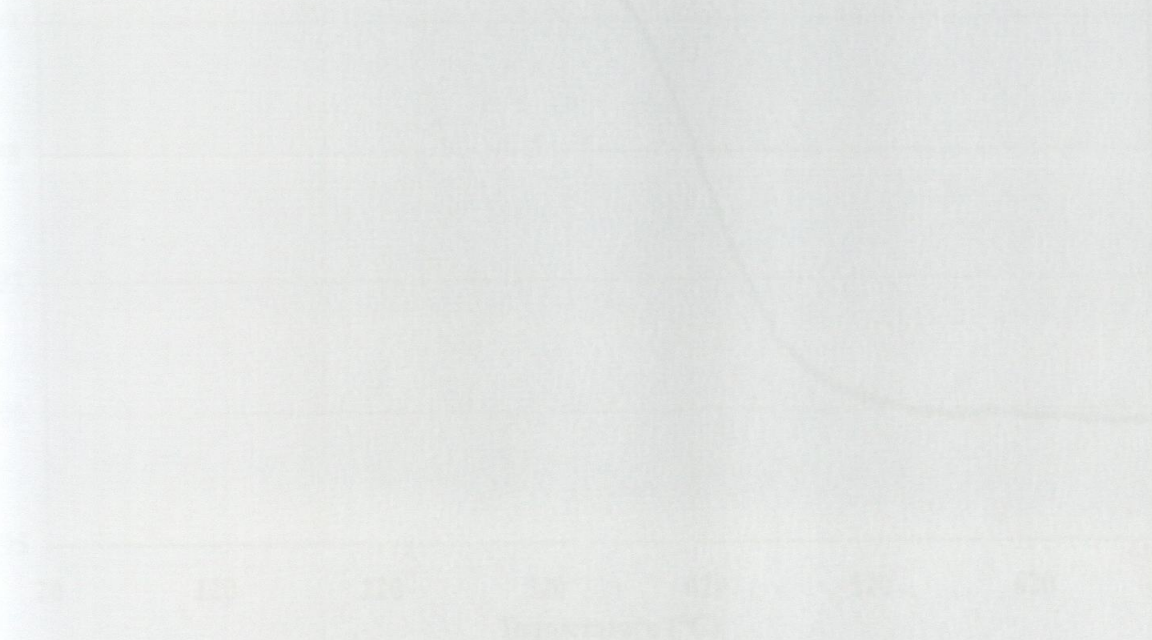
As propene soot has a considerable surface area (BET surface area of about 90 m²g⁻¹). So the reaction is thought to take place at the interface between soot and catalyst.

Figure 3.23, 3.24 and, 3.25 represent the TGA profile of catalyst with commercial soot (printex L), graphite, and activated charcoal respectively. It is obvious from these figures that Fe₂O₃ could catalyze the combustion of all types of carbon samples.

These results clearly show Fe₂O₃ that show much better catalytic activity to propene soot combustion than printex L, activated charcoal, and graphite. The reason

for this activity is the SOF, and Fe_2O_3 is a good catalyst for the soluble organic fraction (Stanmore et al., 2001). It is worth reporting, at this stage, that Fe_2O_3 is a good catalyst for SOF.

Comparing these TG curves obtained from figures 3.22, 3.23, 3.24, & 3.25 show a single weight lose step occurring at $< 600\text{ }^\circ\text{C}$. These results show that the combustion temperature of soot decreases in the presence of catalyst.



3.22

TGA profile of catalyst and product (SOF) showing a single weight loss step at $< 600\text{ }^\circ\text{C}$ (20 mmol, Fe_2O_3 0.12 g (0.0004 mol), SO_2 0.01 g (0.0001 mol), SO_3 0.01 g (0.0001 mol) (STP), SO_2 0.01 g (0.0001 mol), SO_3 0.01 g (0.0001 mol).

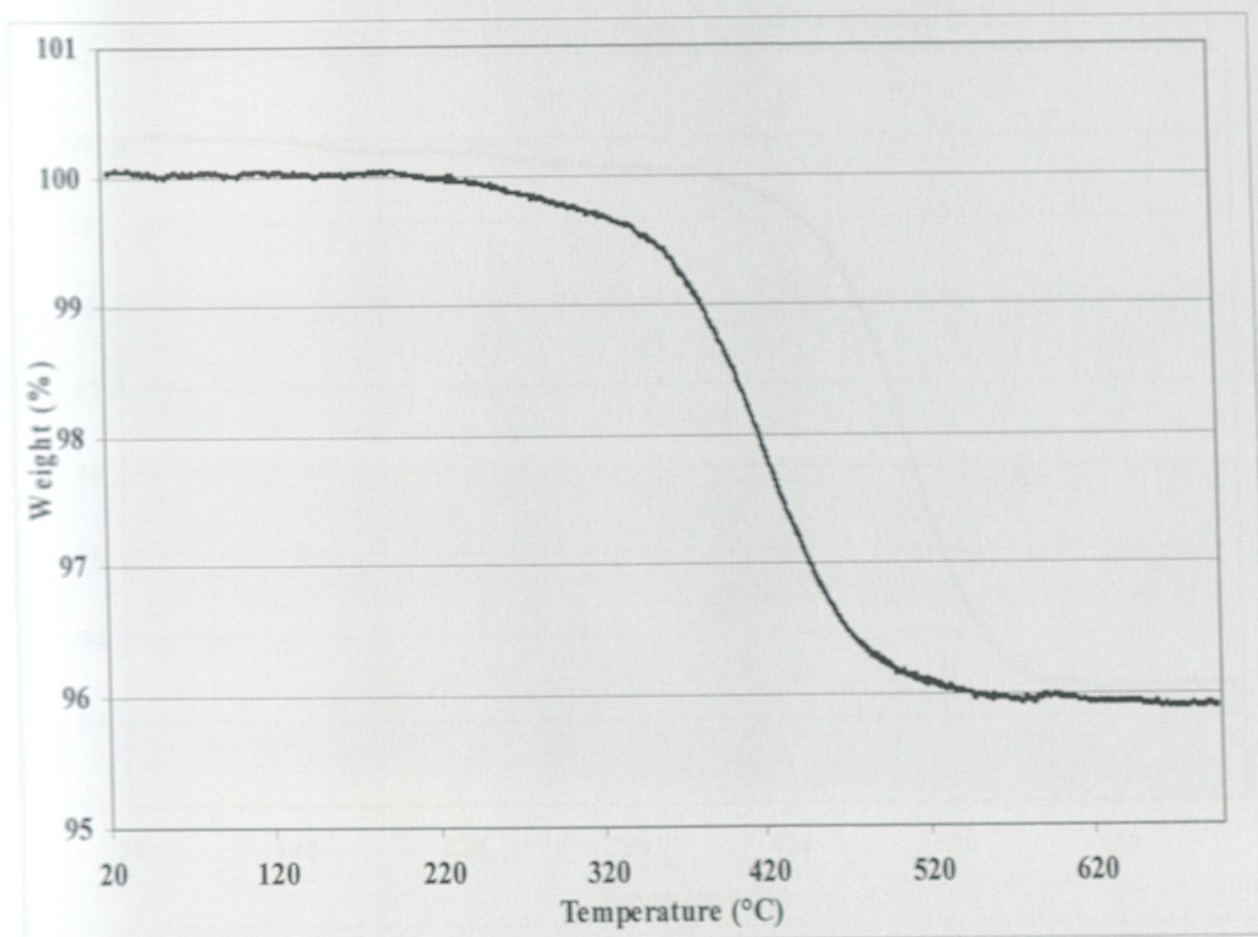


Fig. 3.22.

TGA profile of catalyst and propene soot. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19$ g (20 mmol), $m(\text{C}) = 0.12$ g (10 mmol), $c(\text{O}_2) = 21.0$ vol.%, N_2 balance, $F = 500$ cm^3/min (STP), $\Delta T/\Delta t = 10$ K/min, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

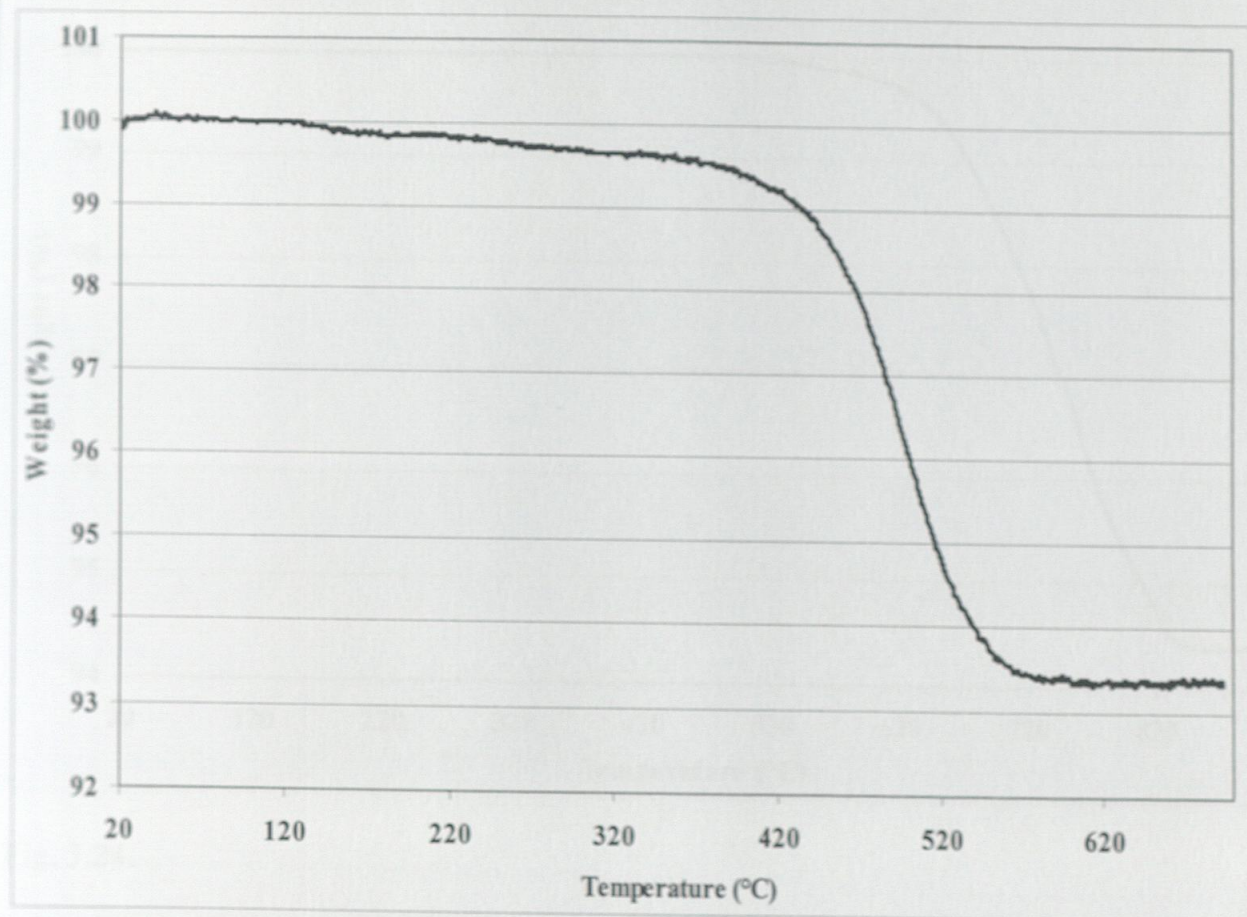


Fig. 3.23.

TGA profile of catalyst and printex. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 10 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

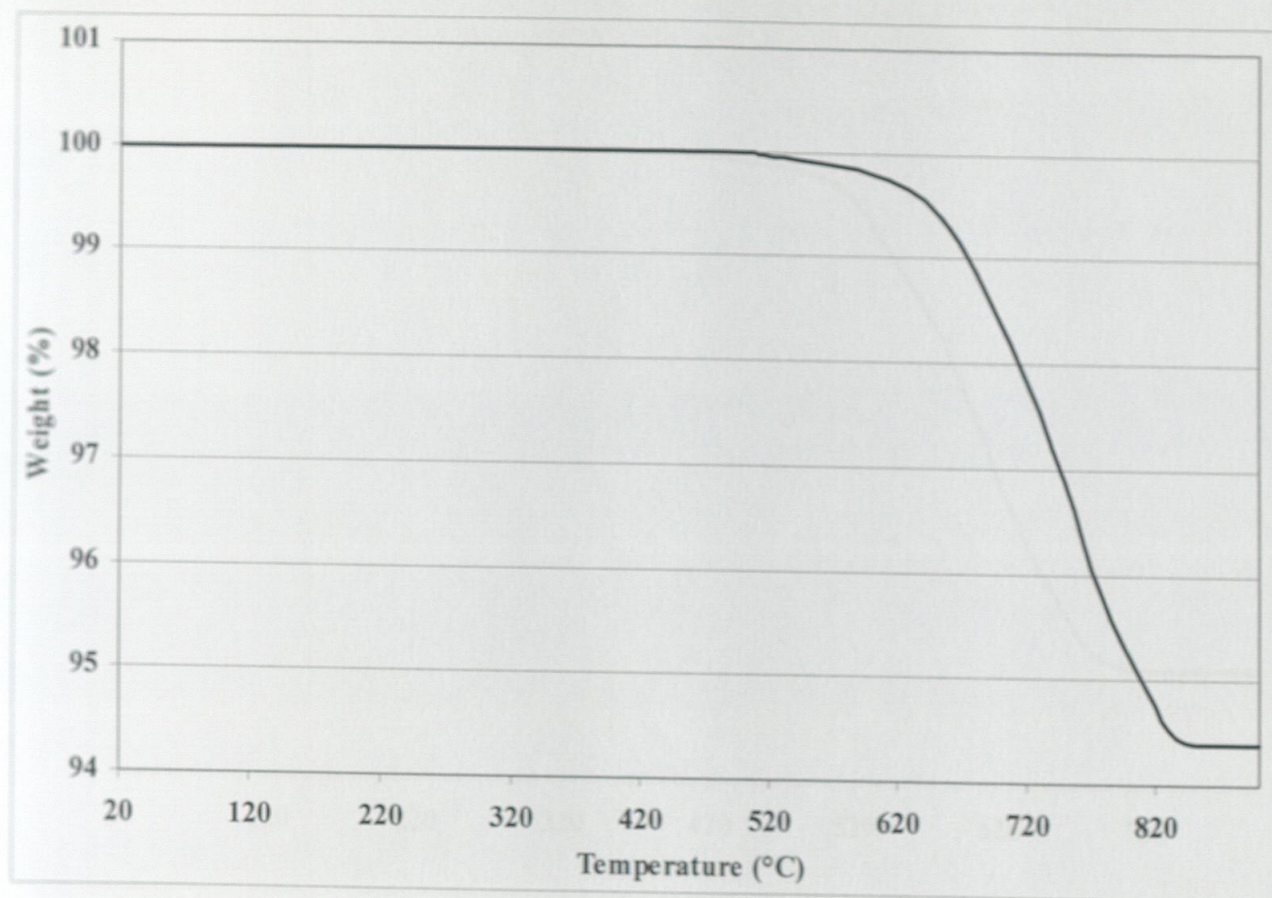


Fig. 3.24.

TGA profile of catalyst and graphite. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 10 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

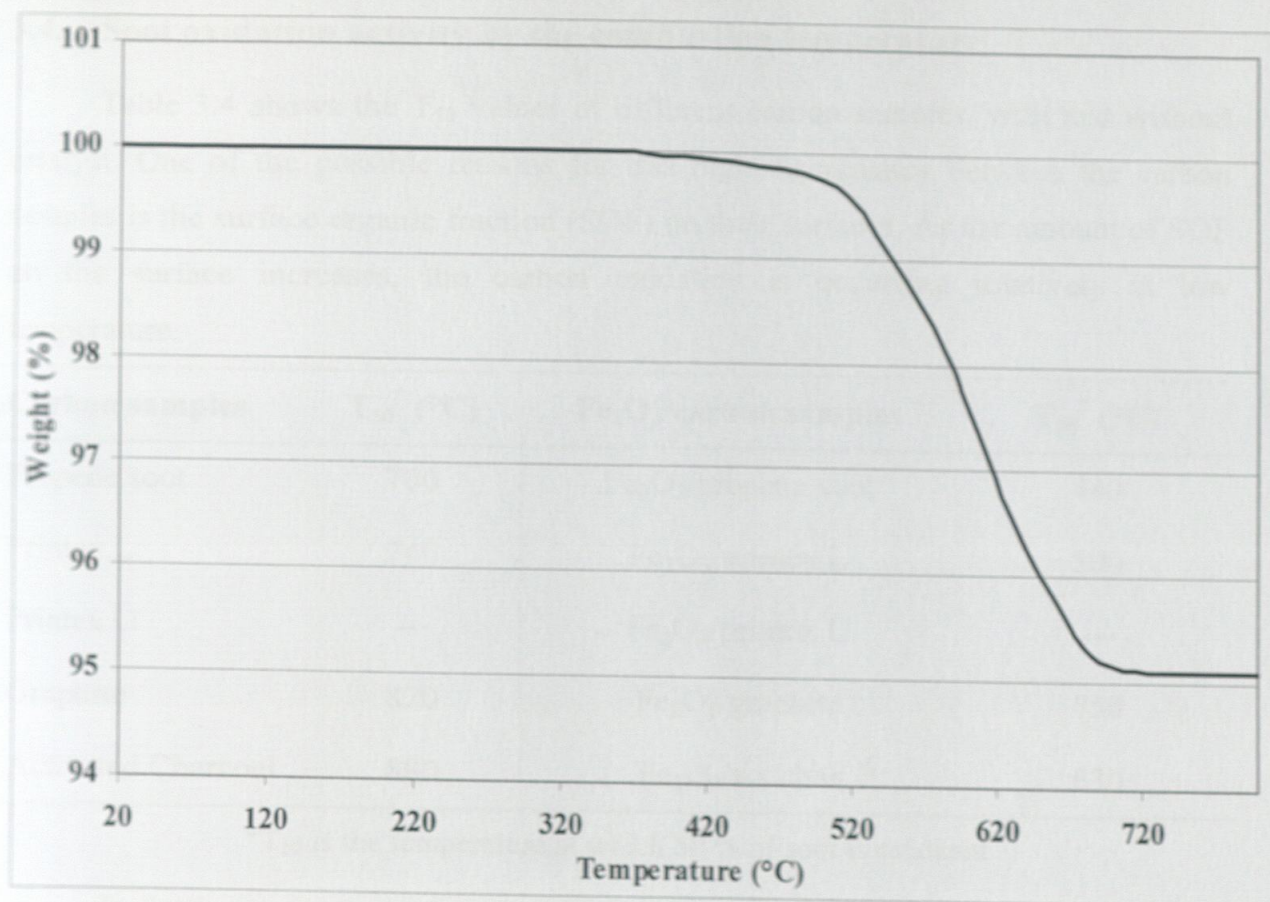


Fig. 3.25.

