DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE REMOVAL OF CARBON MONOXIDE BY IRON OXIDE NANOPARTICLES IN CAR EXHAUST

by
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İZMİR

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ABSTRACT

With the implementation of cars into our everyday life, a dangerous aspect of this luxury became apparent; exhaust gases. The oxidation of gasoline in the engine to CO_2 and H_2O is far from completely efficient. To fight with this problem, various laws and regulations were made. These emission standards limit the maximum amount of harmful substances a car exhaust can release. The pollutants that are limited today by these regulations are hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x) and particulate matter (PM). Advances in engine and vehicle technology continually reduce the amount of pollutants generated, but this is generally considered insufficient to meet emissions goals. Therefore, technologies to react with and clean up the remaining emissions have long been an essential part of emissions control. This study focuses on the oxidation of soot in diesel exhaust gases using Fe_2O_3 as a model catalyst. The purpose is to establish a thermally stable nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions. Nano-sized Fe_2O_3 was produced using sol-gel method. The synthesis of bulk Fe_2O_3 was carried out by polyvinyl alcohol (PVA) technique. Thermogravimetric analysis (TG) and temperature programmed oxidation analysis (TPO) were conducted. The effect of various dopants (Zr, Ce, Fe) and thermal aging were investigated. Also each sample was analyzed with X-Ray Diffraction (XRD) before and after each experiment. Our analysis show that, nano-sized Fe_2O_3 grants a temperature decrease in peak reaction temperature up to nearly 150ºC.

Key words; Catalysis; Vehicle emissions; Autocatalysts; Nano iron oxide

OTOMOBİL EKSOZUNDAN KARBON MONOKSİTİN NANO DEMİR OKSİT KULLANILARAK AYRIŞTIRILMASI

ÖZ

Arabaların günlük hayatımıza girmesiyle, bu lüksün tehlikeli bir yanı da ortaya çıktı; egzoz gazları. Ne yazık ki benzinin araba egzozunda CO_2 ve H_2O ya oksidasyonu tam verimle gerçekleşmekten uzaktır. Bu problemin önüne geçebilmek için bir çok ülkede değişik yasalar, bir aracın çevreye bırakabileceği maksimum zehirli gaz miktarını denetlemektedir. Günümüzde bu yasalarla denetlenen maddeler hidrokarbonlar (HC), karbon monoksit (CO), nitrojen oksitler (NO_x) ve is tanecikleri (PM) dir. Motor teknolojisindeki gelişimler bu gazların miktarlarını azaltmakla birlikte, genellikle bu azalma yeterli düzeyde değildir. Bu sebepten dolayı egzos gazlarıyla reaksiyona girip onları temzilemeye yönelik teknolojiler, egzos gazı kontrolünün önemli bir parçasıdır. Bu çalışma için dizel egzos gazlarının oksidasyonunu Fe_2O_3 i katalist olarak kullanarak incelemektedir. Burada amaç nano boyuttaki Fe_2O_3 in thermal stabilitesini incelemek ve dizel motorlarında katalist olarak kullanılabileceğini kanıtlamaktır. Nano boyuttaki Fe_2O_3 sol-gel methodu ile, Fe_2O_3 ise polivinil alkol (PVA) tekniği ile üretilmiştir. Örnekler üzerinde thermogravimetrik (TG) ve zaman ayarlı oksidasyon (TPO) analizleri yapılmıştır. Ayrıca ısıl yaşlanmanın ve değişik madde (Zr, Ce, Fe) katkılarının etkileri incelenmiştir. Deneylerimiz nano-Fe_2O_3 in 150ºC lik bir ısıl kazanç sağladığını kanıtlamaktadır.

Anahtar Kelimeler; Kataliz; Egzos gazları; Araba katalizörleri; Nano demir oksit

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CHAPTER ONE
INTRODUCTION

Cars... A car is a wheeled passenger vehicle that carries its own motor. By definition they are designed to run primarily on roads, to have seating for one to seven people, to typically have four wheels, and to be constructed principally for the transport of people rather than goods. Historically the invention of the first automobile is credited to Karl Benz who first built it in 1885. But actually it is estimated that over 100,000 patents created the modern automobile starting with the first theoretical plans for a motor vehicle that had been drawn up by both Leonardo da Vinci and Isaac Newton. Over the years automobiles has seen many changes and improvements. However the number of cars owned change by country (Dargay et al., 1999), as of 2002, there are roughly one car for every eleven people in the world.

With the implementation of cars into our everyday life, a dangerous aspect of this luxury became apparent. Even by the 1940 and 1950s air quality problems were experienced in some urban cities because of the increasing number of cars. By the 1960s cars had been in large scale mass production for many years, and they gave personal mobility to an increasing range of people. However, oxidation of fuel in the engine to CO_2 and H_2O was far from completely efficient. (Figure 1.1)

$$4H_mC_n + (m+4n)O_2 \rightarrow 2mH_2O + 4nCO_2$$
$$4H_mC_n + (m+2n)O_2 \rightarrow 2mH_2O + 4nCO$$
$$N_2 + O_2 \rightarrow 2NO$$

Figure 1.1 Oxidation of fuel in the engine (Twigg, 2007)

So the exhaust gas contained significant amounts of unburned hydrocarbons and lower levels of partially combusted products like aldehydes, ketones, and carboxylic acids, together with large amounts of CO. Unburned fuel and other hydrocarbons formed by thermal cracking, and various oxygenated species are referred to as

‘‘hydrocarbons’’ and designated HC. At the high temperature during the combustion in the cylinder N_2 and O_2 react to establish the endothermic equilibrium with nitric oxide (NO). This equilibrium is then frozen as the hot product gases are rapidly cooled and ejected into the exhaust manifold. The combination of NO and any of its oxidized form nitrogen dioxide (NO_2) is referred to as NO_x and more than a thousand ppm can be present in exhaust of a gasoline engine. The three major primary pollutants in the exhaust gases from cars are therefore NO_x, HC and CO. (Twigg, 2007) Particulate matter (PM), a major pollutant produced by diesel engines is also considered dangerous today by various standards. (Alkemade et al., 2006)

The dangerous materials in an automobile defined, we can take a closer look at the cause; the engine. However since the first car many different types of engines have been used, where as diesel and Internal Combustion engines are the two main engine types in use today. Since different engines will result in different exhaust gases our first priority should be taking a closer look at these engines and also the different types of fuels they use.

1.1 Internal Combustion Engine

The internal combustion engine is an engine in which the burning of a fuel occurs in a confined space called a combustion chamber. This exothermic reaction of a fuel with an oxidizer creates gases of high temperature and pressure, which are permitted to expand. The defining feature of an internal combustion engine is that useful work is performed by the expanding hot gases acting directly to cause movement, for example by acting on pistons, rotors, or even by pressing on and moving the entire engine itself.

This contrasts with external combustion engines, such as steam engines, which use the combustion process to heat a separate working fluid, typically water or steam, which then in turn does work, for example by pressing on a steam actuated piston.

Internal combustion engines are most commonly used for mobile propulsion systems. In mobile scenarios internal combustion is advantageous, since it can provide high power to weight ratios together with excellent fuel energy-density. These engines appear in almost all automobiles, motorbikes, many boats, and in a wide variety of aircraft and locomotives. Where very high power is required, such as jet aircraft, helicopters and large ships, they appear mostly in the form of gas turbines. They are also used for electric generators and by industry.

1.2 Diesel Engine

When a gas is compressed, its temperature rises. A diesel engine uses this property to ignite the fuel. Air is drawn into the cylinder of a diesel engine and is compressed by the moving piston at a compression ratio as high as 25:1, much higher than needed for a spark-ignition engine. At the end of the piston stroke, diesel fuel is injected into the combustion chamber at high pressure through an atomizing nozzle. The fuel ignites directly from contact with the air, the temperature of which reaches 700–900 °C. The combustion causes the gas in the chamber to heat up rapidly, which increases its pressure, which in turn forces the piston outward. The connecting rod transmits this motion to the crankshaft, which delivers rotary power at its output end. Scavenging (pushing the exhausted gas-charge out of the cylinder and drawing in a fresh draught of air) of the engine is done either by ports or valves. To significantly increase the efficiency of a diesel engine, a turbocharger to compress the intake air is often used. Use of an aftercooler/intercooler to cool the intake air after compression by the turbocharger further improves efficiency.