TGA profile of catalyst and activated charcoal. Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 10 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm .

3.4. Soot oxidation activity by the combustion temperature

Table 3.4 shows the T_{50} values of different carbon samples, with and without catalyst. One of the possible reasons for this high discrepancy between the carbon samples is the surface organic fraction (SOF) on their surfaces. As the amount of SOF on the surface increases, the carbon oxidation is occurring relatively at low temperature.

Carbon samples	T_{50}^* (°C)	Fe ₂ O ₃ /carbon samples	T_{50}^* (°C)
Propene soot	700	Fe ₂ O ₃ /propene soot	440
Printex L	740	Fe ₂ O ₃ /printex L	500
Printex U	---	Fe ₂ O ₃ /printex U	---
Graphite	820	Fe ₂ O ₃ /graphite	750
Activated Charcoal	880	Fe ₂ O ₃ /act.char	630

* T_{50} is the temperature at which 50 % of soot is oxidized.

In synthetic air, the weight losses profiles are significant. From figure 3.26, and 3.27, it has to be noted that the weight loss is a simultaneous effect of volatilization, reactive gas adsorption, and oxidation. At higher temperature where soot oxidation expectedly takes place, the weight loss decreases much faster in air and finally nothing left. As it is assumed that the desorption of surface groups might also contribute to the weight loss at higher temperature, which is clear from the figure 3.26 and 3.28.

Figure 3.27 represent the soot treated in nitrogen flow. For the soot combustion with air no residual ash was recorded which means all of the soot was burned. When the soot was treated under nitrogen flow, only 2.6 weight % of the soot was loss. This is useful for the intended examination of the catalytic reaction between NO_x and soot, as parallel reactions and unwanted secondary effects that may both might be caused by pronounced presence of adsorbed hydrocarbons are to be neglected.

Figure 3.28 show that the activated charcoal has high activity than printex and graphite. It can be seen that the activated charcoal show a TG curve that is

dramatically different from that of other carbon samples. It is because of the trace impurities of Cu and Fe in the sample from the manufacturer specification.

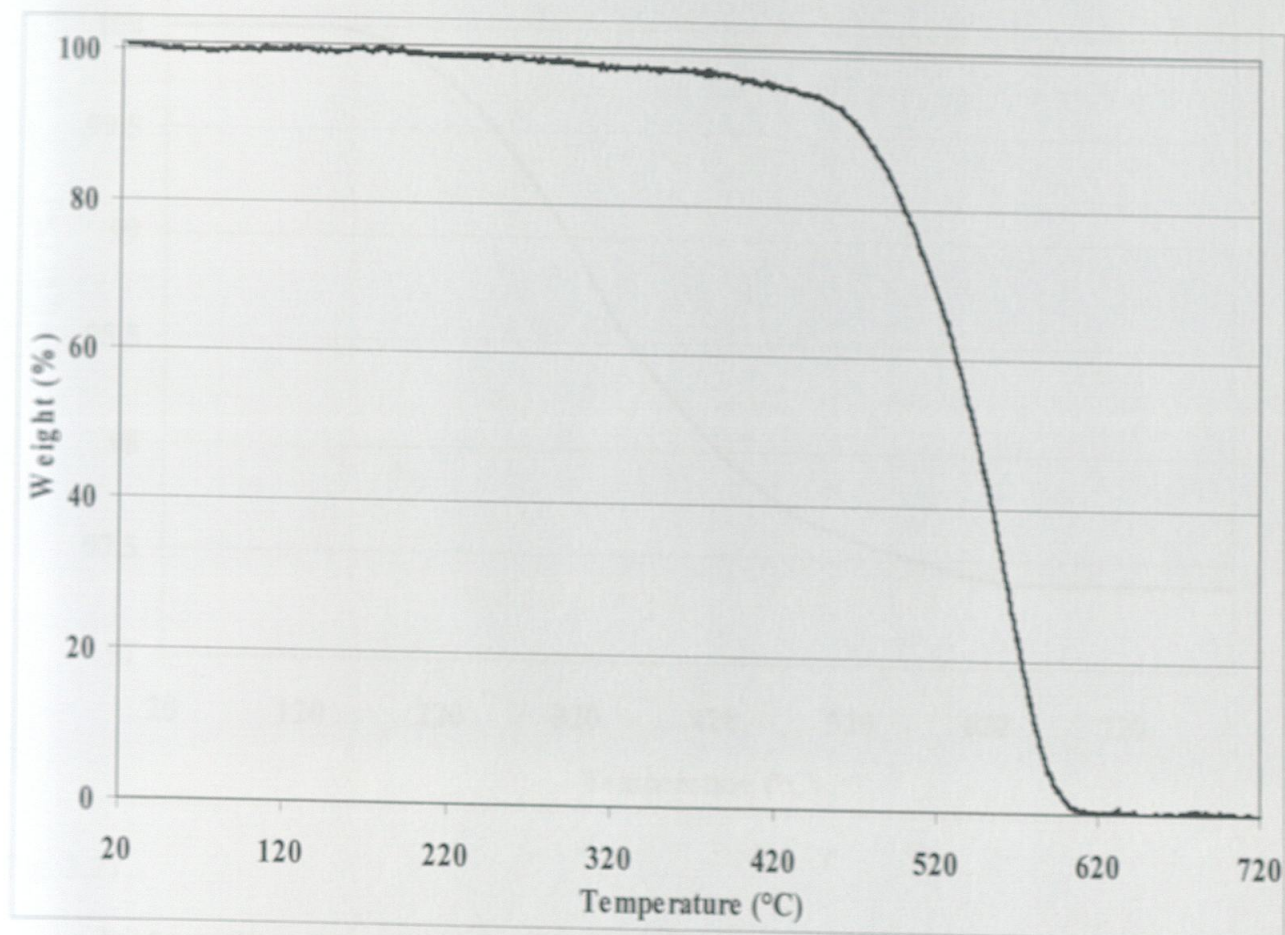


Fig. 3.26.

TGA profile of propene soot. Reaction conditions: $m(\text{C}) = 3.00 \text{ mg}$, $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 10 \text{ K/min}$, soot used of 125-250 μm .

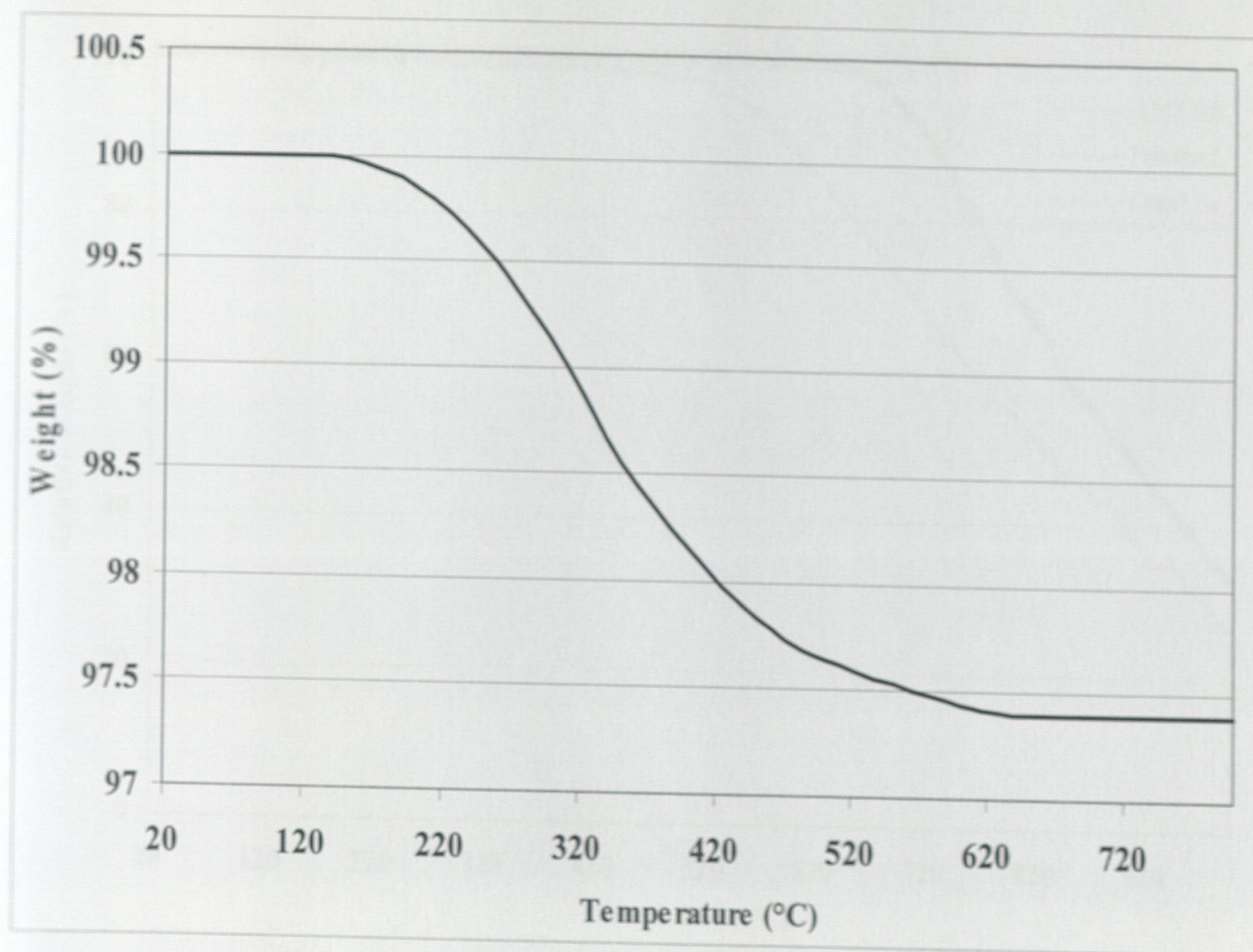


Fig. 3.27.

TGA profile of propene soot. Reaction conditions: $m(C) = 32.00$ mg, $F = 500$ cm^3/min (STP) N_2 , $\Delta T/\Delta t = 10$ K/min, soot used of 125-250 μm .

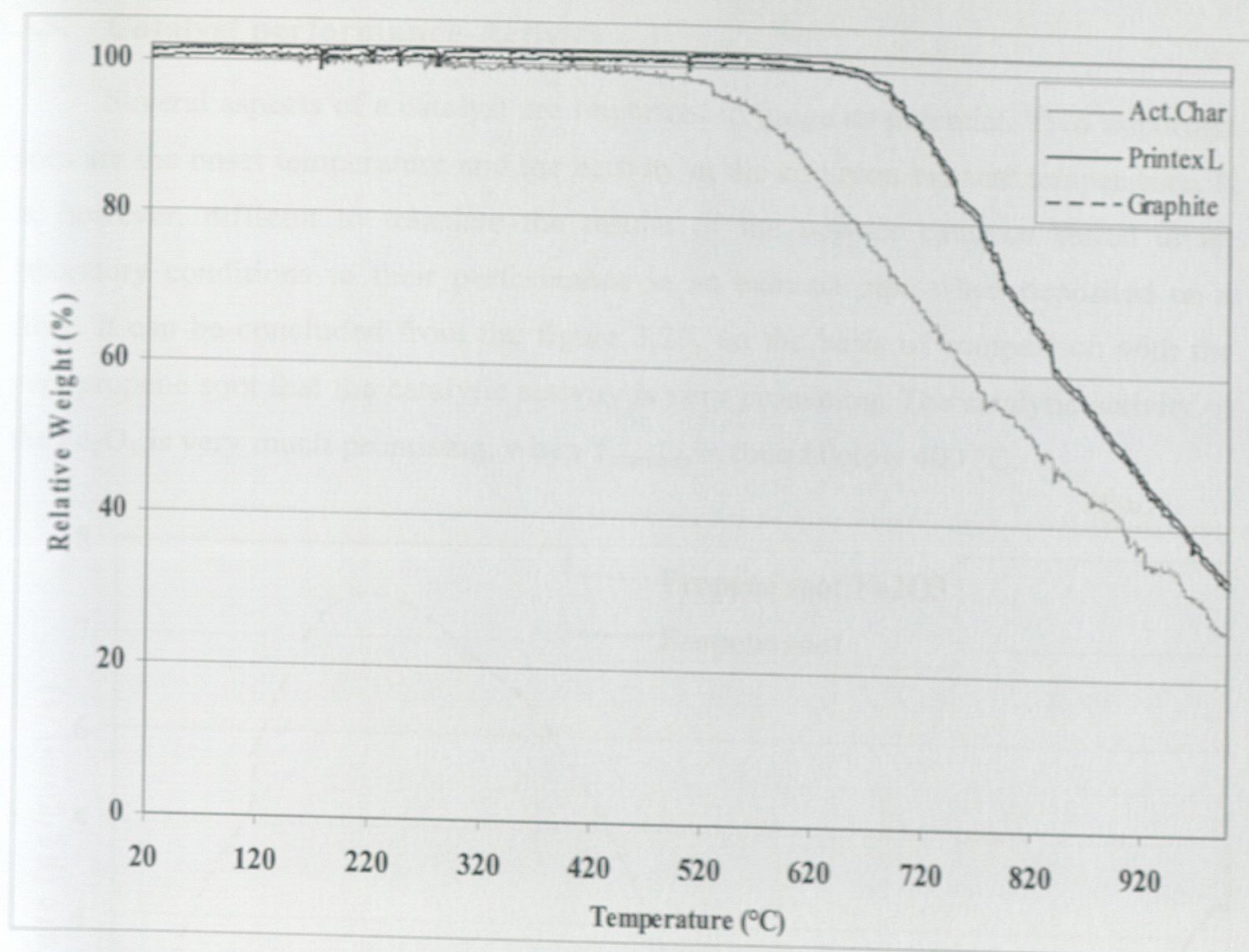


Fig. 3.28.

TGA profile of (...) = Activated Charcoal, (—) = Printex L, and (---) = Graphite. Reaction conditions: $m(C) = 3.00$ mg, $c(O_2) = 21.0$ vol.%, N_2 balance, $F = 500$ cm³/min (STP), $\Delta T/\Delta t = 10$ K/min, carbon samples used of 125-250 μ m.

3.5. Catalyst performance-Activity

Several aspects of a catalyst are important to judge its potential. Two important ones are the onset temperature and the activity at the common exhaust temperature. It is, however, difficult to translate the results of the powder catalysts tested under laboratory conditions to their performance in an exhaust pipe when deposited on a filter. It can be concluded from the figure 3.29, on the basis of comparison with the pure propene soot that the catalytic activity is very promising. The catalytic activity of the Fe_2O_3 is very much promising, when $T_{\text{max.rate}}$ is found below 400 °C.

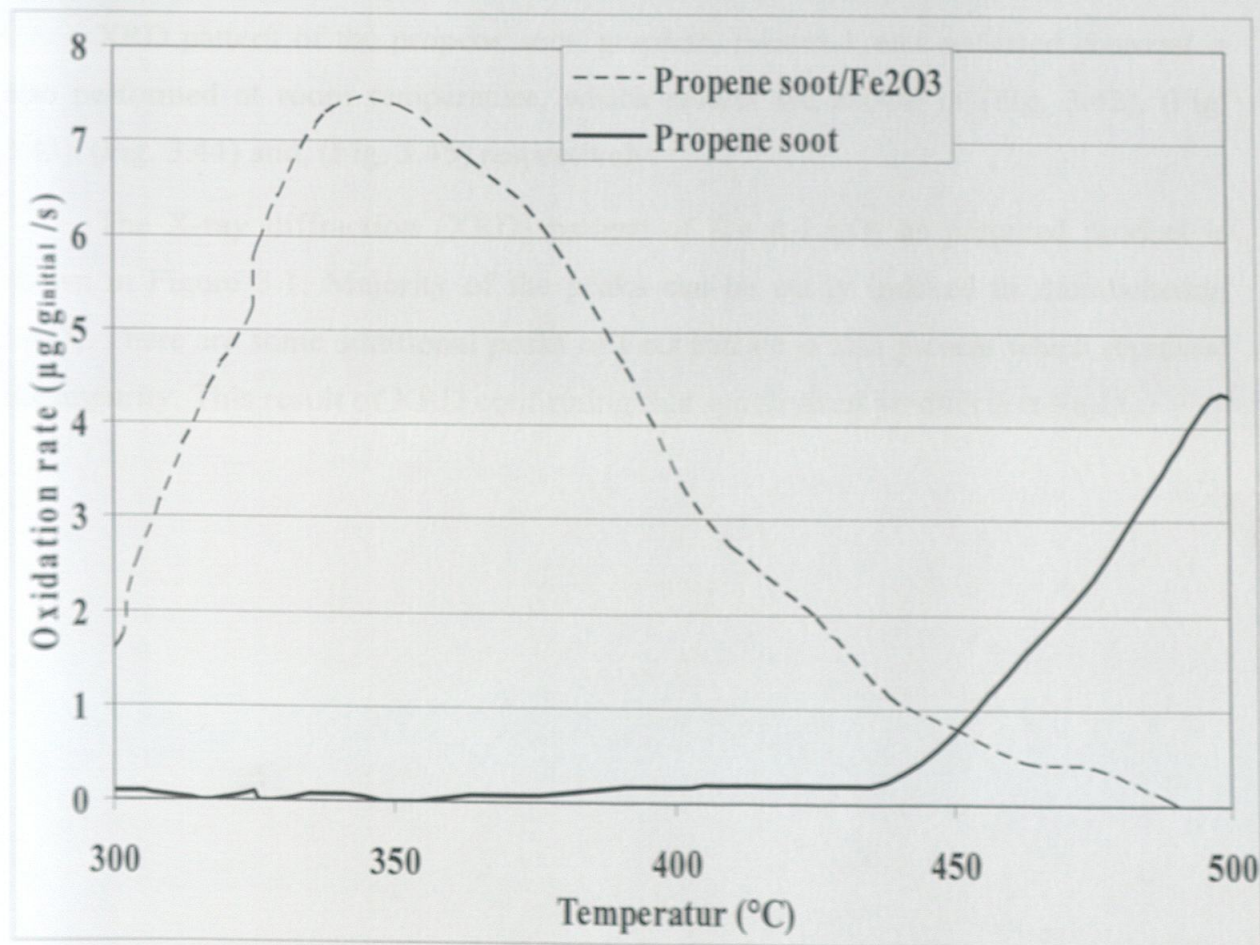


Fig. 3.29.

Oxidation rate as a function of temperature of propene soot (—) and Fe_2O_3 /propene soot mixture (---). Reaction conditions: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$, $m(\text{C}) = 0.120 \text{ g}$, $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, propene soot used of 125-250 μm .

3.6. Morphology of α -Fe₂O₃ & soot particles

Hematite has a rhombohedrally centred hexagonal structure of the corundum type with a closed packed oxygen lattice in which two-thirds of the octahedral sites are occupied by Fe (III) ions (Wang et al., 2004).

The crystal structure is confirmed by powder X-ray diffraction that is performed at room temperature on a siemens D 501 employing Ni filtered Cu K α radiation. Fe₂O₃ and different forms of the carbon have been studied by X-ray diffraction (XRD). XRD analysis revealed that α -Fe₂O₃ obtained was the hexagonal phase (Fig. 3.41).

XRD pattern of the propene soot, graphite, printex l, and activated charcoal is also performed at room temperature, which results are shown in (Fig. 3.42), (Fig. 3.43), (Fig. 3.44) and, (Fig. 3.45) respectively.

The X-ray diffraction (XRD) pattern of the α -Fe₂O₃ as prepared product is shown in Figure 3.1. Majority of the peaks can be easily indexed to rhombohedral Fe₂O₃. There are some additional peaks of FeO and Fe is also present which represent the impurity. This result of XRD confirming that synthesised product is α -Fe₂O₃.

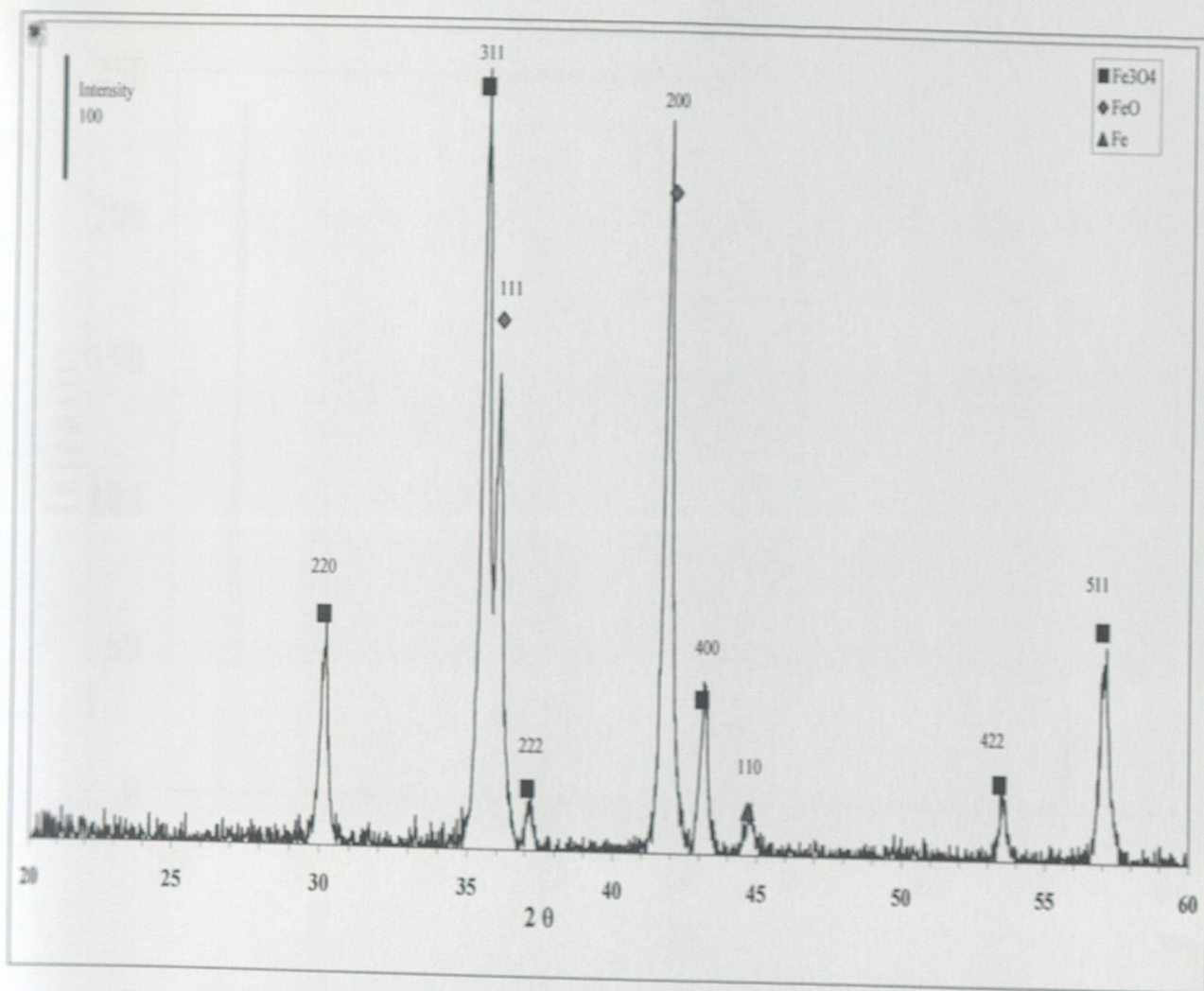


Figure 3.41

X-ray diffraction pattern of freshly prepared α -Fe₂O₃.

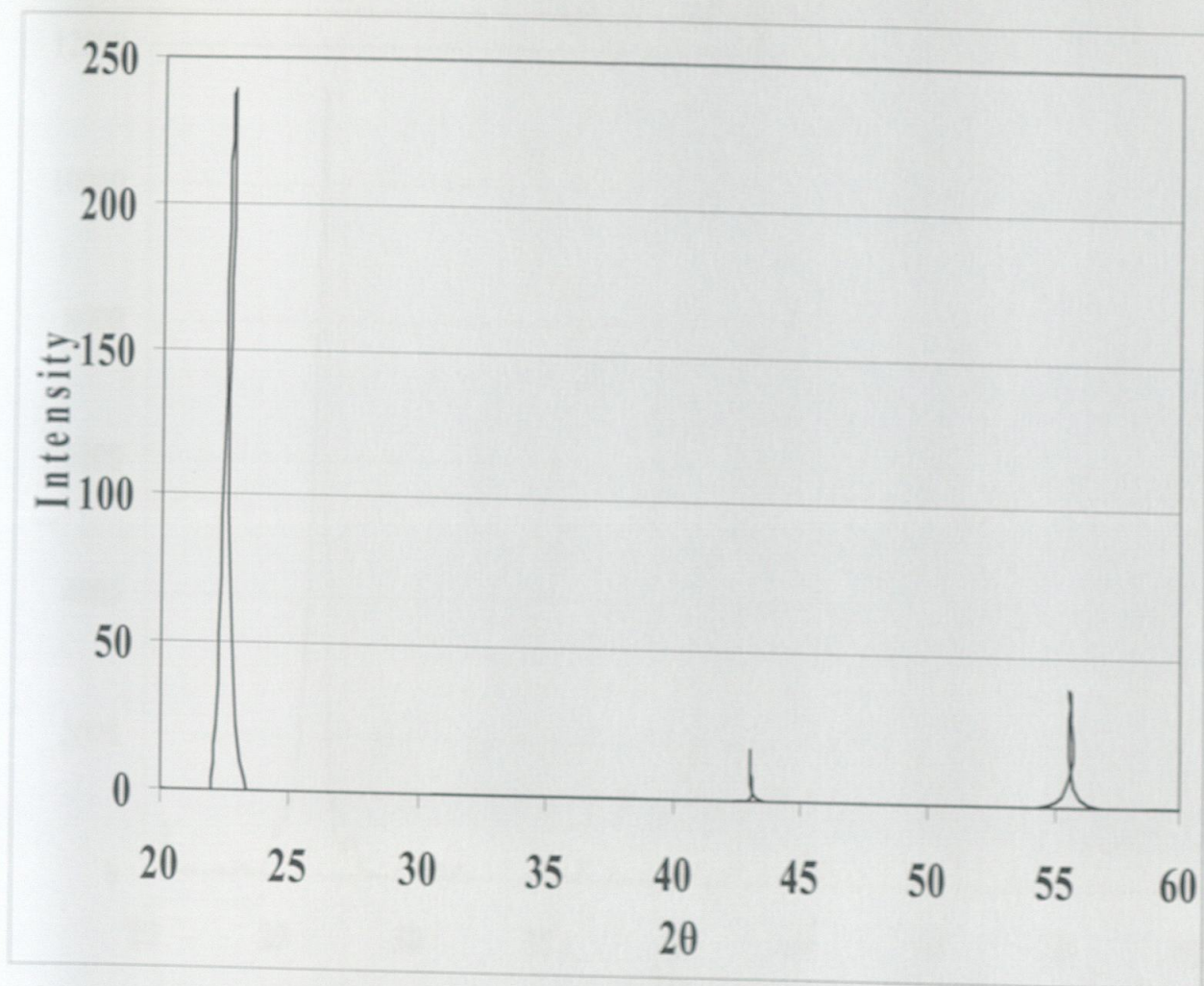


Figure 3.42

X-ray diffraction pattern of propene soot.

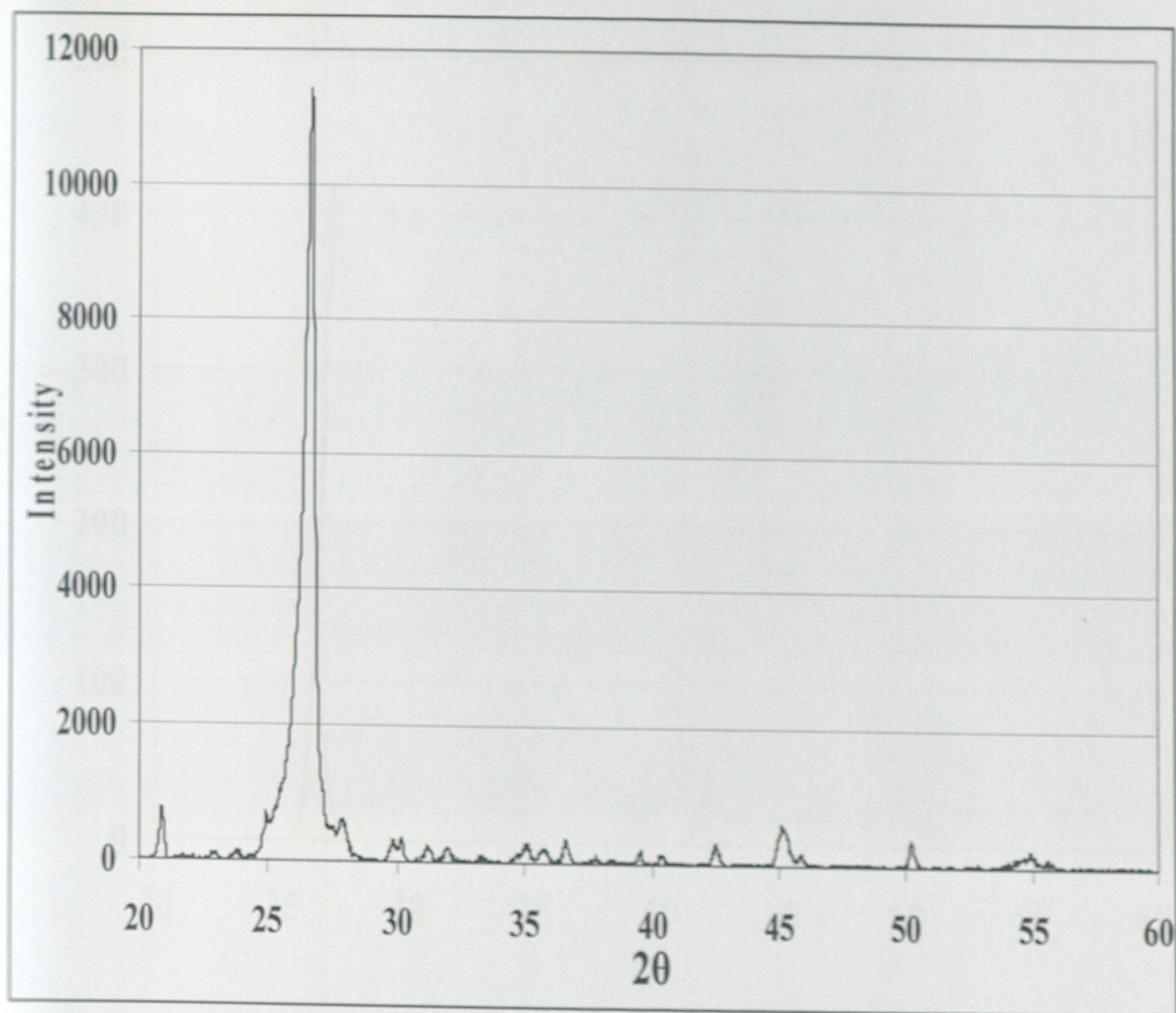


Figure 3.43

X-ray diffraction pattern of graphite.

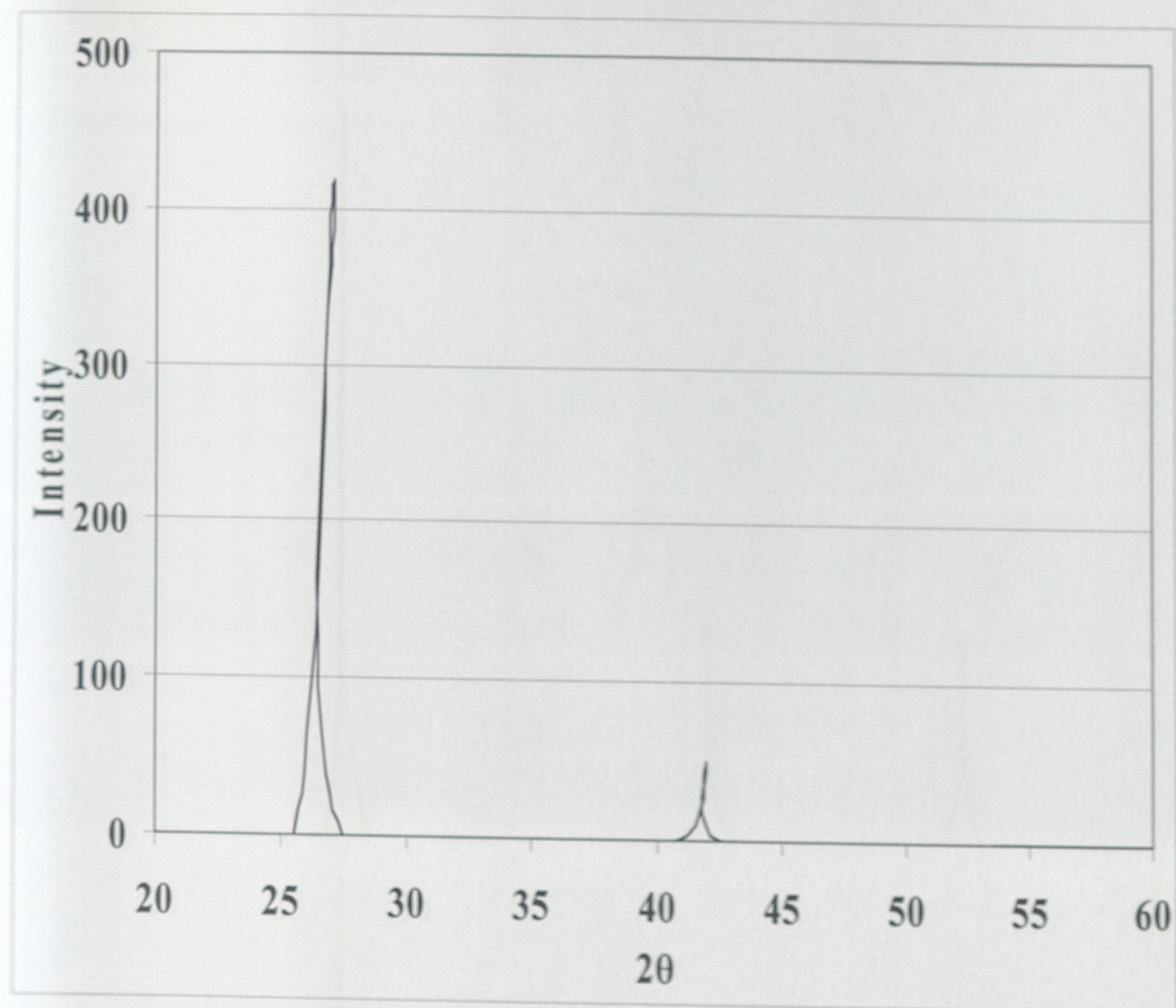


Figure 3.44

X-ray diffraction pattern of printex L.