1.3 Fuels

Gasoline or petrol is a petroleum-derived liquid mixture consisting mostly of hydrocarbons and enhanced with benzene or iso-octane to increase octane ratings, used as fuel in internal combustion engines.

Diesel is produced from petroleum, and is sometimes called petrodiesel when there is a need to distinguish it from diesel obtained from other sources such as biodiesel. It is a hydrocarbon mixture, obtained in the fractional distillation of crude oil between 200 °C and 350 °C at atmospheric pressure.

The density of diesel is about 850 g/L whereas gasoline has a density of about 720 g/L, about 15% less. When burnt, diesel typically releases about 40.9 MJ/L, whereas gasoline releases 34.8 MJ/L, about 15% less. Diesel is generally simpler to refine than gasoline and often costs less (although price fluctuations sometimes mean that the inverse is true; for example, the cost of diesel traditionally rises during colder months as demand for heating oil, which is refined much the same way, rises). Also, due to its high level of pollutants, diesel fuel must undergo additional filtration which contributes to a sometimes higher cost.

Table 1.1 The energy contents of different fuels. (Bosch , 1996)

Fuel type	MJ/L	MJ/kg	BTU/Imp gal	BTU/US gal	Research octane number (RON)
Regular Gasoline	31.60	42.70	151,6	126,2	91
Premium Gasoline	32.84	43.50	157,5	131,2	95
Autogas (LPG)	24.85	46.02	119,2	99,3	115
Ethanol	21.17	26.80	101,6	84,6	129
Methanol	15.56	19.70	74,6	62,2	123
Gasohol	30.63	41.11	146,9	122,3	93/94
Diesel	35.50	42.50	170,2	141,7	25(*)

(*) Diesel is not used in a gasoline engine, so its low octane rating is not an issue; the relevant metric for diesel engines is the cetane number

1.4 Exhaust Gasses and Emission Standards

However different variations of engines and fuels exist, one fact remains true; each of them produces pollutants, NO_x, HC, CO and PM. Considering the huge number of cars in use today, it is safe to assume, automobile exhaust gasses is the major reason of air pollution. To fight with this problem, various laws and regulations were made. These emission standards limit the maximum amount of harmful substances a car exhaust can release. The pollutants that are limited today by these regulations are Hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x) and particulate matter (PM) (Alkemade et al., 2006).

In the United States, emissions standards are managed by the Environmental Protection Agency (EPA) as well as some state governments. Currently, vehicles sold in the United States must meet "Tier II" standards that went into effect in 2004 (Goralski et al., 2002). "Tier II" standards are currently being phased in a process that should be complete by 2009. The former Tier I standards that were effective from 1994 until 2003 were different between automobiles and light trucks (SUVs, pickup trucks, and minivans), but Tier II standards are the same for both types.

The European Union has its own set of emission standards that all new vehicles must meet. Currently, emissions of NO_x, HC, CO, and PM are regulated for most vehicle types, including cars, lorries, trains, tractors and similar machinery, barges, but excluding seagoing ships and airplanes (Figure 1.2). The stages are typically referred to as Euro 1 (1993), Euro 2 (1996), Euro 3 (2000), Euro 4 (2005) and Euro 5 (2008/9), or alternatively using Roman numerals instead of numbers.

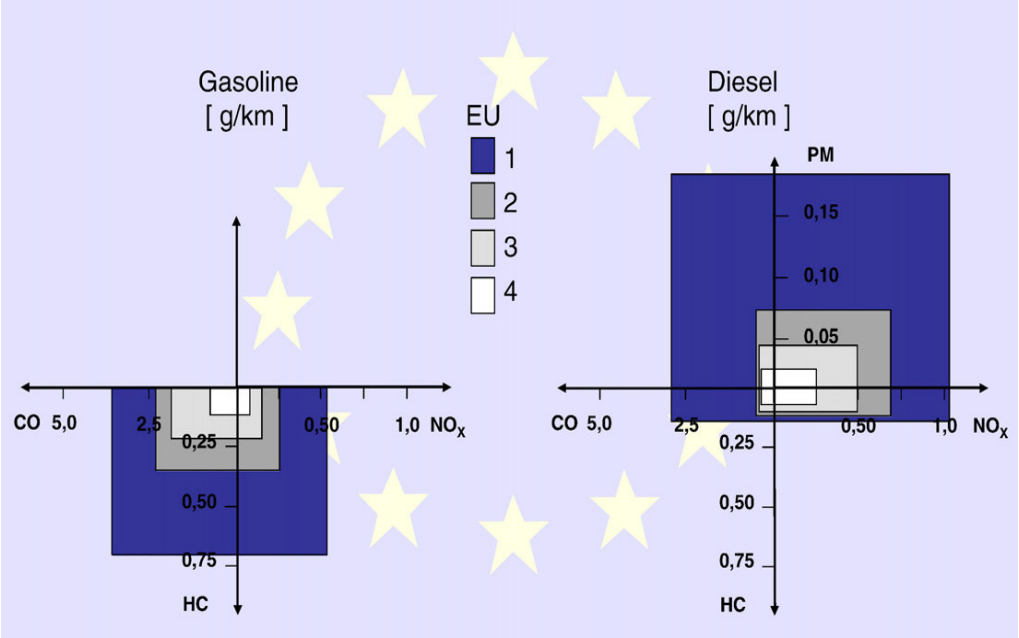


Figure 1.2 Emission control regulations for passenger cars in the European union (Alkemade et al., 2006)

In order to keep up with these regulations, automobile industry uses three basic approaches;

- Increasing engine efficiency
- Increasing vehicle efficiency
- Cleaning up the emissions

Each area presents its own unique research potential. Electronic ignition, Fuel injection systems and Electronic control unit technologies has improved engine efficiency. On the other hand lightweight vehicle design, minimized air resistance, reduced rolling resistance, improved power train efficiency, increasing spark to the spark plug has increased vehicle efficiency.

In line with the purpose of our study we are going to focus on the third approach.

1.5 Cleaning Up The Emissions

Advances in engine and vehicle technology continually reduce the amount of pollutants generated, but this is generally considered insufficient to meet emissions goals. Therefore, technologies to react with and clean up the remaining emissions have long been an essential part of emissions control.

1.5.1 Air injection

A very early emissions control system, the air injection reactor (AIR) reduces the products of incomplete combustion (hydrocarbons and carbon monoxide) by injecting fresh air into the exhaust manifolds of the engine. In the presence of this oxygen-laden air, further combustion occurs in the manifold and exhaust pipe. Generally the air is delivered through an engine-driven 'smog pump' and air tubing to the manifolds. This technology was introduced in 1966 in California, and was in use for the next several decades. It is not generally in use any longer, having been supplanted by cleaner burning engines and better catalytic converters.(Goralski et al., 2002, Ghoniem et al., 2005)

1.5.2 Exhaust Gas Recirculation

Engines produced after the 1973 model year have an exhaust gas recirculation valve on the intake manifold; its sole purpose is to reduce NO_x emissions by introducing exhaust gases into the fuel mixture, lowering peak combustion temperatures.

Around 1990, the Jeep division's power plants eliminated the EGR system. Some other engines also have dispensed with EGR, such as GM's Ecotec engine which was able to meet LEV emissions standards without requiring EGR. In some cases, the valve timing has been set to hold some exhaust in the combustion chamber after the exhaust stroke to perform a similar function to EGR.