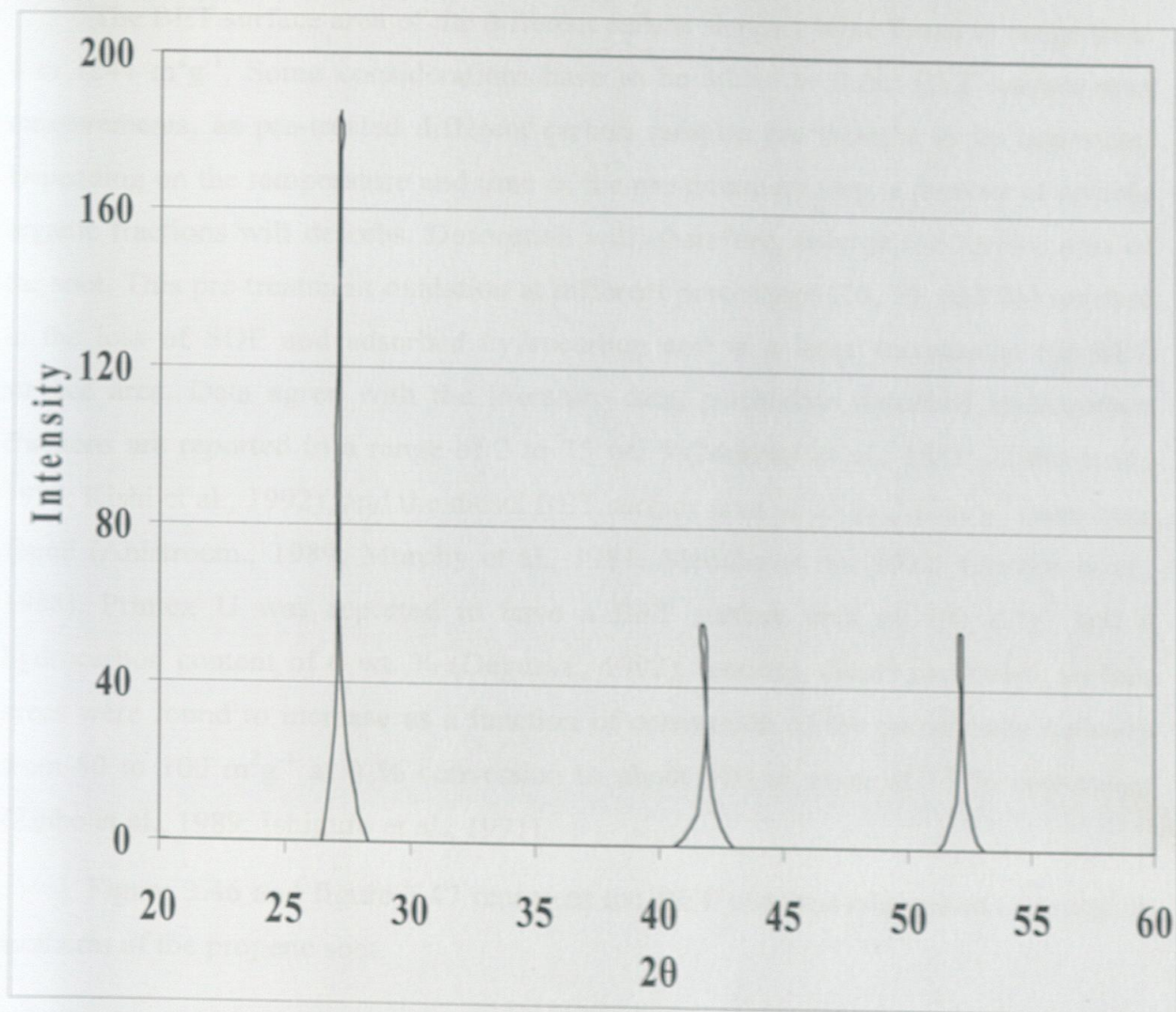


Figure 3.45

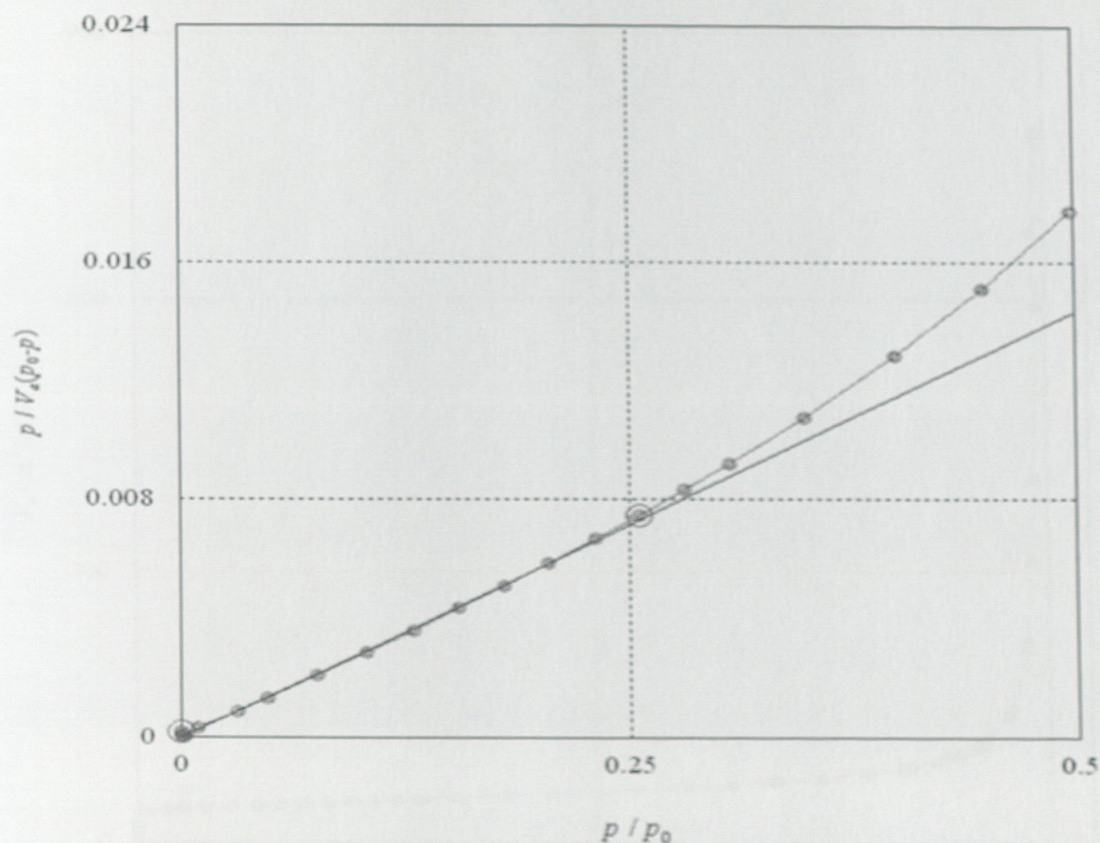
X-ray diffraction pattern of activated charcoal.

The BET surface area of the different carbon samples were found to range from 4 to 1244 m²g⁻¹. Some considerations have to be added to these BET surface area measurements, as pre-treated different carbon samples are thought to be important. Depending on the temperature and time of the pre-treatment step, a number of soluble organic fractions will desorb. Desorption will; therefore, enlarge the surface area of the soot. This pre-treatment oxidation at different percentage (25, 50, and 75) resulted in the loss of SOF and adsorbed hydrocarbon and in a large increase in the BET surface area. Data agree with the literature data, particulate desorbed hydrocarbon fractions are reported in a range of 2 to 75 wt. % (Murphy et al., 1981; Zinbo et al., 1989; Kishi et al., 1992), and the diesel BET surface area of 35 to 270 m²g⁻¹ have been found (Ahlstroem., 1989; Murphy et al., 1981; Medalia et al., 1982; Glasson et al., 1988). Printex U was reported to have a BET surface area of 100 m²g⁻¹ and a hydrocarbon content of 6 wt. % (Degussa., 1992). Besides, diesel particulate surface areas were found to increase as a function of conversion of the particulates typically from 50 to 100 m²g⁻¹ at 0 % conversion to about 300 or more at 75 % conversion (Zinbo et al., 1989; Ishiguro et al., 1991).

Figure 3.46 and figure 3.47 represent the BET plot and adsorption / desorption isotherm of the propene soot.

Samples	Oxidation (%)	BSA (m ² g ⁻¹)
Propene Soot	0	91
	25	385
	50	484
	75	544
Printex L	0	152
	25	490
	50	563
	75	667

Printex U	0	90
	25	484
	50	766
	75	1244
Graphite	0	4
	25	5
	50	6
	75	4



BET-Plot

Adsorptive N₂

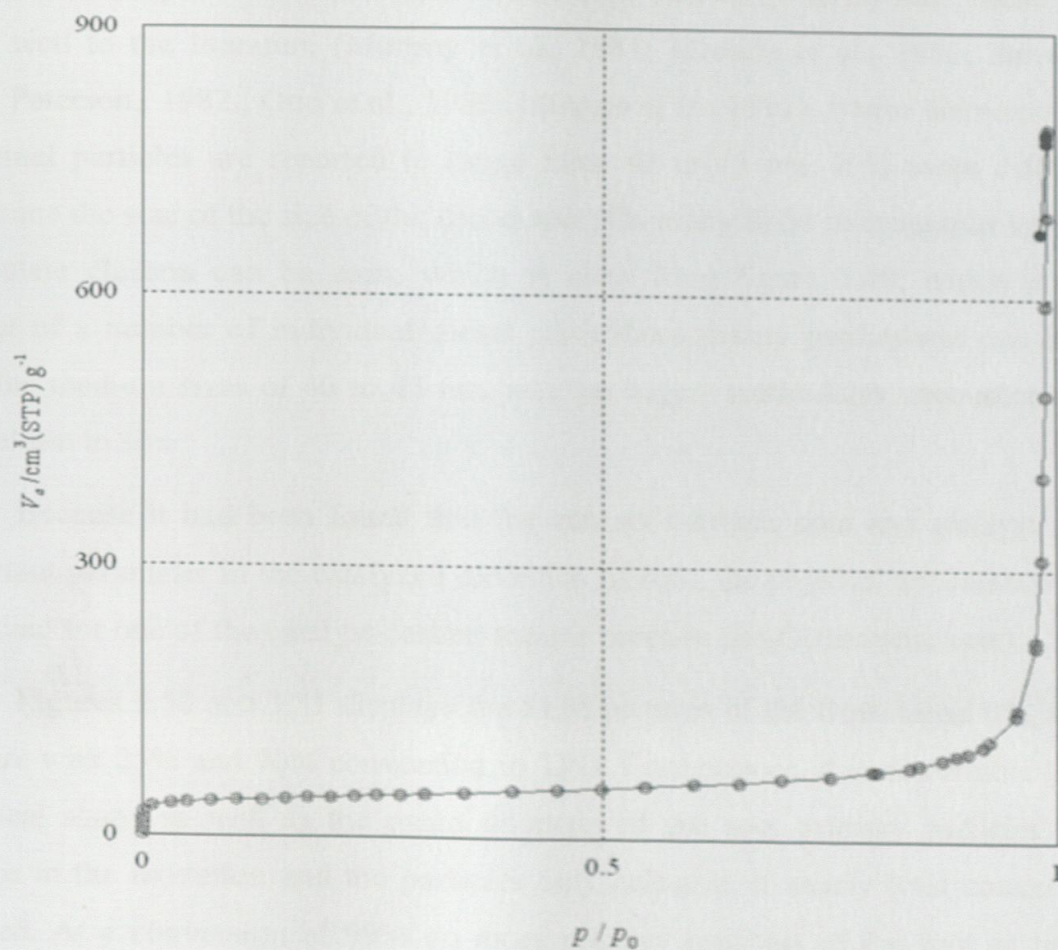
Adsorption temperature 77 [K]

©PrintexL.DAT

Sample weight	0.2063	[g]	Date of measurement	09/12/14
Saturated vapor pressure	101.78	[kPa]	Time of measurement	8:44:41
V_m	34.908	[cm ³ (STP) g ⁻¹]	$a_{s,BET}$	1.5193E+02 [m ² g ⁻¹]
C	2642.7		Total pore volume ($p/p_0=0.990$)	1.1315 [cm ³ g ⁻¹]
Mean pore diameter	29.790	[nm]		

Figure 3.46

BET plot of the propene soot .



Adsorption / desorption isotherm

Adsorptive N2

Adsorption temperature 77 [K]

©●PrintexL.DAT

Sample weight	0.2063	[g]	Date of measurement	09/12/14
Saturated vapor pressure	101.78	[kPa]	Time of measurement	8:44:41

Figure 3.47

Adsorption / desorption isotherm of the propene soot.

According to the SEM micrographs, which are shown in figure 3.48 and 3.49, propene soot is a very fluppy material. It consists of agglomerates of the individual, small elemental particles which have the average size of 10 to 20 nm. These results agree well to the literature (Murphy et al., 1981; Medalia et al., 1982; Stevenson., 1982; Peterson., 1982., Otto et al., 1980; Ishiguro et al., 1991), where diameters of the elemental particles are reported to range from 40 to 45 nm. It is more difficult to determine the size of the size of the diesel soot. On many SEM micrographs very large particulate clusters can be seen, which is clear from figure 3.49, which probably consist of a number of individual diesel particulates. Many particulates can be seen with the medium sizes of 40 to 45 nm, and the largest particulates encountered were several μm in size.

Because it had been found that the contact between soot and catalyst is very important parameter in the catalyzed oxidation of soot, the physical appearance of this is studied for one of the catalyst-carbon sample mixture (Fe_2O_3 /propene soot).

Figures 3.50 and 3.51 displays the SEM pictures of the fresh blend 0%, and the mixture with 25% and 90% conversion in TPO. Furthermore, it is discernible that the spherical shape as well as the mean diameter of the soot primary particles do not change in the oxidation and the particles only collapse, if nearly total conversion is reached. At a conversion of 99% no more primary particles of the soot or resulting fragments or observed in the micrograph.

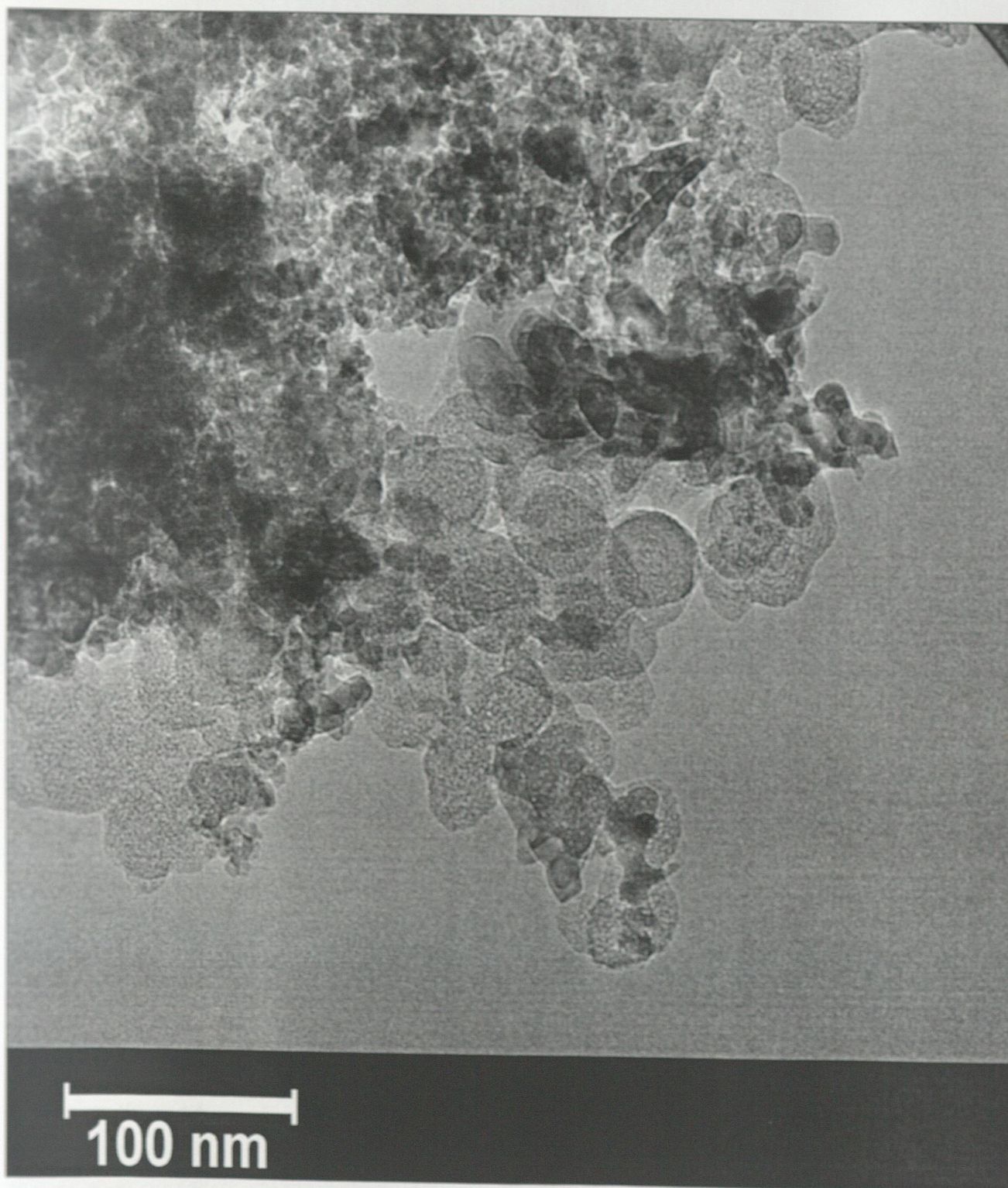


Figure 3.48.

SEM micrograph of the propene soot at 100 nm magnification.