1.5.3 Catalytic Converters

The catalytic converter is a device, placed in the exhaust pipe, which converts various emissions into less harmful ones using, generally, a combination of platinum, palladium and rhodium as catalysts. Catalytic converters have been steadily improved over the years. They make for a significant, and easily applied, method for reducing tailpipe emissions. Their other significant effect on pollution was that they were incompatible with the use of tetraethyl lead as an octane booster in gasoline, prompting the phasing-out of that additive as converter-fitted cars became more prevalent. The lead emissions were highly damaging to human health, and its virtual elimination has been one of the most successful reductions in air pollution. (Twigg, 2007, Twigg, 2006, Ozawa, 1998)

1.6 Diesel Engine Exhaust Control

A characteristic of old diesel engines was ‘‘black soot’’ in their exhausts caused by the combustion process itself in which very small ‘‘atomised’’ droplets of fuel burning in hot compressed air left an unburnt core of fine carbon particles onto which other species in the exhaust gas, including HCs, sulphur compounds NO_x and water adsorbed. Recently tremendous advances were made in the fuelling and combustion processes of modern high-speed diesel engines used in passenger cars. This involved very high pressure pumps, an increased number of smaller injector nozzles, and multiple injections. As a result soot or particulate matter (PM), emissions have been reduced to low levels. Nevertheless, there are still concerns about the possible health effects of diesel PM and there is a move to eliminate this by filtration. (Twigg, 2007)

So far three procedures were mainly examined in detail; classical selective catalytic reduction (SCR), HC SCR procedure and NO_x storage catalyst (NSC) technology, respectively. In case of SCR technique, nitrogen oxides are selectively reduced by ammonia into nitrogen over TiO_2 supported V_2O_5/WO_3 catalysts. The

required ammonia can be produced “on board” by decomposition for example of urea. (Kureti et al., 2003)

In the HC SCR procedure nitrogen oxides are reduced by hydrocarbons over platinum catalysts. In this process hydrocarbons can be generated from the fuel, and therefore no additional tank for its storage is required. However, NO_x reduction takes place with smaller conversion and lower nitrogen selectivity than occurred by NH_3 SCR procedure. Furthermore,large quantities of unwanted greenhouse gas N_2O are also formed.

The NSC technology is based upon periodic adsorption and subsequent reduction of NO_x. These catalysts contain a precious metal component which promotes the oxidation of NO into NO_2. The resulting NO_2 is then stored by basic adsorbents, e.g. Al_2O_3 and $Ba(OH)_2$. When the storage capacity is reached, rich exhaust conditions are established momentarily by engine management systems. As a result NO_x desorbs from the adsorbent and is reduced by H2, CO and HC present over the precious metal. However, a serious constraint of NSC technique is the susceptibility of the basic adsorbents to sulfur poisoning.

The emission of soot, which is thought to be carcinogen, can be diminished substantially by application of soot filters, which work efficiently in the CRT system (continuously regenerating trap). The CRT technique was developed by Johnson Matthey and is actually applied for heavy duty vehicles. The soot is separated on filters and is later on oxidized by NO_2 to CO_2 , whereby NO_2 is reduced into NO. In this process NO_2 is produced by oxidation of NO in the exhaust gas over a platinum catalyst. Considering the overall NO_x reactions there is no significant removal of nitrogen oxides. This CRT system shows an excellent performance during a road test over 700,000 km in the presence of ultra-low sulphur diesel fuel. Another possibility of soot removal is the use of oxidation catalysts, e.g. Cs_2SO_4 and V_2O_5, which accelerate the O_2–soot reaction.

A soot filter system fitted as standard equipment of diesel passenger cars has been developed by both PSA Peugeot Citroen and Toyota. The PSA Peugeot Citroen system has already been introduced and it comprises a particle filter that is linked with a pre-catalyst, i.e. an oxidation catalyst. The filter is discontinuously regenerated by temperature rise caused by post-injection of fuel as well as oxidation of the resulting unburnt hydrocarbons over the catalyst. The ignition temperature of the soot is lowered by a cerium containing fuel additive. The diesel particulate NO_x reduction (DPNR) technique provided by Toyota is based upon a filter system that contains an oxygen releasing agent as well as a NSC. By post-injection molecular oxygen and oxygen radicals desorb from the oxygen adsorbent and promote oxidation of the soot. Furthermore, the precious metal of the NSC component supports NO oxidation into NO_2 leading to a continuous soot oxidation like in the CRT system.

CHAPTER TWO
CATALYSIS

2.1 Catalysts

A catalyst is a substance that alters the rate of a chemical reaction without appearing in the products. Catalysts accelerate reactions but do not change equilibria. Increasing the rate of a desired reaction relative to unwanted reactions maximizes the formation of a desired product. (Othmer, 1985, Considine, 1974)

Catalysts are believed to function through an unstable chemical complex formed between the catalyst and reactant molecules. This complex reacts to produce new compounds with dissociation of the complex and regeneration of the catalyst which can then bring about the transformation of additional reactant molecules. The rate of a chemical reaction is proportional to a rate constant (k):

$$k = Ae^{-E/RT}$$

Because of the exponential form of the equation, even a small decrease in E, the activation energy, can bring about a large increase in rate. The catalytic pathway is a series of three chemical reactions: formation of the complex (activated adsorption), surface reaction, and desorption.

Solid catalysts invariably adsorb reactant molecules, adsorption and chemical reaction occurring on active sites identified as certain types of lattice defects.

The activity and selectivity of a catalyst can be affected by its pore structure, e.g., in a very slow reaction molecules can diffuse through a pore system to the catalytically active site center of a catalyst particle before they react. (Othmer, 1985)

2.1.1 Poisons

A poison, present in small amounts, adversely affects the catalyst performance. Most poisons are strongly adsorbed and react quantitatively with active sites to form stable inactive surface compounds. For instance, acidic catalysts are poisoned by basic nitrogen compounds and alkali metal ions, and metallic catalysts by sulfides, arsenic, and lead compounds, and sometimes by carbon monoxide, chlorides, and water.

Some poisons cause loss of selectivity, such as the nickel, vanadium, iron, and copper present in gas oils used in catalytic cracking. These deposit on the catalyst and because of their dehydrogenation ability, increase gas and coke formation and decrease gasoline production.

In some instances, a poison minimizes an undesired reaction while permitting a desired reaction. Thus in dehydrocyclization of paraffins to aromatics. potassium oxide is added to chromium oxide-aluminum oxide to neutralize acid sites active in cracking.

2.1.2 Reactivation

Decomposition or desorption of poison can sometimes be accomplished by steaming or evacuation at the maximum temperature permissible, or hydrogenation. More often, cokelike deposits are burned off with air. However, sintered catalysts cannot be regenerated. Removal of heavy metals by leaching restores cracking catalysts' selectivity can sometimes be economically justified.

2.1.3 Maintenance of Catalytic Efficiency

The maintenance of efficient performance during the lifetime of a catalyst can be more important than initial catalytic efficiency. In industrial use, catalysts loose not only activity but sometimes selectivity as well, i.e., the ability to produce a desirable distribution of products (quality).

In general, heterogeneous catalysts loose effectiveness because of overheating and contamination. Overheating causes sintering with loss of surface area and consequently of activity. Finely divided oxides and metals sinter at temperatures much lower than their melting points.

Contaminants affecting catalytic efficiency are metals entrained in the feedstock; oxygen, nitrogen, or sulfur compounds; and polynuclear aromatic compounds or coke. The latter can be removed by calcination. Nickel catalysts are notoriously susceptible to sulfur poisoning. However, cracking catalysts are not inactivated by sulfur compounds at the operating temperatures since they promote the formation of hydrogen sulfide which is eliminated.

2.2 Choosing a Catalyst

The factors that are considered when choosing a catalyst for a specific reaction are (Othmer, 1985);

- Selectivity
- Activity
- Stability
- Physical suitability
- Regenerability
- Cost

2.2.1 Selectivity

Selectivity means the efficiency in catalyzing a desired transformation. It is usually expressed by a factor representing the amount of desired product formed, divided by the amount of reactants converted. Low selectivity represents waste of reactants. It often decreases as the percentage of converted charge increases. Thus in industrial practice, a compromise is frequently made between selectivity and conversion. Nevertheless, selectivity often exceeds 90%. Another measure of selectivity is in product quality, e.g., the octane number of gasoline or the desirable properties of a plastic polymer.

2.2.2 Activity

Activity is frequently expressed as the amount of reactant in contact with the catalyst under a given set of conditions converted to all products. Activity is less desirable than might be thought since construction of a larger catalyst reactor, of say twice the size, is ordinarily inexpensive. However, a catalyst that is active at low temperatures may contribute to selectivity since this permits operation with minimum thermal degradation.

2.2.3 Stability

Stability is the ability to retain initial activity and selectivity, over the catalysts' lifetime. Activity is usually lost either by overheating (frequently in the presence of steam) which causes sintering with loss of surface area, or by poisons that deactivate active centers. Loss of selectivity is usually caused by chemical transformation in the catalyst, frequently by addition of poisons which cause unwanted reactions.

2.2.4 Physical Suitability

Catalysts require not only appropriate porosity, which can affect diffusion and thus the activity and regenerability, but also mechanical strength in moving-bed reactors.