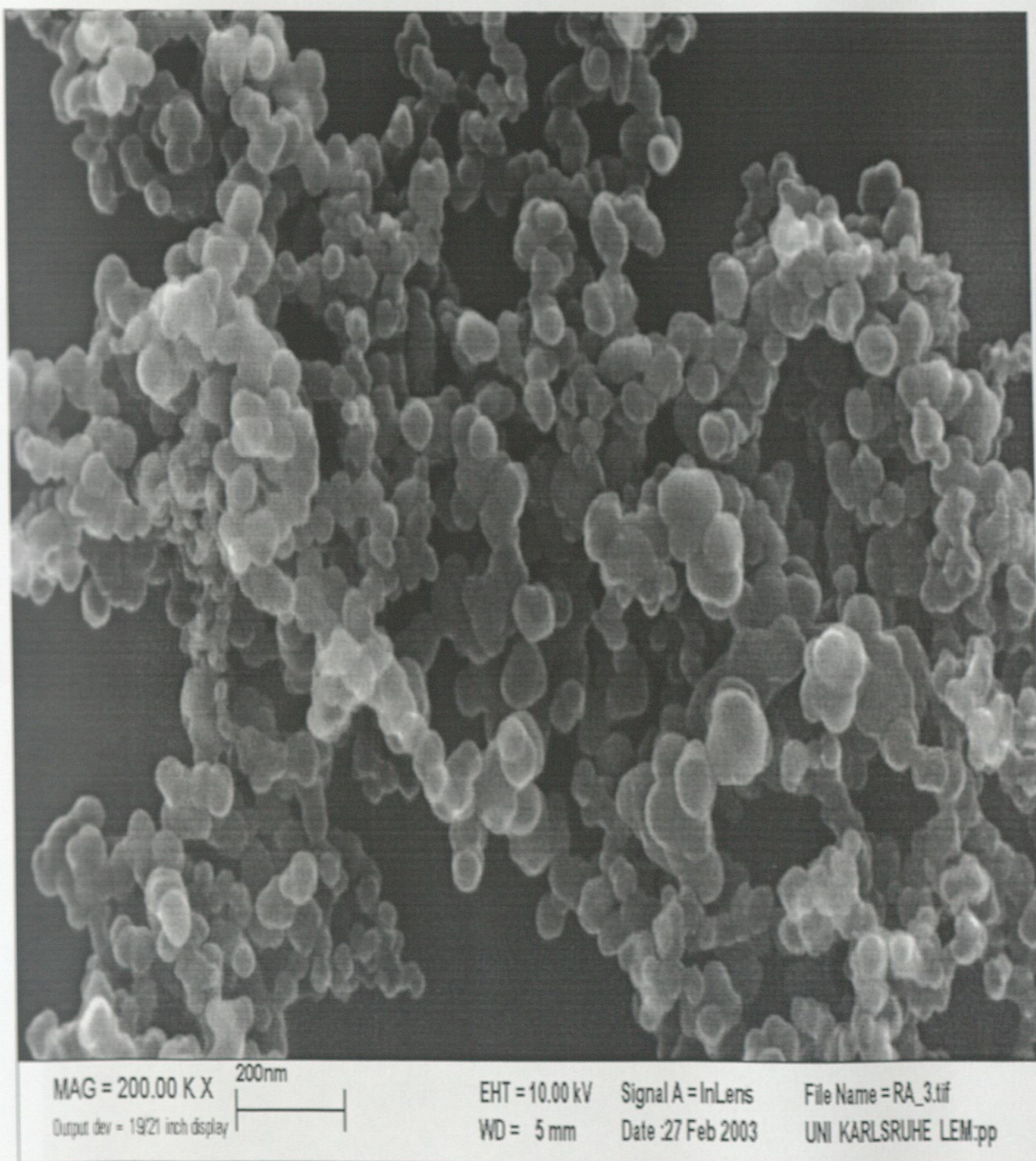


Figure 3.49.

SEM micrograph of the propene soot agglomerates at 200 nm magnification.

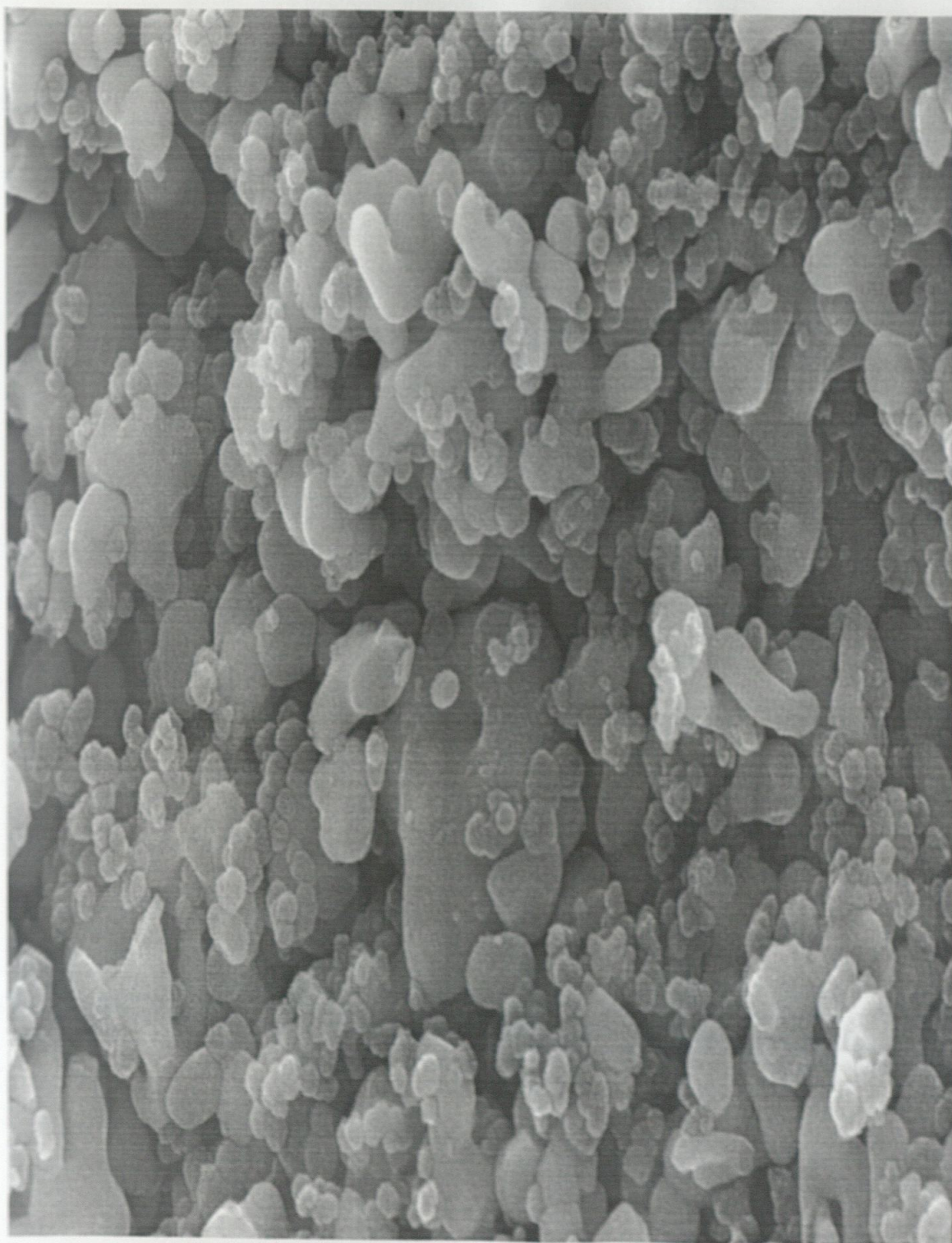


Figure 3.50.

SEM micrograph of 25% oxidized propene soot at 200 nm magnification.

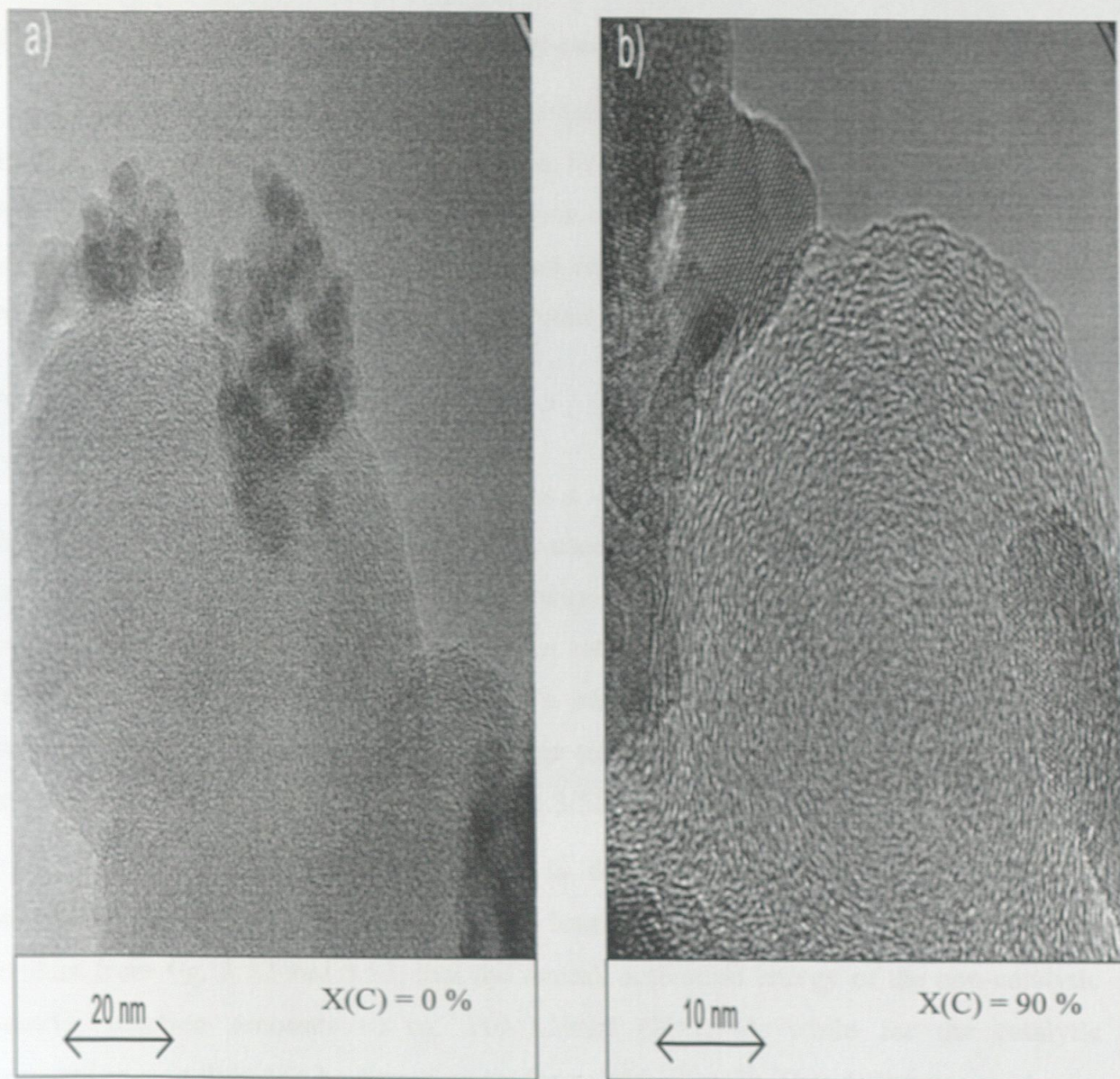


Figure 3.51

SEM pictures of the unreacted mixture of nano-sized Fe_2O_3 and soot at 20 nm magnification (left) and of the corresponding mixture that is obtained after quenching the TPO at a soot conversion of 90% at 10 nm magnification (right), (Reichert et al., 2008).

3.7. Kinetics of the catalytic and non-catalytic soot/O₂ reaction

The soot oxidation always show a maximum of CO_x followed by a continuous decline, i.e. a steady state is never observed. From the CO_x traces which correspond to the conversions between 10 and 15% the rate of soot oxidation is derived as there the concentration of carbon oxides is measured reliably (Equation 3.1); V_m is the molar volume at 20°C and n₀ the initial molar amount of soot.

$$r(\text{CO}_x) = \frac{(c(\text{CO}) + c(\text{CO}_2))FV_m}{n_0} \quad 3.1$$

The catalytic soot oxidation indicates a very similar CO_x profile as compared to the non-catalytic reaction, where CO is detected in rather low concentration only. This effect is associated with the high CO oxidation activity of the Fe₂O₃ catalyst (Reichert et al., 2008). As no steady state appears in catalytic as well as non-catalytic soot/O₂ reaction the kinetic data are analysed in a particular passion, which is the rates of certain conversion level obtained at different temperatures are summarised and plotted in an Arrhenius diagram as shown in figure 3.52 and 3.53.

Apparent activation energy (E_A) is then deduced from the slope of the regression lines; error propagation of the least square fitting is less than 10%. It is evident from fig. 3.52 and 3.53, that the overall activation energy of the non-catalytic soot/O₂ reaction amounts to ca. 210 kJ/mol (X=15%), while for the catalytic conversion it is found to be significantly lower (56 kJ/mol). This difference evidences the enhancing effect of the Fe₂O₃ catalyst (Reichert et al., 2008).

Our group recently reported that the Fe₂O₃ catalyst act as an oxygen pump which continuously transfers oxygen from the gas phase via its surface to the soot (Reichert et al., 2008). The oxygen transfer occurs at the contact points of both solids and is maintained up to high conversion levels. This release of oxygen produces vacancies on the Fe₂O₃ that are refilled by neighbouring surface oxygen leading to a kind of cascade of formation and refilling of the surface vacancies. Finally vacancies produced in a certain distance to the contact points are refilled by gas-phase oxygen. It has been shown that the dissociative adsorption of O₂ on Fe₂O₃ reveals on activation

energy which is very close to 0 kJ/mol, whereas the thermal desorption necessitates activation energy of about 210 kJ/mol (Wagloehner et al., 2008).

It is therefore concluded that adsorption and desorption of oxygen does not represent the rate-determining step in the catalytic soot/O₂ reaction. Moreover, for surface diffusion on solids it is generally accepted that the activation energy is in order of 10-20% of the binding energy of the adsorbate (Atkins., 1990). As the adsorption enthalpy of O₂ on Fe₂O₃ is reported to be ca.120 kJ/mol, our group estimate the activation energy of surface diffusion to be in the range of ca. 10-25 kJ/mol (Jarvis et al., 2007). These values are very similar to the apparent activation energy determined above. Thus, it is assumed that the surface diffusion of oxygen is the rate-determining step of soot/O₂ reaction on Fe₂O₃ when carried out under isothermal conditions. Furthermore, it is speculated that the decrease in activation energy refers to the adsorption of CO₂ on the catalyst. It is well-known that in CO₂ adsorption on oxide surfaces carbonate species are produced, in which the carbonate ligand is coordinated to one or two Lewis acid Fe³⁺ sites representing oxygen vacancies (Wagloehner et al., 2008). Thus, the formation of these carbonate complexes should immediately cause the inhibition of surface diffusion of oxygen.

The comparison of the activation energy of the soot oxidation in the present work with the literature data is difficult as the kinetic parameters strongly depends on numerous factors, for instance the type of carbonaceous material, its production conditions and reaction temperature. In general, the activation energy of soot/O₂ reaction decreases in the order: soot > activated carbon > chars > graphite (Neeft et al., 1997). For the oxidation of soot below 700 °C apparent activation energies of ca. 100-210 kJ/mol are reported (Neeft et al., 1997; Otto et al., 1980; Stanmore., 2001; Atamny et al., 1992; Smith., 1978). Thus, present value of 210 kJ/mol is in the range of the reference data.

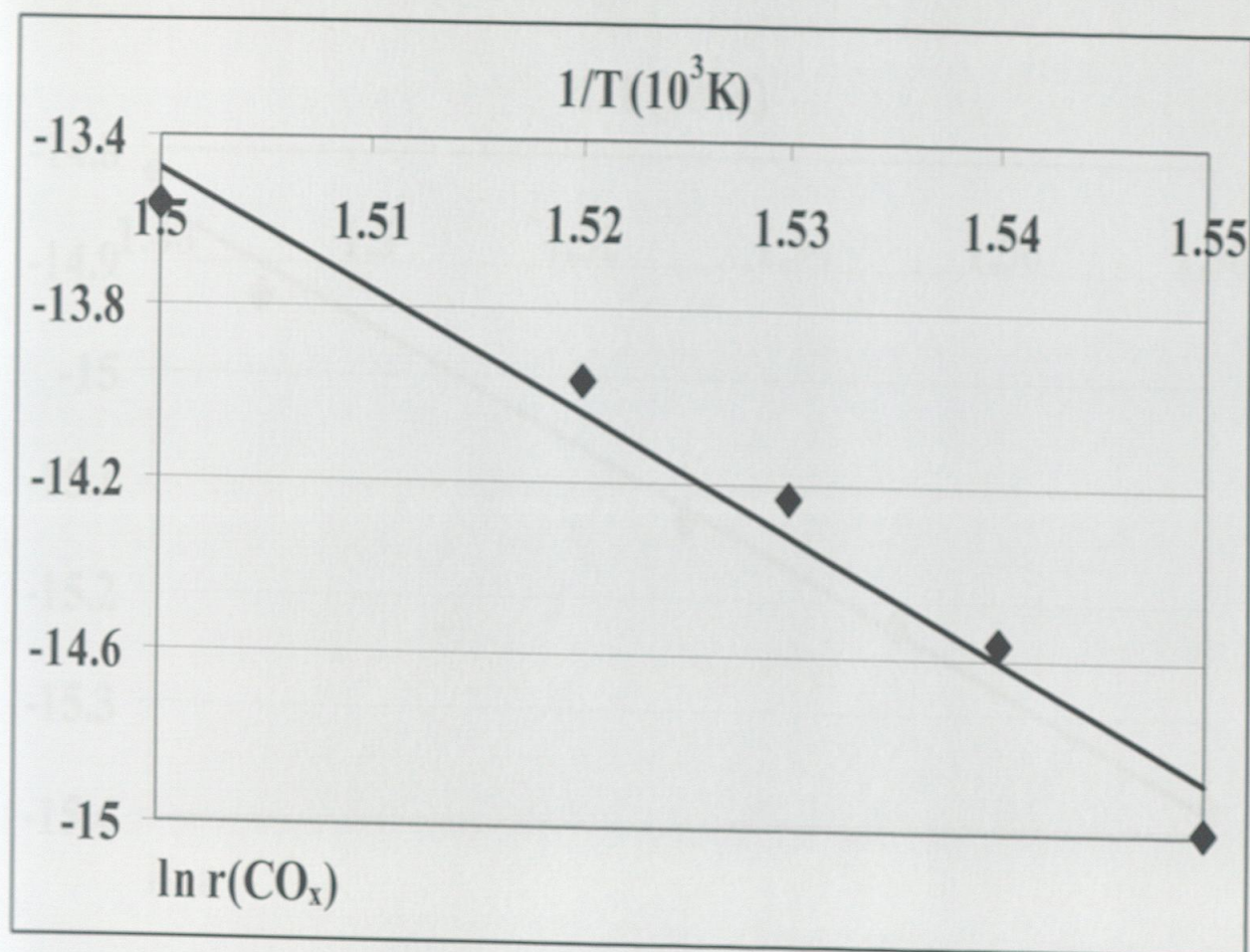


Figure 3.52

Arrhenius plot of $\ln r(\text{CO}_x)$ for non-catalytic soot/ O_2 reaction. Reaction conditions: $m(\text{C}) = 5.64 \text{ mg}$, $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, carbon samples used of $125\text{-}250 \text{ }\mu\text{m}$.