2.2.5 Regenerability

A catalyst may lose activity or selectivity because of coke deposition, which in petroleum refining, may include sulfur and nitrogen residues. Even on a small scale, coke can gradually build up to unacceptable levels. It should then be possible to regenerate the catalyst; this is most readily achieved by burning in air. Less frequently, the catalyst is chemically treated to restore activity. In the case of platinum catalysts, the platinum is usually recovered, and its reuse represents complete chemical regeneration.

2.2.6 Cost

Cost calculations can be made from the product value and costs of raw material processing, plant amortization, and catalyst. The latter is usually quite small.

2.3 Applications of Catalysis

Catalysis is of paramount importance in the chemical industry. The production of most industrially important chemicals involves catalysis. Catalysis is also a major field in applied science, and involves many fields of chemistry, notably in organometallic chemistry, and physics. Catalysis is important in many aspects of environmental science, from the catalytic converter in automobiles to the causes of the ozone hole. Catalytic, rather than stoichiometric reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated.

There are two general types of catalytic processes, homogeneous and heterogeneous. In the homogeneous case, the chemical reaction is said to take place in a single phase, usually a liquid environment. In the heterogeneous case, the process takes place in a multiple phase, usually in a gaseous environment, and usually in the presence of a solid catalyst phase, which is either present as an undiluted material or on the surface of an inert substance (such as charcoal) called a support. The support allows the catalyst to have improved properties. For instance, a supported catalyst can be prepared with a higher active surface and greater physical strength than the original unsupported catalyst. (Considine, 1974)

In many cases a catalyst cannot be used by itself, as for instance mercuric acetate in the reaction of acetylene and acetic acid in the vapor phase, to yield vinyl acetate, a component of many polymers and plastics. Mercuric acetate has poor physical characteristics, and in the pure state is quite costly. However, a solution containing mercuric acetate can be absorbed onto and into small pieces of activated carbon which can have a surface area of up to 1,200 m^2/g. The resultant supported catalyst now has mercuric acetate spread over 1,200 m^2/g with a great deal more activity than mercuric acetate powder, which normally has a small surface area of less than 1 m^2/g. (Considine, 1974)

2.3.1 Examples of Catalytic Processes

2.3.1.1 Inorganic Chemicals

Modern industrial catalysis may be said to date from the introduction of the lead-chamber process in 1746. Nitric oxide is added to accelerate the oxidation of sulfur dioxide to sulfur trioxide. Almost seventy years later, Davy discovered that platinum hastens the combustion of mine gases and around 1832 it was found that platinum is also a catalyst for the conversion of sulfur dioxide to sulfur trioxide. The Deacon process for the catalytic oxidation of hydrogen chloride to molecular chlorine was an important milestone in 1860. The platinum-catalyzed oxidation of ammonia for nitric acid production was developed by Ostwald in 1905. The synthesis of ammonia was

accomplished by Haber and Mittasch just before World War I. More recently, the catalytic productions of hydrogen and hydrogen peroxide have been notable inorganic developments.(Othmer, 1985)

2.3.1.2 Organic Chemicals

Sabatier studied the hydrogenation of unsaturated compounds with the aid of nickel catalysts. The hardening of fat by hydrogenation was accomplished commercially by Normann in 1902. Ipatieff introduced high pressure technique that he applied successfully to catalytic hydrogenation in the early 1900s. The synthesis of methanol from carbon monoxide and hydrogen was achieved in Germany in 1923. Phthalic anhydride was produced by the oxidation of naphthalene in a process that is still used extensively. During World War II, Roelen and co-workers discovered the oxo reaction whereby carbon monoxide and hydrogen are added to olefinic materials, making possible production of aldehydes. These in turn can be catalytically hydrogenated to the corresponding alcohols. During World War II, processes were also developed for the production of butadiene by dehydrogenation of butene or butane. The most successful process for butane dehydrogenation, devised by Houdry, is still being used on a worldwide basis.

Catalytic reforming of petroleum became the dominant process for aromatics following World War II. More recently, large-scale production of benzene and naphthalene by hydrodealkylation of corresponding methyl homologues has been introduced. Large-scale manufacture of other aromatics include the alkylation of benzene with ethylene and subsequent dehydrogenation to styrene , isomerization of xyieres and transalkylation and toluene disproportionation. A new feature is the sophisticated integrated petrochemicals manufacture that uses hydrogen obtained from reforming.

Catalytic polymerization for production of plastics and synthetic rubber has enjoyed great industrial success. Catalysis by sodium polymerization of butadiene was introduced around 1925 by Lebedev in the Union of Soviet Socialist Republics,

followed by development of emulsion polymerization techniques in Germany in the mid 1930s employing peroxide catalysts. This was developed further using redox systems. More recently olefins, notably ethylene, have been polymerized at high pressures and even at lower pressures using Ziegler-type or solid catalysts such as molybdena-alumina or ehromia-silica-alumina. Of greatest interest is stereospecific polymerization catalyzed by lithium metal or aluminum alkyl and titanium chloride.

The tremendous increase in the production of polyurethane plastics, especially as flexible and rigid foam products, has been accelerated by the discovery of high activity catalyst systems, notably triethylenediamine plus tin compounds that make possible rapid one-shot polymerization. Also important is the direct conversion of nitroaromatics to isocyanates which are used in polyurethane manufacture.

In a new catalytic reaction of olefins, first described in 1964, propylene was disproportionated to ethylene and butene at 94% efficiency at 43% conversion. The mechanism is considered to proceed by a four-center (quasicyclobutane) intermediate involving the four doubly bonded carbon atoms of the two molecules of olefin and the catalyst, alumina-molvbdena, although recently a carbene mechanism has also been proposed.

The large-scale production of acrylonitrile from propylene by air oxidation in the presence of ammonia is a good example of a complex catalyzed reaction. (Othmer, 1985)

Table 2.1 Catalytic processes (Othmer, 1985)

Process & Product	**Reactants**	**Catalyst**	**Yield**
Amination:			
Amines	Alcohols + ammonia	Al_2O_3(Co)	90+
Ammoxidation:			
Acrylonitrile	Propylene + O_2 + NH_3	Bi-Mo-P CuO, SbSn	60-80
Benzonitrile	Toluene + O_2 + NH_3	V_2O_5-Sb	90+
Phthalonitrile	o-Xylene + O_2 + NH_3	V_2O_5	90+
Chlorination:			
Chlorobenzene	Benzene + Cl_2	Fe	70-75
Chloroacetic acid	Acetic acid + Cl_2	Red P	90
Benzyl chloride	Toluene + Cl_2	Ultraviolet light	95+
Hydration:			
Acetaldehyde	Acetylene + H_2O	Hg_2SO_4	95
Ethanol (alcohols)	Ethylene + H_2O	H_3PO_4, WO_3	95
Dehydration:			
Styrene	Methylethyl carbinol	TiO_2	80+
Ethylene (olefins)	Ethanol (alcohols)	Al_2O_3, ThO_2	90+
Acrylonitrile	Ethylene cyanohydrin	Al_2O_3	90+
Hydrogenation:			
Aniline	Nitrobenzene	Fe-HCl, Cu·SiO_2	90-95
Butanol	Butyraldehyde	Co, Ni-SiO_2	98+

Cyclohexane	Benzene	Ni-Al_2O_3, PtO_2	96+
Ethylene	Acetylene	Fe, Ni, Cu, Pd-$BaSO_4$	99
Methanol	Carbon monoxide	ZnO-CrO_3, Ni-Co	60
Dehydrogenation:			
Acetaldehyde	Ethanol + H_2	Cu, Ag, $FeMoO_4$	85-95
Benzene	Cyclohexane	Nu-Al_2O_3, Pt-Al_2O_3	95+
Butadiene	Butenes	Fe, Cr, K, $CaNiPO_4$	75-85+
Butene	Butane	Cr_2O_3-Al_2O_3	
Methyl ethyl ketone	Sec-Butanol	ZnO-ZnCu	85-92
Styrene	Ethyl benzene Phenyl methyl carbinol	$ZnCrO_2$-FeMgO $CaNiPO_4$ TiO_2	86-92 80+
Multiple reactions			
Reductive amination (with hydrogen):			
Isopropylcyclohexylamine	Acetone + cyclohexylamine + Cyclohexanone + isopropylamine	Ni	90+
Reductive dehydration:			
Butane	Butanol + H_2	Ni-Al_2O_3	90+
Reforming:			
Aromatic	Naphthenes + H_2	Mo-Al_2O_3 Pt-Al_2O_3-halides	
Desulfurization:			
Butane	Thiophene + H_2S + H_2	Co-Mo-Al_2O_3	

Oxidation:			
Acetaldehyde	Ethylene	$PdCl_2$-MgO-Cu	95+
Acetic acid	Acetaldehyde Butane	Mn^{++} Co, Bi	88-95 20-40
Acetic anhydride	Acetaldehyde	Cu, Co	70-75
Acetone	Isopropanol	Cu, Ag, Zno	85-90
Adipic acid	Cyclohexanone	Cu-Mn, V-Cu	70-90
Benzoic acid	Toluene Phenol	Co^{++} Cu	90 90
Benzaldehyde	Toluene	UO_2-MoO_3-Cu	30-50
Ethylene oxide	Ethylene	Ag, AgO	70
Propylene oxide	Propylene	Mo, W, Ti, V	90
Phthalic anhydride	Naphthalene o-Xylene	V_2O_5-K_2SO_4	70-80
Maleic anhydride	Benzene Butene	Mo-V-P-Na V-P	85 60
Terephthalic acid	p-Xylene	Mn-Co	90+

2.4 Catalysts in Environmental Control

The use of catalysts for the abatement of noxious emissions has increased substantially over the last several years. In the area of automotive emissions control, this has resulted in major growth for the catalyst manufacturing industry. Similarly, catalysis is being applied to a number of other environmental problems including nitrogen oxide reduction, odor control, and the "development of stationary-source catalytic combustors.

2.4.1 Nitric Acid Plant Tail Gas Cleanup

Nitric acid is manufactured by the catalytic oxidation of ammonia with air to produce nitrogen oxides which are then absorbed in water to give nitric acid. Large amounts of unabsorbed nitrogen oxides in the tail gas from the absorption tower

result in a pollution problem which has been solved in some cases by the catalytic processing of this tail gas over platinum-group metals to yield useful energy in the form of steam, power, or both. The tail gas reactor outlet temperature is usually between 650 and 750°C. Support materials for the catalyst include nichrome wire, alumina pellets, and alumina honeycomb materials. (Ramírez et al., 2005, Cabrera et al., 2005, Xu et al., 2004, Sadykov et al., 2000)

2.4.2 Industrial Odors

The elimination of organic fumes is desirable for air pollution and fire safety reasons. The platinum metals (particularly Pt and Pd) supported on SiO_2, Al_2O_3, and carbon have been used as catalysts for the oxidation of carbon monoxide and a wide range of organic compounds in the presence of air or oxygen. Most odors are caused by low concentrations of organic sulfur, nitrogen, and oxygen compounds. The catalyst lowers the temperature needed to remove odors and accelerates the process.(Schlegelmilch et al., 2005, Miedema et al., 2000)

2.4.3 Catalytic Combustors

The use of catalysts to promote hydrocarbon oxidation reactions has a number of advantages for emissions control. For example, flame combustion places a limit on the lower level of NO_x control that can be achieved economically for clean fuels (approximately 25-30 ppm NO_x for small sources), whereas with catalytic combustion much lower levels of NO_x can be reached (perhaps <10 ppm). This is caused primarily by the lower temperatures of catalytic combustion. Additionally catalytic combustion is soot-free, depending on the kind of fuel. Overall high combustion efficiency is possible if the excess air can be limited in some way, such as two-stage combustion, flue-gas recirculation, or cooling of the catalyst bed. Furthermore, the presence of a catalyst permits much more efficient and complete combustion at air-fuel ratios that are unacceptable for a homogeneous combustion system. (Hwang et al., 2004, Spadaccini et al., 2003, Cittadini et al., 2001)

2.4.4 Hydrogen Sulfide Conversion to Sulfur

Hydrogen sulfide is ubiquitous to many refinery and chemical waste streams, and can be converted to sulfur using the Claus process. There are three major variations of this process, namely partial combustion, split stream, and direct oxidation. In these processes, part of the H_2S stream is oxidized to SO_2 and S, and the SO_2 then reacts with the remaining H_2S over a bauxite catalyst to give S and H_20. The process is generally run at atmospheric pressure and GHSV (space velocity) in the range of 1000-5000 h^{-1}. Catalyst life ranges from 1 to 5 years, depending on usage. (Henshaw et al., 1998, Li et al., 1996)

2.4.5 Automotive Emissions

The exhaust of an automobile is a demanding environment, and very unlike the steady-state operation of most chemical plant catalytic processes. The catalyst must function at low temperature, resist effects of thermal excursions up to about 1000 C (for diesel 600 C), tolerate the presence of poisons (especially sulphur species) and not be affected by gas flow pulsations and severe mechanical vibrations (Twigg, 2007,Twigg, 2006)Distilled to its essence, however, the story of automotive exhaust catalysis revolves around three noble metals—platinum (Galisteo et al., 2005, Skoglundh et al., 1999, Adams et al., 1996, Lin et al., 237-254, Stone et al., 2003), palladium (Skoglundh et al., 1996, Uenishi et al., 2005, Nishihata et al., 2005, Papadakis et al., 1996, Farrauto et al., 1995), and rhodium (Mannila et al., 1996, Cuong et al., 1994, Tremont et al., 1990, Schlatter et al., 1977, Heeb et al., 2000, Lassi et al., 2004) that have been dispersed, stabilized, promoted, alloyed, and segregated in increasingly sophisticated ways over the years to achieve extraordinary advances in performance and durability.(Gandhi et al., 2003)

Much of the early research and development on automotive catalysts, prior to commercialization in the 1975 time frame, was devoted to non-noble metal catalysts (so-called base metal catalysts), largely due to concerns over the cost and availability of noble metals. However, it quickly became apparent that the base metals (oxides of

Ni, Cu, Co, Mn, and Cu/Cr, for example) lacked the intrinsic reactivity, durability, and poison resistance required for automotive applications (Gandhi et al., 2003).

Platinum group metal catalysts were found to be very active, and a huge amount of work was done with ruthenium, but its oxides are so volatile such that it was not possible to prepare a catalyst that did not lose ruthenium during use. Even iridium oxides are too volatile at high temperatures, so this metal could not be used in practical catalysts. (Twigg, 2006) Thus, Pt and Pd were left as clear choices for the oxidation catalysts employed during the first phase of catalytic emission controls, especially since Rh is scarce relative to Pt and Pd and exhibits lower activity for olefin conversion under oxidizing conditions (Gandhi et al., 2003). Of these platinum is the most noble, but catalysts containing it when very hot and exposed to oxygen for long periods can sinter through a process involving migration of oxide species. Palladium forms a more stable oxide, and this is catalytically active in oxidation reactions. (Twigg, 2007)

Table 2.2. lists some of the physical properties of platinum group metals together with those for base metals that are used in industrial catalysts. Frequently two or more metals are used in combination in autocatalysts. Today three-way catalysts most commonly contain palladium/rhodium although platinum/rhodium is still used on some cars.(Twigg, 2007)

Table 2.2 Physical properties of some metals and their oxides relevant to their behaviour in autocatalysts

Metal	**An***	**Atomic Weight**	**Density (g cm^{-3})**	**Mp* (K)**	**Reduction Potential**	**Oxide stability**
Platinum	77	195.08	21.45	2045	1.19 (2)	Unstable
Iridium	46	192.22	22.56	2683	1.16 (3)	Nearly stable
Palladium	45	106.42	12.02	1825	0.92 (2)	Stable
Rhodium	76	102.91	12.41	2239	0.76 (3)	Stable
Osmium	44	190.2	22.59	3327	N/A (2)	Very volatile
Ruthenium	29	101.07	12.37	2583	N/A (2)	Very volatile
Copper	27	63.33	8.96	1357	0.34 (2)	Stable
Cobalt	28	58.93	8.90	1768	-0.28 (2)	Stable
Nickel	26	58.69	8.90	1726	-0.30 (2)	Stable
Iron	78	55.85	7.87	1808	-0.44 (2)	Stable

* mp = melting point, an = atomic number

2.4.5.1 Three-way gasoline catalysts

The engines with the earliest catalytic emissions control systems were fuelled via carburettors that could not precisely control the amount of fuel that was mixed with the intake air. Often the air/fuel ratio moved randomly either side of the stoichiometric point, and it was observed a platinum/rhodium catalyst could, under appropriate conditions, simultaneously convert CO and HC oxidations and reduce NO_x with high efficiency. This catalyst concept became known as a three way catalyst (TWC), because all three pollutants are removed from the exhaust gas simultaneously. Application of the TWC required three elements:

- Electronic fuel injection (EFI) so precise amounts of fuel could be metered to provide a stoichiometric air/fuel mixture.
- An oxygen sensor in the exhaust to provide an electrical signal indicating if the engine is running rich or lean.