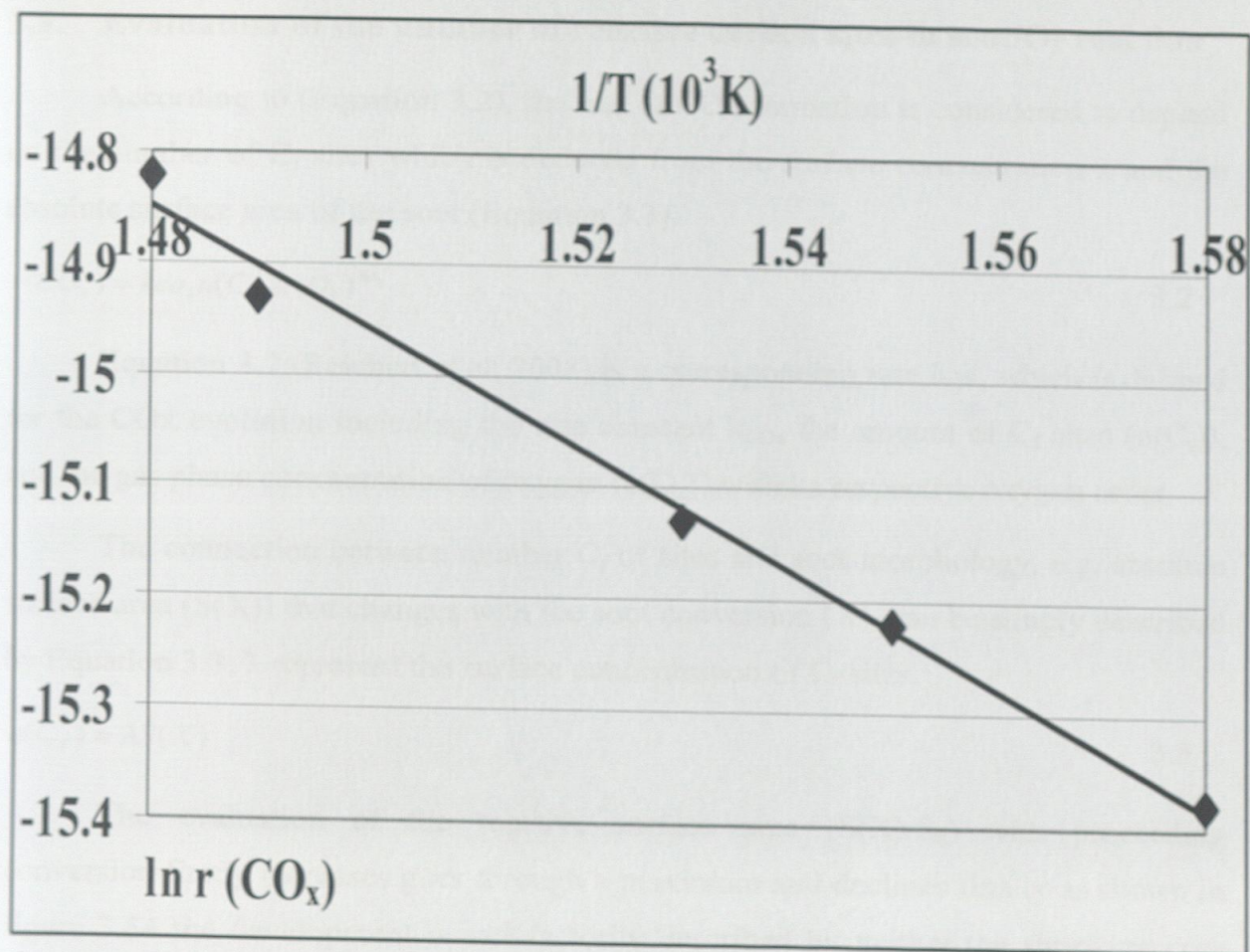


Figure 3.53

Arrhenius plot of $\ln r(\text{CO}_x)$ for Fe_2O_3 catalyst-soot/ O_2 reaction. $m(\text{Fe}_2\text{O}_3) = 53.787 \text{ mg}$, $m(\text{C}) = 2.023 \text{ mg}$, $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of $125\text{-}250 \mu\text{m}$, $(n(\text{Fe}_2\text{O}_3)/n(\text{C}))=2$.

3.8. Evaluation of the number of reactive carbon sites in soot/O₂ reaction

According to (Equation 3.2), the rate of CO_x formation is considered to depend on the number of C_f sites which is deduced from the surface concentration λ and the absolute surface area of the soot (Equation 3.3).

$$r(\text{CO}_x) = k_{\text{CO}_x} n(\text{C}_f) c(\text{O}_2)^{n_{\text{O}_2}} \quad 3.2$$

Equation 3.2 (Reichert et al; 2008) is a corresponding rate law, which is defined for the CO_x evolution including the rate constant k_{CO_x} the amount of C_f sites ($n(\text{C}_f)$), and the gas phase concentration of oxygen ($c(\text{O}_2)$) with its respective oxygen order.

The connection between number C_f of sites and soot morphology, e.g. absolute surface area ($S(X)$) that changes with the soot conversion (X), can be simply described by Equation 3.3; λ represent the surface concentration of C_f sites.

$$n(\text{C}_f) = \lambda S(X) \quad 3.3$$

The evaluation of the reactive surface area ($S(X)/S_0$) with proceeding conversion firstly increases goes through a maximum and declines finally as shown in figure 3.54 the development is satisfactorily described by neither the shrinking core nor the random pore model, whereas the later reveals a much better approximation. Hence our group empirically advance the formula from Bhatia et al., 1980; by implementing the factor f and the exponent $1/q$ (Equation 3.4); with $f = 300$ and $q = 3$ the experimental data are described well as shown in figure 3.54.

$$\frac{S(X)}{S_0} = (1 - X)(1 + fX)^{\frac{1}{q}} \quad 3.4$$

Where $S(X)$ is simply calculated from the BET surface area and the mass of soot ($m(X)$), (Equation 3.5) remaining in oxidation.

$$m(X) = m_0(1 - X) \quad 3.5$$

In accordance with the literature (Marcucilli., 1994), the surface the surface concentration of the C_f sites is estimated by TPD. λ is then obtained by coupling the amount of CO_x released and the mass of soot with BET surface area. It is obvious that this approach is a rather rough approximation which involves the following

assumption: (a) each desorbed COx molecule leads to the formation of one C_f site; (b) the production of H₂O in TPD is not considered to produce C_f sites; (c) the number of COx desorbed directly after the O₂ pre-treatment is neglected; (d) in soot oxidation present SOC species desorb to form C_f sites.

The total amount of COx respective BET surface area (S_{BET}) and the resulting surface concentration of SOC species of the fresh and pre-treated soot samples are summarized in table 3.1. From the assumptions stated above a very similar surface concentration of C_f sites is inferred regardless of the pre-treatment of the sample, the average value of λ is 8.7 $\mu\text{mol}/\text{m}^2$. This result is in the same order of magnitude as reported by Ahmad amounting to 18-57 $\mu\text{mol}/\text{m}^2$ (Ahmad et al., 1985).

Table 3.1 BET surface area and the total amount of SOC species of the soot samples oxidized to the specific conversion levels (Reichert et al., 2008).

	X %			
	0	25	50	75
S _{BET} (m ² /g)	91	385	484	544
n(COx) (mmol/g)	0.86	3.73	3.88	4.24
n(COx) ($\mu\text{mol}/\text{m}^2$)	9.4	9.7	8.0	7.8

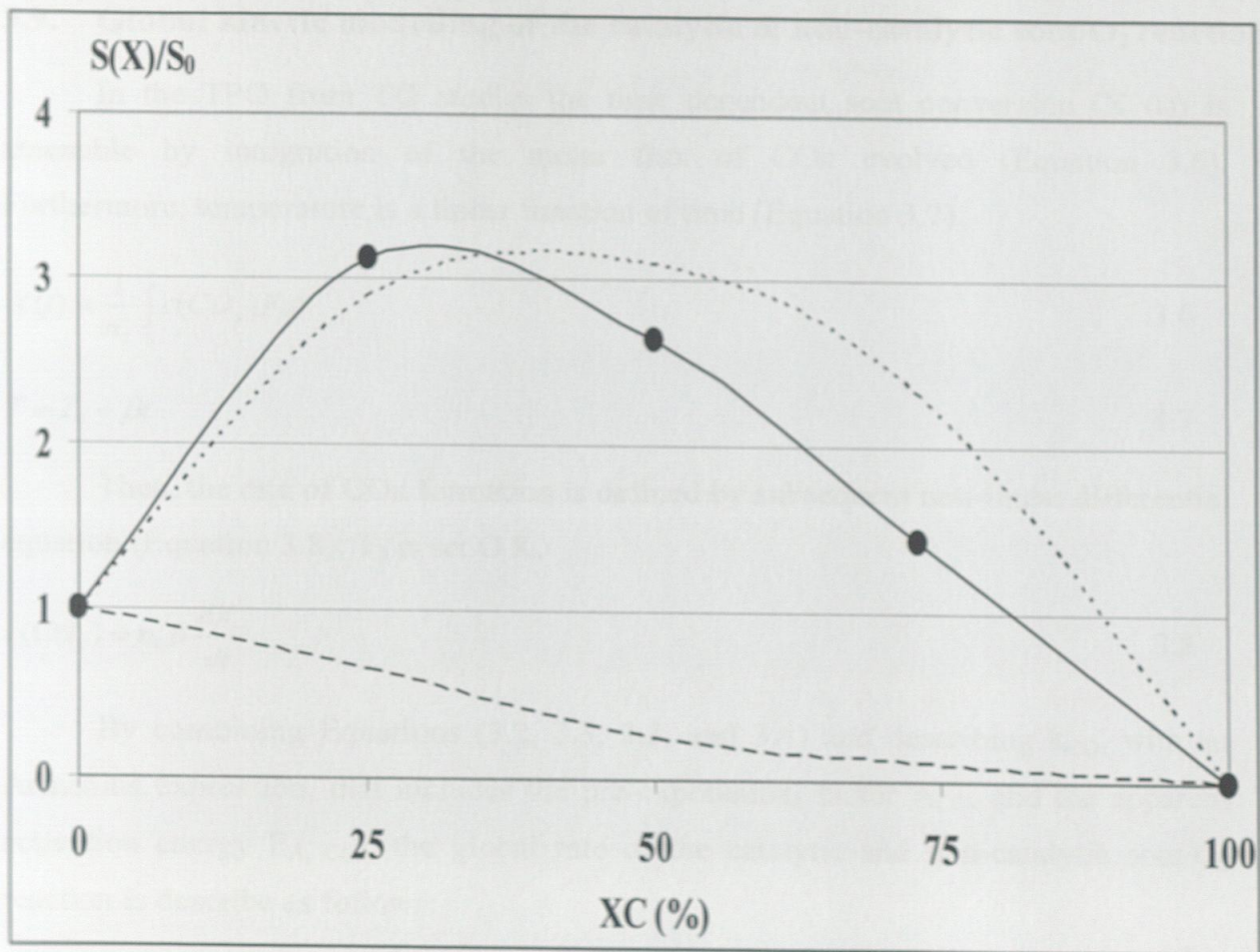


Figure 3.54

Evolution of $S(X)/S_0$ with proceeding conversion of soot; experimental data (•), are compared with the shrinking core model (....), random pore model from Bhatia ($\alpha=50$;---), and the empirical model defined by equation 3.4 (Reichert et al., 2008).

3.9. Global kinetic modelling of the catalytic & non-catalytic soot/O₂ reaction

In the TPO from TG studies the time dependent soot conversion ($X(t)$) is amenable by integration of the molar flux of CO_x evolved (Equation 3.6). Furthermore, temperature is a linear function of time (Equation 3.7).

$$X(t) = \frac{1}{n_0} \int_0^t c(\text{CO}_x) F dt \quad 3.6$$

$$T = T_0 + \beta t \quad 3.7$$

Then, the rate of CO_x formation is defined by subsequent non-linear differential equation (Equation 3.8); T_0 is set 0 K.

$$r(\text{CO}_x) = n_0 \beta \frac{dX}{dt} \quad 3.8$$

By combining Equations (3.2, 3.3, 3.3, and 3.4) and describing k_{CO_x} with an Arrhenius expression, that includes the pre-exponential factor A_{CO_x} and the apparent activation energy E_{A, CO_x} , the global rate of the catalytic and non-catalytic soot/O₂ reaction is describe as follows:

$$n_0 \beta \frac{dX}{dt} = A_{\text{CO}_x} e^{(-E_{A, \text{CO}_x} / RT)} \lambda S_0 m_0 (1 - X)(1 + fX)^{1/q} c(\text{O}_2)^{n_{\text{O}_2}} \quad 3.9$$

For the catalytic conversion λ , f and q are adopted from the non-catalytic reaction. Additionally, with the exception of the different pathway of the chemisorption of oxygen our model includes the same mechanism of the soot oxidation and changes in morphology in the absence and the presence of the Fe₂O₃ catalyst.

In accordance with the literature the apparent reaction order of this assumed to be 1 ($n = 1$) (Stanmore et al., 2001). Additionally, for the non-catalytic soot/O₂ reaction, the apparent activation energy is taken from the TPO of TG experiments. A_{CO_x} is kept as free parameter which is estimated by non-linear regression method. The results of the calculation are shown in figure 3.55, and 3.56 respectively, indicating satisfactory description of the TPO profile of soot/O₂ conversion.

In the presence of catalyst the soot oxidation is significantly enhanced as shown in figure 3.56, for instance the peak concentration of is shift to ca. 210 K to lower temperatures.

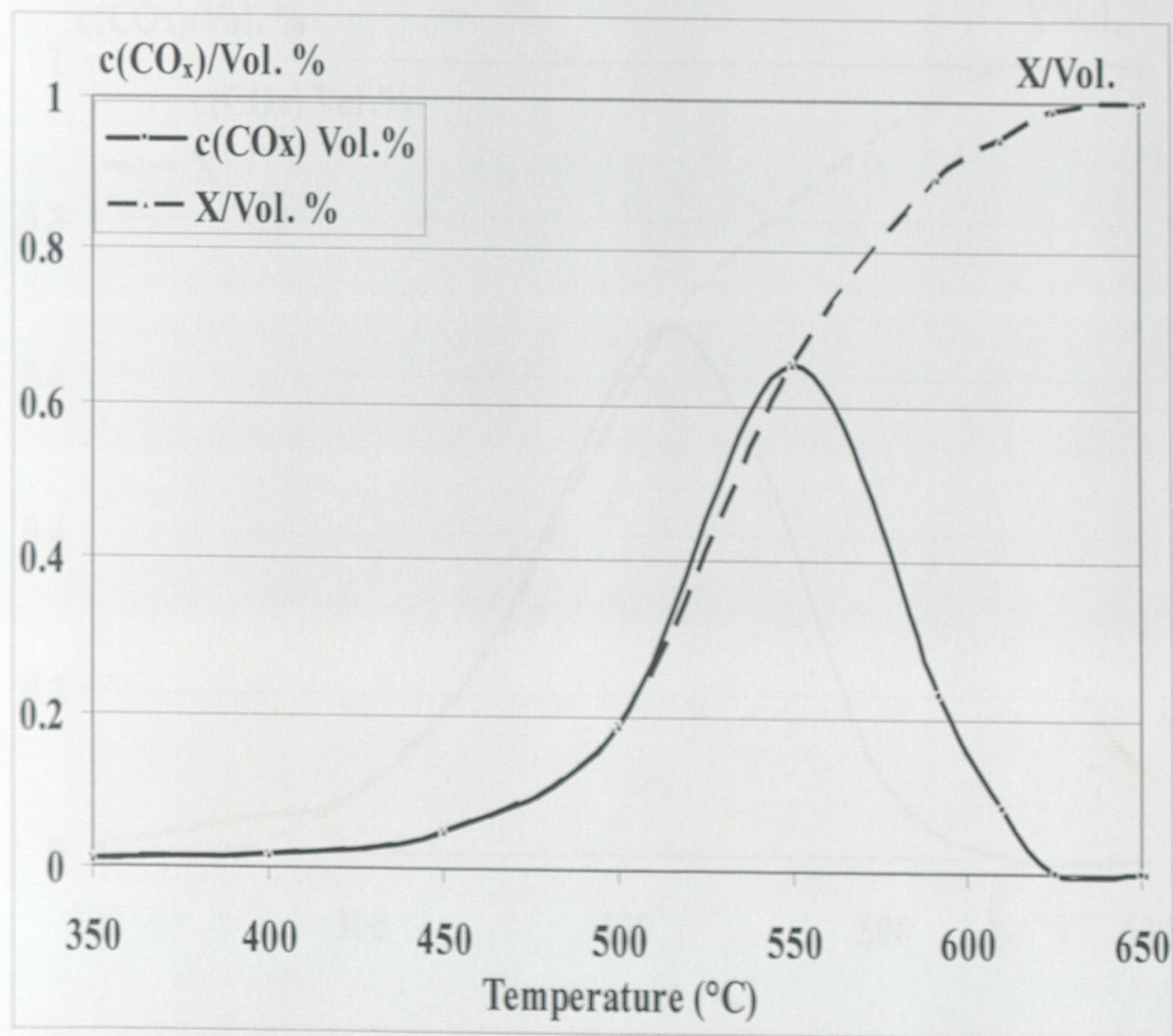


Figure 3.55

Comparison of the experimental CO_x concentration (—) and soot conversion (---) in the non-catalytic soot/ O_2 reaction. Reaction condition: $m(\text{C}) = 0.120 \text{ g}$ (10 mmol), $c(\text{O}_2) = 21.0 \text{ vol. \%}$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, Soot used of 125-250 μm .