- A microprocessor to control a feedback-loop using oxygen sensor signals to determine the amount of fuel to be injectedunder specific conditions to maintain the exhaust gas close to the stoichiometric point.

By the early 1980s all of the elements necessary for the operation of TWCs were available. This became a more efficient means of controlling HC, CO and NO_x emissions than the earlier catalyst systems, and it was also more cost effective. Soon TWCs were universally adopted. (Twigg, 2007, Twigg, 2006)

CHAPTER THREE
IRON AND IRON OXIDES

3.1 Iron

Iron is a chemical element with the symbol Fe and atomic number 26. Iron is a group 8 and period 4 metal. Iron is a lustrous, silvery soft metal. Iron and nickel are notable for being the final elements produced by stellar nucleosynthesis, and thus the heaviest elements which do not require a supernova or similarly cataclysmic event for formation. Iron and nickel are therefore the most abundant metals in metallic meteorites and in the dense-metal cores of planets such as Earth.

Iron is believed to be the tenth most abundant element in the universe, and fourth most abundant on earth. The concentration of iron in the various layers in the structure of the Earth ranges from high (probably greater than 80%, perhaps even a nearly pure iron crystal) at the inner core, to only 5% in the outer crust. Iron is second in abundance to aluminium among the metals and fourth in abundance in the crust. Iron is the most abundant element by mass of our entire planet, making up 35% of the mass of the Earth as a whole.

Iron is a metal extracted from iron ore, and is almost never found in the free elemental state. In order to obtain elemental iron, the impurities must be removed by chemical reduction. Iron is the main component of steel, and it is used in the production of alloys or solid solutions of various metals, as well as some non-metals, particularly carbon.

3.2 Iron Oxides

Iron oxides are common compounds which are widespread in nature. They are present in almost all of the different compartments of the global system - the atmosphere, hydrosphere, lithosphere, pedosphere and biosphere - and take part in the manifold interactions between these compartments. (Cornell et al., 1996)

Initially, formation of Fe^{III} oxides mainly involves aerobic weathering of surface magmatic rocks in both terrestrial and marine environments; redistribution between the various global compartments may follow. Redistribution may involve mechanical transport by wind/water erosion from the pedosphere into the hydrosphere or atmosphere or, more importantly, reductive dissolution followed by oxidative reprecipitation in a new compartment. Iron ore formation and iron oxide precipitation in biota are important examples of such redistribution processes. Man participates in these processes not only as a living organism, but also as a consumer of iron metal and Fe oxides for various industrial purposes. The overall result of all these processes is a continuous net increase in Fe oxides in the global system at the expense of the iron in the magmatic ("primary") rocks. (Cornell et al., 1996)

The logical consequence of the widespread distribution of Fe oxides is that they are of interest to many scientific disciplines (Figure 3.1). Naturally this has led to much fruitful, interdisciplinary communication and interaction. (Cornell et al., 1996)

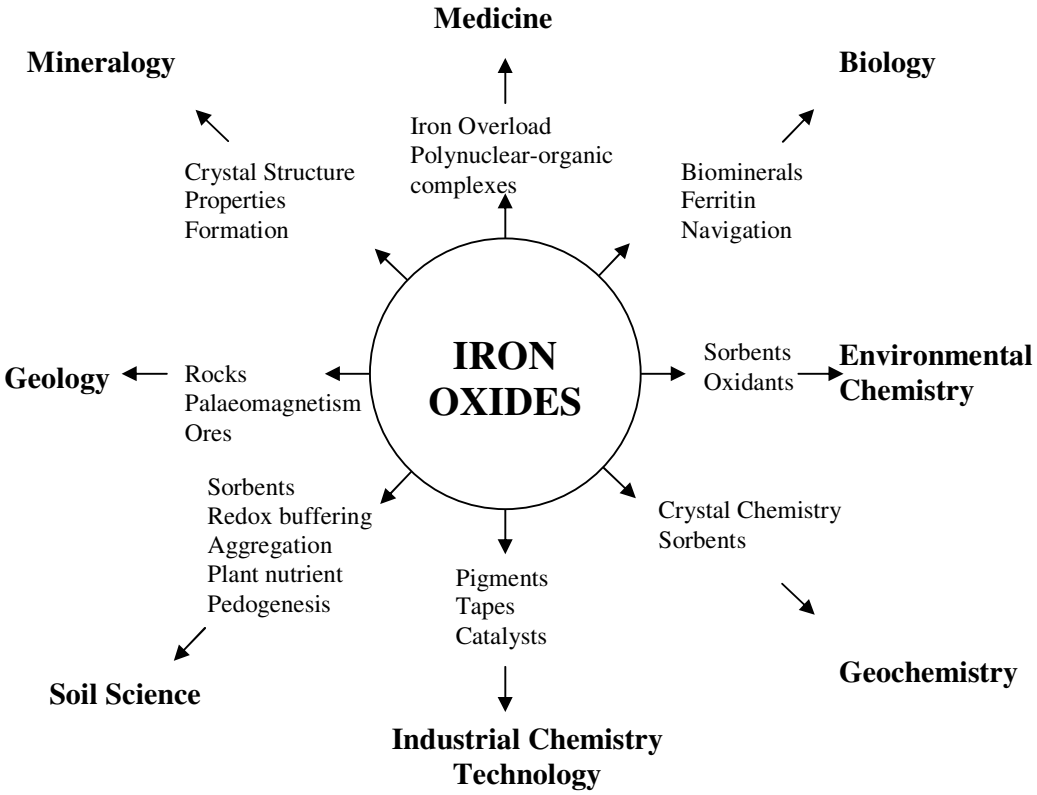


Figure 3.1 Scientific disciplines related to iron oxides

3.3 Types of Iron Oxides

There are sixteen iron oxides. These compounds are in fact either oxides, hydroxides or oxide hydroxides. They are composed of Fe together with O and/or OH. In most compounds iron is in the trivalent state. Iron oxides consist of close packed arrays of anions (usually in hexagonal (hep) or cubic (ccp) close packing) in which the octahedral and, in some cases, the tetrahedral interstices are partly filled with tri-valent or divalent Fe. The various oxides differ mainly in the way in which the basic structural units are arranged in space. In some cases, anions (Cl^-, SO_4^{2-}) participate in the structure. (Cornell et al., 1996)

Table 3.1 Selected properties of the iron oxides

	Goethite	Lepidocrocite	Akaganeite	Feroxyhyte	Ferrihydrite	Haematite	Magnetite	Maghemite	Wüstite
Crystal system	ortho-rhombic	ortho-rhombic	Tetragonol (monoclinic)	hexagonal	hexagonal	trigonal	cubic	cubic or tetragonol	cubic
Cell dimensions(nm)	a=0,4608 b=0,9956 c=0,30215	a=0,388 b=1,254 c=0,307	a=1,000 b=0,3023 c=1,0513	a=0,293 c=0,460	a=0,508 c=0,94	a=0,5034 c=1,3752	a=0,839	a=0,854	a=0,430 2-0,4275
Formula units per unit cell,Z	4	4	8	2	4	6	8	8	4
Density(g/cm^3)	4,26	4,09	3,56	4,2	3,96	5,26	5,18	4,87	5,9-5,99
Octahedral occupancy	1/2	1/2	1/2	1/2	<2/3	2/3	-	-	-
Colour	yellow brown	orange	yellow brown	red-brown	red-brown	red	black	reddish brown	black
Hardness	5-5 1/2	5	-	-	-	6 1/2	5 1/2	5	-
Type of magnetism	antiferromag	antiferromag	antiferromag	ferrimag	speromag	weakly ferromag or antiferromag	ferrimag	ferrimag	anti-ferrimag
Neel(curie) temperature(K)	400	77	290	440-460	25-115	956	850	820-986	203-211
Standard free energy of formation ΔG_f^o	-488,6	-477,7	-752,7	n.k	-699	-742,7	-1012,6	-711,1	-251
Solubility product (pFe+3pOH)	40-44	-42	34,8	n.k	38-39,5	42,2-43,3	35,7	40,4	

There are five polymorphs of FeOOH and four of Fe_2O_3. The oxide hydroxides are readily dehydroxylated to their oxide counterparts. Dehydroxylation proceeds relatively easily owing to the similarity between the anion frameworks which ensures that rearrangement of the cations and loss of OH are often all that is required to effect a transformation. Other characteristics of these compounds include the low solubility (high stability) of the Fe^{III} oxides, the brilliant colors, the partial replacement of Fe in the structure by other cations, in particular Al^{3+} and the catalytic activity. Owing to their high energy of crystallization, Fe oxides often form only minute crystals both in natural environments and when produced industrially. They have, therefore, a high specific surface area, often > 100 m^2/g, at which the so called functional groups are exposed: this makes them effective sorbents for a large range of dissolved ions, molecules and gases. Selected properties of the iron oxides are summarized in Table 3.1

3.3.1 Goethite

α-FeOOH, occurs throughout the various compartments of the global ecosystem. It has the diaspore structure which is based on hep packing of anions. Goethite is one of the thermodynamically most stable iron oxides at ambient temperatures and is, therefore, the first oxide to form and also the end member of many transformations. In massive crystal aggregates, goethite is dark brown or black, whereas the powder is yellow and is responsible for the colour of many rocks, soils and ochre deposits. Industrially, goethite is an important pigment.