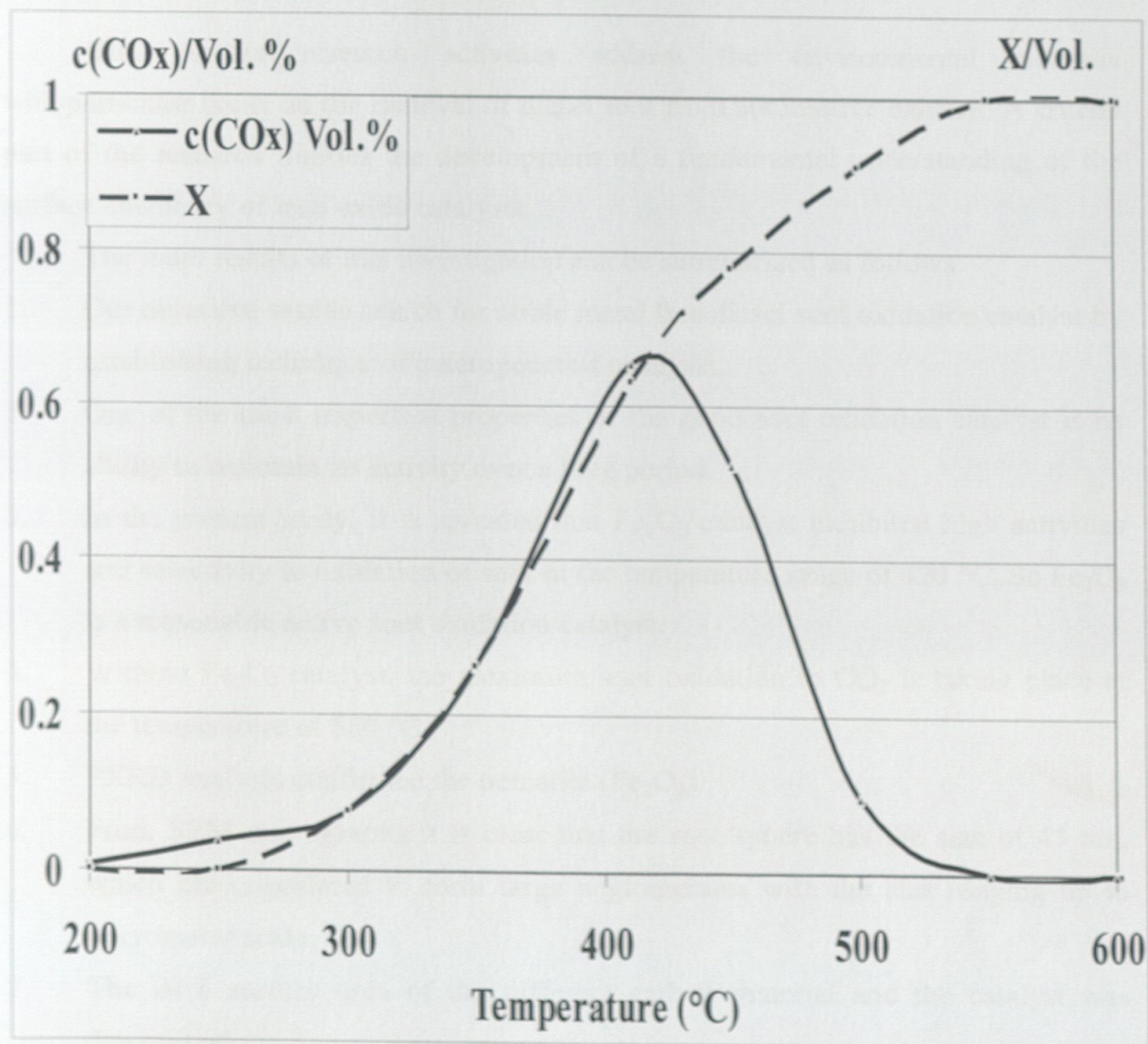


Figure 3.56

Comparison of the experimental COx concentration (—) and soot conversion (---) in the presence of Fe_2O_3 catalyst soot/ O_2 reaction. Reaction condition: $m(\text{Fe}_2\text{O}_3) = 3.19 \text{ g}$ (20 mmol), $m(\text{C}) = 0.12 \text{ g}$ (10 mmol), $c(\text{O}_2) = 21.0 \text{ vol.}\%$, N_2 balance, $F = 500 \text{ cm}^3/\text{min}$ (STP), $\Delta T/\Delta t = 1.5 \text{ K/min}$, $\text{Fe}_2\text{O}_3/\text{soot}$ used of 125-250 μm , $(n(\text{Fe}_2\text{O}_3) / n(\text{C})) = 2$.

CHAPTER – 4

CONCLUSIONS

The current research activities address the environmental catalysis with particular focus on the removal of diesel soot from automotive exhaust. A crucial part of the research implies the development of a fundamental understanding of the surface chemistry of iron oxide catalysts.

The main results of this investigation can be summarized as follows:

1. Our objective was to search for noble metal free diesel soot oxidation catalyst by establishing technique of heterogeneous catalysis.
2. One of the most important properties of the good soot oxidation catalyst is its ability to maintain its activity over a long period.
3. In the present study, it is revealed that Fe_2O_3 catalyst exhibited high activities and selectivity to oxidation of soot in the temperature range of 420 °C. So Fe_2O_3 is a reasonable active soot oxidation catalyst.
4. Without Fe_2O_3 catalyst, the maximum soot oxidation to CO_2 is taking place at the temperature of 580 °C.
5. PXRD analysis confirmed the hematite (Fe_2O_3).
6. From SEM micrographs it is clear that the soot sphere has the size of 45 nm, which are coagulated to form large agglomerates with the size ranging up to micrometer scale.
7. The BET surface area of the different carbon material and the catalyst was determined.
8. The role of O_2 in the combustion of soot is investigated by analysing the soot combustion characteristics and the FTIR spectra of the surface oxygen complexes (SOFs) as soot oxidation intermediate.
9. Oxidation of soot in oxygen yields several oxygen complexes (SOCs). The amount of SOCs increases with soot conversion.
10. In TG experiments, the sharp mass loss attribute to the thermal runaway reaction (ignition).

11. The chemical form of the surface complexes was estimated from the results obtained from TPD/FTIR study.
12. Soot from the various sources is structurally similar, and similar to commercial carbon blacks.
13. The reactivity towards oxygen is similar to that of other carbon (printex 1, graphite, and activated charcoal).
14. The control of soot emissions from automotive engines can now be achieved by installing filter monoliths in the exhaust line. These traps must be periodically regenerated by burning the deposited soot. This filtration device can be associated with the use of fuel additives to decrease the ignition temperature of the soot material by a catalytic effect.
15. The particulate emission, particularly soot, can be removed substantially by the application of soot filters, which can work efficiently in the CRT-system (Continuously Regenerating Trap).
16. Hence, the present work is aimed to develop a non-hazardous CRT catalyst showing high performance as well as physical stability even at elevated temperature. Looking to the thermal stability and remarkable CRT activity, (Because it is known that Fe_2O_3 is thermally stable up to 1200 °C and exhibits remarkable CRT activity) iron oxide will be used as catalyst.

CHAPTER – 5

REFERENCES

1. Ahlstrom, A.F.; Odenbrand, C.U.I.; *Carbon*, 27, (1989) 475.
2. Ahmad, S.; Back, M.H.; *Carbon*, 23, (1985) 513.
3. Ahmad, S.; Back, M.H.; Roscoe, J.M.; *Combust Flame*, 70, (1987) 1.
4. Akhtar, M.S.; Keifer, J.R.; Chughtai, A.R.; Smith, D.M.; *Carbon*, 23, (1985) 589.
5. Akhter, M.S.; Chughtai, A.R.; Smith, D.M.; *Appl. Spect.*, 39, (1985) 154.
6. Akhter, S.; Chughtai, A.R.; Smith, D.M.; *Appl. Spec.*, 39, (1985) 143.
7. Allansson, R.; Goerrsmann, C.; Lavenius, M.; Phillips, P.R.; Uusimaki, A.J.; Walker, A.P.; *SAE Techn. Papers*, (2004) 01-0072.
8. Allen, D.; Hayhurst, A.N.; In: *Twenty-third international symposium on combustion*, Pittsburg: The combustion Institute, (1990) 935.
9. Astarita, M.; Corcione, F.E.; Vaglieco, B.M.; *Experimental thermal and fluid science*, 21, (2000) 142.
10. Atamny, F.; Bloecker, J.; Duebtzky, A.; Curt, H.; Timpe, O.; Loose, G.; Mahdi, W.; Schloegl, R.; *Mol. Phys.*, 76, (1992) 851.
11. Atkins, P.W.; *Phys. Chem., Oxford University Press*, (1990).
12. Badini, C.; Saracco, G.; Specchia, V.; *Catal. Lett.*, 55, (1998) 201.
13. Balle, P.; Bockhorn, H.; Geiger, B.; Jan, N.; Kureti, S.; Reichert, D.; Schröder, T.; *J. Chem. Eng. Proc.*, 45, (2006) 1065.
14. Bandyopadhyay, M.; Korsak, O.; Van den Berg, M.W.E.; Gruenert, W.; Birkner, A.; Li, W.; Schueth, F.; Gies, H.; *Microporous Mesoporous Mater.* 89, (2006) 158.
15. Baumgarten, E.; Schuck, A.; *Appl. Catal.*, 37, (1988) 247.
16. Bhatia, S.K.; Perlmutter, D.D.; *J. Am. Inst. Chem. Eng.*, 26, (1980) 379.
17. Bond, G. C.; Dias, C. R.; Portela, M. F.; *J. Catal.*, 156, (1995) 295.
18. Brunauer, S.; Emmet, P.H.; Teller, E.; *J. Amer. Chem. Soc.*, 60, (1938) 309.

19. Campbell, C.T.; Ertl, G.; Kuipers, H.; Segner, J.; *J. Chem. Phys.*, 73, (1980) 5862.
20. Cavaliere, A.; Barbella, R.; Ciajolo, A.; D'Anna, A.; Ragucci, R.; *In: Twenty-fifth international symposium on combustion, Philadelphia: The combustion Institute, (1994) 167.*
21. Cerfontain, M. A.; Moulijn, J. A.; *Fuel*, 65, (1986) 1349.
22. Chang, J.; Park, S.; Park, M.; *Chem. Lett.*, 11, (1997) 1123.
23. Chatterjee, D.; Deutschmann, O.; Warnatz, J.; *Faraday Discuss.*, 119, (2001) 371.
24. Che, M.; Bennet, C.O.; *Advances in Catalysis, Academic Press Inc.*, 36, (1989) 55.
25. Cooper, B.J.; Thoss, J.E.; *SAE Techn. Papers*, (1989) 890404.
26. Courcot, D.; Abi-Aad, E.; Capelle, S.; Aboukais, A.; *In. CaPOC 4, Brussels, (1997) 303.*
27. Cvetanovic, R.J.; Amenomiya, Y.; *Catal. Rev. -Sci. Eng.*, 6, (1972) 21.
28. Davydov, A.A.; *Infrared spectroscopy of adsorbed species on the surface of transition metal oxides*, Wiley, New York, (1990).
29. De Castro, A.J.; Meneses, J.; Briz, S.; Lopez, F.; *Review of scientific instruments*, 70, (1999) 3156.
30. De Soete, G.; *In: Western States section meeting, Salt Lake City, The Combustion Institute 21-22 March (1988).*
31. Degussa AG, *Pigment Blacks*, Product information, (1992).
32. Donnet, J-B.; *In. Second international conference on Carbon black (Mulhouse) (1993) 1.*
33. Du, Z.; Sarofim, A.F.; Longwell, J.P.; *Energy and Fuels*, 4, (1990) 296.
34. Du, Z.; Sarofim, A.F.; Longwell, J.P.; Mims, C.A.; *Energy and Fuels*, 51, (1991) 214.
35. Fagel, G.A.; El-Shobaky, G.A.; El-Khouly, S.M.; *Colloids Surf. A*, 178, (2001) 287.
36. Falconer, J.A.; Schwarz, *Catal. Rev. - Sci. Eng.*, 25, (1983) 141-227.

37. Fanning, E.; Vannice, M. A.; *Carbon*, 31, (1993) 721.
38. Fernandes, V. J.; Araujo, A. S.; *Thermochimica. Acta*, 255, (1995) 273.
39. Fino, D.; Cauda, E.; Saracco, G.; *Catal. Today*, 114, (2006) 31.
40. Fino, D.; Russo, N.; Saracco, G.; Specchia, J.V.; *J. Catal.*, 242, (2006) 38.
41. Flanning, P.E.; Vannice, M.A.; *Carbon*, 31, (1993) 721.
42. Frenklach, M. In: *Twenty-sixth international symposium on combustion, Philadelphia: The combustion Institute*, (1996) 2285.
43. Friedel, R.A.; Durie, R.A.; Shewchyk, Y.; *Carbon*, 5, (1967) 559.
44. Fuller, E.L.; Smyrl, N.R.; *Fuel*, 64, (1985) 1143.
45. Galdeano, N.F.; Carrascull, A.L.; Ponzi, M.I.; Lick, I.D.; Ponzi, E.N.; *Thermochimica Acta.*, 421, (2004) 117.
46. Galuszka, J.; Sano, T.; Sawicki, J. A.; *J. Catal.*, 136, (1992) 96.
47. Gayubo, A. G.; Arandes, J. M.; Aguayo, A. T.; Olazar, M.; Bilbao, J.; *J. Chem. Eng. J. & Bio. Eng.*, 54, (1994) 35.
48. Genc, E.V.; Altay, E.F.; Uner, D.; *Catal. Today*, 105, (2005) 537.
49. Gilot, P.; Bonnefoy, F.; Marcuccilli, F.; Prado, G.; *Combust. Flame*, 85, (1993) 87.
50. Gilot, P.; Bonnefoy, F.; Marcucilli, F.; Prado, G.; *Combust. Flame*, 95, (1993) 87.
51. Gilot, P.; Brillard, A.; Stanmore, B.R.; *Combust. Flame*, 102, (1995) 471.
52. Glasson, D.R.; Seebold, C.; Horn, N.J.; Millword, G. E., In: *Proceeding of Carbon 88 conference*, 18-23 september, Newcastle upon Tyne, 34 (1988).
53. Goldenberg, E.; Prigent, M.; *J. Caillod, Oil & Gas Sci. Techn. -Rev. IFP*, 38, (1983) 793.
54. Guyon, M.; Blanche, P.; Bert, C.; Philippe, L.; Messaoudi, I.; *SAE Paper* (2000)-01-2910.
55. Hashiguchi, Sakai, S.; In *Acid-Base Catalysis*, (Eds: K. Tanabe, H. Hattori, T. Yamaguchi, T. Tanaka), Kodansha, Tokyo, (1989), p 191.
56. Herzberg, G.; *Molecular, Spectroscopy and Molecular Structure II. Infrared and Raman Spectra of polyatomic Molecules*, Van Nostrand, Princeton (1945).

57. Heywood, J.B.; *Internal combustion engine fundamentals*, New York, McGraw Hill (1990).
58. Imanari, M.; Watanabe, Y.; Matsuda S.; Nakajima, F.; *In: Proc. 7th Intern. Congr. Catal.* T. Seiyama and K. Tanabe, Eds. Elsevier, Amsterdam, (1981) 641.
59. Ishiguro, T.; Suzuki, N.; Fujitani, Y.; Morimoto, H.; *Combust. Flame*, 85, (1991) 1.
60. Jacquot, F.; Logie, V.; Brilhac, J.F.; Gillot, P.; *Carbon*, 40, (2002) 335.
61. Jacquot, F.; Logie, V.; Brilhac, J.F.; Gilot, P.; *Carbon*, 40, (2002) 335.
62. Jarvis, E.A.; Chaka, A.M.; *Surf. Sci.*, 601, (2007) 1909.
63. Jelles, B.A.; Van Setten, A.L.; Makkee, M.; Moulijn, J.A.; *Appl. Catal. B.*, 21, (1999) 35.
64. Johnson, J.H.; Bagley, S.T.; Gratz, L.D.; Leddy, D.G.; *SAE Techn. Papers*, (1994) 920233.
65. Kabin, S.K.; Muncrief, L.R.; Harold, M.P.; *Catal. Today*, 96, (2004) 79.
66. Kahandawala, M.S.P.; Graham, J.L.; Sidhu, S.S.; *Fuel*, 83, (2004) 1829.
67. Kahlich, M.J.; Gasteiger, H.A.; Behm, R.J.; *J. Catal.*, 182, (1999) 430.
68. Kapteijn, F.; Meijer, R.; Moulijn, J.A.; Cazorla-Amoros, D.; *Carbon*, 32, (1994) 1223.
69. Kapteijn, F.; Moulijn, J.A.; *In: Carbon and coal gasification, NATO ASI, Series -E: Appl. Sci.* No. 105, Martinus Nijhoff publisher 291, (1986).
70. Karge, Dondur, V.; *J. Phys. Chem.*, 94, 7(1990) 65.
71. Khan, M.I.; Wang, C.H.T.; Langridge, B.E.; *Combust. Flame*, 17, (1971) 409.
72. Kim, M.R.; Kim, D.H.; Woo, S.I.; *Appl. Catal. B*, 45, (2003) 269.
73. Kishi, Y.; Tohno, H.; Ara, M.; *SAE Paper*, 920687 (1992).
74. Kittelson, D.B.; *J. Aerosol. Sci.*, 29, (1998) 575.
75. Klos, T.; *Eindimensionale-Mulikomponenten-Raman-Streuung zur Mesung charakteristischer Turbulenzeigenschaften*, VDI-Reihe 8, Fortschr.-Ber. Nr. 692 (1998).