3.3.2 Lepidocrocite

The orange coloured lepidocrocite, γ-FeOOH, is typically formed in nature i.e. in soils, biota and rust, as an oxidation product of Fe^{2+}. It has the boehmite structure which is based on ccp packing of anions.

3.3.3 Akaganeite

β-FeOOH, occurs rarely in nature. It is found mainly in Cl-rich environments such as hot brines. Unlike the other FeOOH polymorphs, it has a structure based on body centered cubic anion close packing (hollandite structure) and contains a low level of either chloride or fluoride ions. Its colour is brown to bright yellow.

3.3.4 Schwertmannite

Schwertmannite is closely related with akaganeite. However in this compound the chloride ions have been replaced by sulphate ions. This recently recognized mineral can be synthesized by inorganic or bacterial oxidation. It is also found in nature, e. g., in acid mine waters, as an oxidation product of pyrite.

3.3.5 δ-FeOOH

δ-FeOOH (synthetic) is a ferrimagnetic materials. Its structure is based on hep anion arrays. The compound is reddish brown.

3.3.6 Feroxyhyte

Feroxyhyte (δ′-FeOOH) is the poorly crystalline mineral form of δ-FeOOH is also a ferrimagnetic material. The structures of both compounds are based on hep anion arrays and differ in the ordering of the cations. These compounds are reddish brown. Feroxyhyte occurs (rarely) in various surface environments.

3.3.7 Ferrihydrite

Ferrihydrite, a reddish-brown mineral is widespread in surface environments. Unlike the other iron oxides it is poorly ordered and, unless stabilized in some way, transforms into more stable members of the group. Until recently, ferrihydrite was often termed amorphous iron oxide or hydroxide or hydrous ferric oxide (HFO).

Neither the structure nor the formula has been fully established; the former resembles that of haematite, but contains structural cation vacancies together with some OH.

3.3.8 Bernalite

$Fe(OH)_3$ is a recently identified, greenish iron oxide that to date, has only been found as a mineral sample in a museum.

3.3.9 $Fe(OH)_2$

$Fe(OH)_2$, does not exist as a mineral. The structure is similar to that of brucite and is based on hep anion packing with the cation in the divalent state. Pure Fe(OH)2 is white. It is, however, readily oxidized, upon which it develops into the greenish-blue, so called green rust or, upon further oxidation into black magnetite.

3.3.10 Haematite

α-Fe_2O_3, is the oldest known Fe oxide mineral and is widespread in soils and rocks. Its colour is red, if finely divided and black or sparkling grey, if coarsely crystalline. Haematite has the corundum structure which is based on hep anion packing. Like goethite, haematite is extremely stable and is often the end member of transformations of other iron oxides. It is an important pigment, a valuable ore and an important constituent of the banded iron formations.

3.3.11 Magnetite

Fe_3O_4, is a black, ferrimagnetic mineral containing both Fe^{II} and Fe^{III}. It has an inverse spinel structure. Magnetite is an important ore. Together with titanomagnetite it is responsible for the magnetic properties of rocks.

3.3.12 Maghemite

γ-Fe203, is a red-brown, ferrimagnetic material, isostructural with magnetite, but with cation deficient sites. It occurs in soils as a weathering product of magnetite and as the product of heating other Fe oxides in the presence of organic matter. Maghemite is an important magnetic pigment.

3.3.13 β- Fe_2O_3

β-Fe_2O_3 is a rare compound that have only been synthesized in the laboratory. It was obtained by dehydroxylation of β-FeOOH at 170 °C under high vacuum.

3.3.14 ε- Fe_2O_3

The second laboratory synthesized iron, was produced by reaction of alkaline potassium ferri-cyanide solution with sodium hypochlorite.

3.3.15 High pressure FeOOH

High pressure FeOOH is another rare, laboratory compound that has been prepared by hydrothermal conversion of haematite in NaOH at 500 °C and pressures of 80-90 kb.

3.3.16 Wüstite;

Wüstite, FeO, is a black iron oxide containing only divalent Fe. It is usually non-stoichiometric (oxygen deficient). The structure is similar to that of rock salt and is based on a ccp anion array. Wustite is an important intermediate in the reduction of iron ores.

CHAPTER FOUR
MATERIALS AND METHODS

Throughout this study various chemicals and equipment was used. This section will detail these in short detail.

4.1 Bulk α- Fe_2O_3 and nano-α- Fe_2O_3

The production of both bulk α-Fe_2O_3 and nano-sized α-Fe_2O_3 will discussed more widely in chapter 5. Bulk α-Fe_2O_3 was produced using the technique detailed there. Because we couldn't succeed in polyol-method, and time limitations did not let us have samples with the sol-gel method, we have acquired nano-sized α-Fe_2O_3 samples from another group of the institute. All the experimental work was conducted using these samples.

4.2 Dopants

This study focuses on the oxidation of soot in diesel exhaust gases using nano-sized α-Fe_2O_3 as catalysts that are more active than conventional bulk Fe_2O_3. However a general constraint of nano-solid materials is their susceptibility towards thermal aging and thus the aim is also to increase thermal stability by modification with dopants. In present work Zr, Ce, and Fe were taken as dopants. The following are some short explanations regarding these dopants.

4.2.1 Zirconium (Zr)

Zirconium is a chemical element in the modern periodic table that is assigned the symbol Zr and has the atomic number 40. A lustrous gray-white, strong transition metal that resembles titanium, zirconium is obtained chiefly from zircon and is very corrosion resistant. Zirconium is primarily used in nuclear reactors due to its resistance to corrosion and low neutron cross-section.

4.2.2 Cerium (Ce)

Cerium is a chemical element in the periodic table that has the symbol Ce and atomic number 58. Cerium is a silvery metallic element, belonging to the lanthanide group. It is used in some rare-earth alloys. It resembles iron in color and luster, but is soft, and both malleable and ductile. It tarnishes readily in the air. Only europium is more reactive than cerium among rare earth elements. Alkali solutions and dilute and concentrated acids attack the metal rapidly. The pure metal is likely to ignite if scratched with a knife. Cerium oxidizes slowly in cold water and rapidly in hot water.

4.2.3 Iron (Fe)

Iron is a chemical element with the symbol Fe (Latin: ferrum) and atomic number 26. Iron is a group 8 and period 4 metal. Iron is a lustrous, silvery soft metal. Iron and nickel are notable for being the final elements produced by stellar nucleosynthesis, and thus the heaviest elements which do not require a supernova or similarly cataclysmic event for formation. Iron and nickel are therefore the most abundant metals in metallic meteorites and in the dense-metal cores of planets such as Earth.

4.2.4 Doping of the Fe_2O_3 catalyst

For both thermogravimetric analysis and temperature programmed oxidation analysis, 95 mg of catalyst was mixed with 5 mg of soot. The catalyst was modified with the dopants where appropriate. Table 4.1 shows the amount of material used for doping nano-α-Fe_2O_3. Doping is performed by incipient wetness method. The mixture was left in a laboratory oven for a few hours to dry it. After that the samples were calcinated at 350 C in a calcination oven with flow in order to remove the nitrates completely.