76. Krestinin, A.V.; *Combust. Flame* 121, (2000) 513.
77. Kureti, S.; Hizbullah, K.; Weisweiler, W.; *Chem. Eng. Technol.*, 26, (2003) 9.
78. Lahaye, J.; Boehm, P.; Chambrion, P.; Ehrburger, P.; *Combust. Flame* 104, (1996) 199.
79. Le Minh, C.; Jones, R.A.; Craven, I. E.; Brown, T. C.; *Energy & Fuels*, 11, (1997) 463.
80. Lee, K.B.; Thring, M.W.; Beer, J.M.; *Combust. Flame*, 6, (1962) 137.
81. Leocadio, I.C.L.; Braun, S.; Schmal, M.; *J. Catal.*, 223, (2004) 114.
82. Lies, K.H.; Postulka, A.; Gring, H.; *SAE Paper* , 840361 (1984).
83. Lies, K.H.; Schultz, J.; Winneke, H.; Kuhler, M.; Kraft, J.; *Volkswagen AG*, Wolfsburg, (1988).
84. Lisa, K.; Hufa, M.; Yrjas, P.; *In: Twenty-fourth international symposium on combustion, Pittsburg: The combustion Institute*, (1992) 1349.
85. Ma, M.C.; Haynes, B.S.; *In: Twenty-sixth international symposium on combustion, Philadelphia: The combustion Institute*, (1996) 3119.
86. Marcucilli, F.; Gilot, P.; Stanmore, B.R.; Prado, G.; *In: Twenty-fifth international symposium on combustion, Philadelphia: The combustion Institute*, (1994) 619.
87. Marcucilli, F.; Gilot, P.; Stanmore, B.R.; Prado, G.; *In: Twenty-fifth international symposium on combustion, Philadelphia: The combustion Institute*, (1994) 619.
88. Marsh, H.; Kuo, K.; *In: H. Marsh editor, Introduction to Carbon science*, London: Butterworths, (1989) 107.
89. Masoudi, M.; *SAE Techn. Papers*, (2005) 01-0971.
90. Mckee, D.W.; *Fuel*, 62, (1983) 170.
91. Mckee, D.W.; *In: Chemistry and physic of Carbon*, Vol. 16, (Eds: P.L. Walker and P.A. Thrower), Marcel Dekker, New York 1, (1981).
92. Medalia, A.I.; Rivin, D.; *Carbon*, 20, 4(1982) 81.
93. Meldrum, B. J.; Rochester, C. H.; *J. Chem. Soc, Faraday Trans.* 86, (1990) 861.

94. Meldrum, B. J.; Rochester, C.H.; *Fuel*, 70, (1991) 57.
95. Meldrum, B. J.; Rochester, C.H.; *J. Chem. Soc. Faraday Trans.*, 86, (1990) 861.
96. Meldrum, B. J.; Rochester, C.H.; *J. Chem. Soc. Faraday Trans.*, 86, (1990) 2997.
97. Meldrum, B. J.; Rochester, C.H.; *J. Chem. Soc. Faraday Trans.*, 86, (1990) 3647.
98. Menon, P.G.; In: *Hydrogen Effects in Catalysis; Fundamentals and Practical Applications* (Eds: Z. Paal, P.G. Menon), Dekker, New York 31 (4) (1987) 117.
99. Mimura, N.; Takahara, I.; Ando, M.; *Catal. Today*, 45, (1998) 61.
100. Miyamoto, N.; Ogawa, H.; Goto, N.; Sasaki, H.; *SAE Paper*, (1990) 900640.
101. Mol, G.; Neeft, J.P.A.; Kapteijn, F.; Moulijn, J.A.; *Carbon*, 36, (1998) 1269.
102. Mol, G.; *Ph. D Thesis*, Delft University, Nederland (1997).
103. Morterra, C.; Low, M.J.D.; *Carbon*, 23, (1985) 311.
104. Morterra, C.; Low, M.J.D.; *Carbon*, 23, (1985) 335.
105. Morterra, C.; Low, M.J.D.; *Langmuir*, 1, (1985) 320.
106. Morterra, C.; Low, M.J.D.; *Mater. Lett.*, 2, (1990) 289.
107. Morterra, C.; Low, M.J.D.; *Spectrosc. Lett.*, 15, (1982) 689.
108. Moulijn, J.A.; Cerfontain, M.B.; Kapteijn, F.; *Fuel*, 63, (1984) 1043.
109. Moulijn, J.A.; Kapteijn, F.; *Carbon*, 33, (1995) 1155.
110. Mul, G.; Kapteijn, F.; Doornkamp, C.; Moulijn, J.A.; *J. Catal.*, 179, (1998) 258.
111. Mul, G.; Neeft, J.P.A.; Kapteijn, F.; Moulijn, J.A.; *Carbon*, 36, (1998) 1269.
112. Mul, G.; Neeft, J.P.A.; Kapteijn, F.; Moulijn, J.A.; *J. Catal.*, 170, (1998) 258.
113. Murphy, M.J.; Hillenbrand, L.J.; Trayser, D.A.; Wasser, J.H.; *SAE Paper*, 810112 (1981).
114. Neeft, J.P.A.; Makkee, M.; Moulijn, J.A.; *Appl. Catal. B*, 8, (1996) 57.
115. Neeft, J.P.A.; Makkee, M.; Moulijn, J.A.; *Fuel*, 77, (1998) 111.
116. Neeft, J.P.A.; Makkee, M.; Moulijn, J.A.; *J. Chem. Eng.*, 64, (1996) 295.
117. Neeft, J.P.A.; Nijhuis, T.X.; Makkee, M.; Moulijn, J.A.; *Fuel*, 76, (1997) 1129.

118. Neeft, J.P.A.; Nijhuis, T.X.; Smakman, E.; Makkee, M.; Moulijn, J.A.; *Fuel*, 76, (1997) 1129.
119. Neeft, J.P.A.; Van Pruissen, O.P.; Makkee, M.; *Appl. Catal. B.*, 12, (1997) 21.
120. Neoh, K.G.; Howard, J.B.; Sarofim, A.F.; *In: Twentieth international symposium on combustion, Pittsburgh: The combustion Institute*, (1984) 951.
121. Neri, G.; Bonaccorsi, L.; Donato, A.; Milone, C.; Musolino, M.G.; Visco, A.M.; *Appl. Catal. B*, 11, (1997) 217-31.
122. Neri, G.; Rizzo, G.; Galvagno, S.; Donato, A.; Musolino, M.G.; Pietropaolo, R.; *Appl. Catal. B*, 42, (2003) 381.
123. Oberdoerster, G.; Sharp, Z.; Atudorei, V.; Elder, A.; Gelein, R.; Kreyling, W.; *COx Inhal. Toxicol.* 16, (2004) 437.
124. Oi-Uchisawa, J.; Obuchi, A.; Wang, S.; Nanba, T.; Ohi, A.; *Appl. Catal. B*, 42, (2003) 117.
125. Otake, Y.; Jenkins, R.G.; *Carbon*, 31, (1993) 109.
126. Otto, K.; Sieg, M.H.; Zinbo, M.; *SAE Paper*, (1980) 800336.
127. *Panorama Road transport fuels in Europe: The explosion of demand for diesel fuel* (2005).
128. Peterson, R.C.; *SAE Paper*, (1982) 870628.
129. Pieck, C. L.; Verderone, R. J.; Jablonski, E. L.; Parera, J. M.; *Appl. Catal.*, 55, (1989) 1.
130. Politou, A.S.; Morterra, C.; Low, M.J.D.; *Carbon*, 28, (1990) 529.
131. Prest, M.W.; Mosher, R.A.; *ACS Symp. Ser.*, 200, (1982) 225.
132. Querini, C.A.; Cornaglia, L.M.; Ulla, M.A.; Miro, E.E.; *Appl. Catal. B*, 20, (1999) 165.
133. Querini, C.A.; Cornaglia, L.M.; Ulla, M.A.; Miro, E.E.; *Catal. Today*, 53, (1999) 631.
134. Querini, C.A.; Cornaglia, L.M.; Ulla, M.A.; Miro, E.E.; *Stud. Surf. Sci. Catal.*, 130, (2000) 731.
135. Randall, H.; Doepper, R.; Renken, A.; *Ind. Eng. Chem. Res.*, 36, (1997) 2996.

136. Reichert, D.; Bockhorn, H.; Kureti, S.; *Appl. Catal. B.*, 80, (2008) 248.
137. Reichert, D.; *Diplomarbeit Universität Karlsruhe (TH)* (2003).
138. Reichert, D.; Finke, T.; Atanassova, N.; Bockhorn, H.; Kureti, S.; *Appl. Catal. B.*, 84, (2008) 803.
139. Reilly, J.M.; Mosher, R.A.; *Carbon*, 21, (1983) 47.
140. Ruth, P.; Brandt, O.; Von Gersum, S.; *In: Twenty-third international symposium on combustion, Pittsburgh: The combustion Institute*, (1990) 1485.
141. Ruth, P.; Eckhardt, T.; Franz, B.; Patschull, J.; *Combust. Flame*, 115, (1998) 28.
142. Satava, V.; *J. Thermal Anal.*, 5, (1973) 217.
143. Schalow, T.; Brandt, B.; Laurin, M.; Schauermann, S.; Libuda, J.; Freund, H.-J.; *J. Catal.*, 242, (2006) 58.
144. Schlöten, F.; Pijpers, A.P.; Hustings, A.M.L.; *Catal. Rev. -Sci. Eng.*, 27, (1985) 151.
145. Sestak, J.; Berggren, G.; *Thermochim. Acta.*, 3, (1971) 1.
146. Setiabudi, A.; Makkee, M.; Moulijn, J.A.; *Appl. Catal. B.*, 42, (2003) 35.
147. Setiabudi, A.; Makkee, M.; Moulijn, J.A.; *Appl. Catal. B.*, 50, (2004) 185.
148. Setzer, C.; Schuetz, W.; Schueth, F.; *In: proceedings 10th international congress on catalysis Budapest, Hungary, Amsterdam, Elsevier*, (1993) 2629.
149. Sharma, B.L.; Meyers, D.T.; Chen, J.; Miller, J.A.; *Appl. Catal. A*, 102, (1993) 253.
150. Simpson, T.J.; *Master Thesis*, University of Canterbury, New Zealand (2004).
151. Skoog, D.; Holler, F.; Nieman, T.; *Principles of instrumental analysis*, fifth edition, Thomson learning, United States (1998).
152. Smith, D.M.; Chughtai, A.R.; *Colloids surfaces A: Physiochemical and Engineering aspects*, 105, (1995) 47.
153. Smith, I. W.; *Fuel*, 56, (1978) 409.
154. Socrates, G.; *IR Characteristic Group Frequencies*, John Wiley, New York (1980).
155. Stanmore, B.R.; Brilhac, J.F.; Gilot, P.; *Carbon*, 39, (2001) 2247.
156. Stanmore, B.R.; Gilot, P.; Prado, G.; *Thermochim Acta*, 240, (1994) 79.

157. Stanmore, B.R.; Gilot, P.; Prado, G.; *Thermochim Acta*, 261, (1995) 151.
158. Starsinic, M.; Taylor, R.; Walker, P.L.; Painter, P.C.; *Carbon*, 21, (1983) 69.
159. Stevenson, R.; *Carbon*, 20, (1982) 359.
160. Tikhomirov, K.; Kroeher, O.; Elsener, M.; Wokaum, A.; *Appl. Catal. B.*, 64, (2006) 72.
161. Tosaka, S.; Fujiwara, Y.; *J. SAE Review*, 21, (2000) 463.
162. Twigg, M.V.; *Appl. Catal. B.*, 70, (2007) 2.
163. Twigg, M.V.; *Appl. Earth Sci.*, 114, (2005) 159.
164. Uner, D.; Dimerkol, M.K.; Derniaka, B.; *Appl. Catal., B*, 61, (2005) 334.
165. Van Setten, B.A.A.; Makkee, M.; Moulijn, J.A.; *Catal. Rev.*, 43, (2001) 489.
166. Van Setten, B.A.A.; Schouten, J.M.; Makkee, M.; Moulijn, J.A.; *Appl. Catal. B.*, 28, (2000) 253.
167. Veranth, J.M.; Fletcher, T.H.; Pershing, D.W.; Sarofim, A.F.; *Fuel* 79, (2000) 1067.
168. Voorhoeve, R.J.H.; Remeika, J.P.; Trimble, L.E.; *Ann. N.Y. Acad. Sci.*, 272, (1976) 3.
169. Wagloehner, S.; Reichert, D.; Leon-Sorzano, D.; Balle, P.; Geiger, B.; Kureti, S.; *J. Catal.*, 260, (2008) 305.
170. Walker, P.L.; Austin, L.G.; Nandi, S.P.; In: P.L. Walker editor, *Chem. Phys. of Carbon*, Vol. 1 & 2, Marsel Dekker, New York (1966).
171. Walker, P.L.; Rusinko, F.; Austin, L.G.; *Adv. Catal.*, 11, (1959) 133.
172. Wang, X.; Chen, X.; Ma, X.; Zheng, H.; Ji, M.; Zhang, Z.; *Chem. Phys. Lett.*, 384, (2004) 391.
173. Willey, R.J.; Lai, H.; Perry, J.B.; *J. Catal.*, 130 (1988) 319.
174. www.dieselnet.com, accessed in November (2009).
175. www.jmcatalysts.com, accessed in November (2009).
176. Yezerets, A.; Currier, N.W.; Eadler, H.A.; *SAE Techn. Papers*, (2003) 01-0833.
177. Yuang, H.Y.; Yang, R.T.; *J. Catal.*, 185, (1999) 2996.

178. Zawadzki, J.; *In Chemistry and Physics of Carbon*, P. A. Thrower Eds. Marcel Dekker, New York, 21, (1989) 151.
179. Zawadzki, J.; *In chemistry and physics of Carbon*, P.A. Thrower Eds. Marcel Dekkar, New York, 21, (1989) 151.
180. Zelenka, P.; Cartellieri, W.; Herzog, P.; *Appl. Catal. B*, 70, (1996) 3.
181. Zerkel, D.K.; Allendorf, M.D.; Wolf, M.; Deutschmann, O.; *J. Catal.*, 196, (2000) 18.
182. Zhu, J.; Lee, K.O.; Choi, M.Y.; *Proc. Combust. Inst.*, (2005) 2781.
183. Zhuang, Q-L.; Kyotani, T.; Tomita, A.; *Carbon*, 32, (1994) 539.
184. Zinbo, M.; Hunter, C.; Skewes, L.M.; Schuetzle, D.; *Anal. Sci.* 5, (1989) 403.

Nomenclature

n_m^a	monolayer coverage
a_s	specific surface area
a_m	average area
L	Avogadro constant
p	equilibrium pressure
p_0	saturation pressure
n^a	amount of gas adsorbed by unit mass of adsorbent
c	constant
λ	wavelength of X-radiations
d_{hkl}	interlayer spacing
θ	Bragg angle
r	conversion rate
E_A	apparent activation energy
n	reaction order
k	rate constant
n_0	initial molar amount of soot
$m_{c,0}$	representing the initial mass of carbon.
X	soot conversion
$c(O_2)$	gas phase concentration of oxygen
C_f	reactive sites in soot oxidation
F	volume flow rate at standard conditions
V_m	molar volume
$r(CO_x)$	rate of CO_x

CURRICULUM VITAE

PERSONAL

NAME: NAVEED JAN

Father's Name: Shaukat Ali

Date of Birth: May 1, 1975

Home Address: Village and Post Office Prang, Mohalla Sado Khel, Tehsil and District Charsadda, KPK, PAKISTAN
Post Code: 24420

Profession: Scientific Officer,
Environmental Research Section/F.T.C,
PCSIR Laboratories Complex Peshawar, Pakistan.

E-mail Address: naveedjankhan@gmail.com

Academic Achievements: First class in Bachelor and Master of Science examinations, respectively.

Qualification: M.Sc., Ph.D. (thesis submitted, October-2010).

Title of Ph.D. Thesis: Study on the catalytic oxidation of diesel engine soot using iron oxide catalysts.

PRESENTATIONS

1. Catalytic oxidation of soot. Proceedings of the seminar delivered at the International Seminar, University of Karlsruhe, Germany (2004).
2. Catalytic oxidation of soot. Proceeding of the seminar delivered at the 4th Asia Pacific Congress on Catalysis. Nanyang Technical University, Singapore (2006).
3. Thermo-gravimetric analysis of different type of soot presented at the Institute of Technical Chemistry & Polymer Chemistry, University of Karlsruhe, Germany (2009).
4. Preparation & characterization of nano sized catalysts presented at the Institute of Technical Chemistry & Polymer Chemistry, University of Karlsruhe, Germany (2010-11).

PUBLICATION FROM THIS THESIS

- Jan, M.T.; Hizbullah, K.; Kureti, S.; Jan, N.; 2007, *J. of Chemical Engineering and Technology*, 10, 1440-1444.
- Balle, P.; Bockhorn, H.; Geiger, B.; Jan, N.; Kureti, S.; Reichert, D.; Schroeder, T.; 2006, *J. of Chemical Engineering and Processing*, 45, 1065-1073.
- Jan, N.; Kureti, S.; Reichert, D.; Bockhorn, H.; 2004, *Wissenschaftliche Abschlussbericht 39. International Seminar*, 114-122.