Table 4.1The amount of material used for doping nano-α- Fe_2O_3

Dopant	Molar Ratio (Fe:Dopant)	Amount of Dopant (mg)	Dopant in Nitrate Form	Amount of Water (ml)	Amount of α-Fe_2O_3 (mg)
Zr	1:1	200	$ZrO(NO_3)_2$	0,15	100
	1:0,1	20			
	1:0,01	2			
Ce	1:1	350	$Ce(NO_3)_3.6H_2O$		
	1:0,1	35			
	1:0,01	4			
Fe	1:1	266	$Fe(NO_3)_3.9H_2O$		
	1:0,1	27			
	1:0,01	3			

4.3 Soot

The soot used in the experiments was produced using the laboratory bench, the process will be discussed in great detail in chapter 5. The TG data of the collected soot show a small amount of adsorbed species only (2.6 wt.%). The oxygen content of the soot is deduced from the TPD pattern that indicates the desorption of CO (9.2 mg/g soot) and CO_2 (3.3 mg/g soot). The content of H is determined by TPO, in which the hydrogen is detected in the form of H_2O (43 mg/g soot). Furthermore, neither the evolution of NO_x nor ash residues are observed in temperature programmed oxidation. The pictures clearly show the spherical shape of the primary particles that are condensed to form chains. It is obvious that the most probable diameter is at 45 nm being in fair agreement with diesel soot. (Balle et al., 2006)

4.4 Thermogravimetry (TG)

Thermogravimetry (also knows by acronym "TG") 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.

A sample of material is placed on an arm of a recording microbalance, also called thermobalance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile, 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.

The gaseous environment of the sample can be: ambient air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapors of liquids or "self-generating atmosphere". The pressure can range from high vacuum or controlled vacuum, through ambient, to elevated and high pressure; the latter is hardly practical due to strong disturbances.

The commonly investigated processes are: thermal stability and decomposition, dehydration, oxidation, determination of volatile content and other compositional analysis, binder-burnout, high-temperature gas corrosion etc. The kinetic data obtained by TG are reliable only for irreversible processes, whereas reversible ones are grossly affected by diffusion, and only special procedures can handle them. Although many industrial processes could benefit from thermogravimetric investigations, the industry is often discouraged by the natural discrepancies between the data produced by milligram-size samples, and those of the bulk processes. In this respect gram-size and larger TG samples are more suitable for optimization research of industrial processes.

The conventional TG focuses on various aspects of analysis of materials; the other facet of thermogravimetry is studying synthesis, e.g. using a thermobalance for monitoring of making of materials. The industrial processes of CVD, chemical vapor deposition, CVI, chemical vapor infiltration, metallurgical carburization, synthesis of carbon-carbon composites can greatly benefit from modeling them with large-sample TG instruments.

4.4.1 Netzsch STA 409

The STA 409 CD is based on the classic concept of a thermobalance in a vertically-arranged instrument with top-loaded samples. This design ensures total protection of the digital balance, which is on the bottom, through accurate flow of the purge and protective gases in a natural vertical path to the top, with optimal conditions for coupling FTIR and MS gas analysis systems to the heated furnace outlet. The variety of materials available for components and seals that come into contact with the gases means that measurements are also possible in corrosive gas atmospheres.

Single and double hoist systems for the different types of exchangeable furnaces open up the extremely broad temperature range of -160°C to 2000°C, supported by a multitude of sample carriers and crucibles.

The STA sample carriers are always equipped with a thermocouple for direct measurement of the temperature at the sample/reference crucible (DSC/DTA). There are a number of different thermocouple types to choose from, depending on the application.

Figure 4.1 STA 409 CD Thermogravimeter

4.5 Temperature Programmed Oxidation

Temperature programmed reaction methods form a class of techniques in which a chemical reaction is monitored while the temperature increases linearly with time. Several forms are in use. All these techniques are applicable to real catalysts and single crystals and have the advantage that they are experimentally simple and inexpensive in comparison to many other spectroscopies. Interpretation on a qualitative basis is fairly straightforward. However, obtaining reaction parameters such as activation energies or preexponential factors from temperature programmed methods is a complicated matter.

Instrumentation for temperature programmed investigations is relatively simple. The reactor, charged with catalyst, is controlled by a processor which heats the reactor at a rate of typically 0.1-20 °C/min. A thermal conductivity detector measures

the hydrogen or oxygen content of the gas mixture before and after reaction. For TPR one uses a mixture of typically 5% H_2 in Ar, for TPO 5% O_2 in He, to optimize the thermal conductivity difference between reactant and carrier gas. With this type of apparatus, a TPR (TPO) spectrum is a plot of the hydrogen (oxygen) consumption of a catalyst as a function of temperature.

Temperature programmed sulfidation or temperature programmed reaction spectroscopy usually deal with more than one reactant or product gas. In these cases a TCD detector is inadequate and one needs a mass spectrometer for the detection of all reaction products. With such equipment one obtains a much more complete picture of the reaction process, because one measures simultaneously the consumption of reactants and the formation of products.

To summarize, TPO is a highly useful technique, which provides a quick characterization of metallic catalysts. It gives information on the phases present after impregnation and on the eventual degree of reduction. For bimetallic catalysts, TPO patterns often indicate whether or not the two components are mixed. In favorable cases, where the catalyst particles are uniform, TPO yields activation energies for the reduction as well as information on the mechanism of oxidation. (Niemantsverdriet, 2000)

TPO analysis were carried out on laboratory bench (Figure 4.2). Each sample was placed inside a quartz glass tube (I.D. 22 mm) and was fixed with quartz wool. Using this method CO, CO_2 and inlet, outlet temperatures were measured constantly.

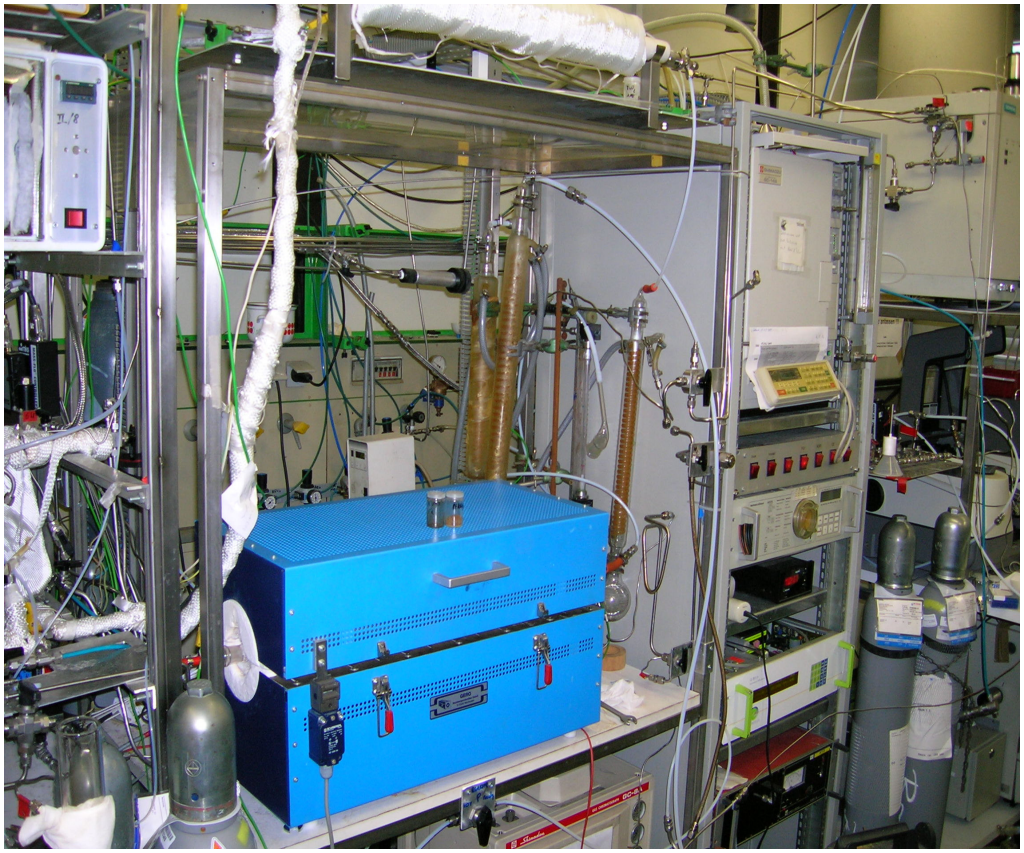


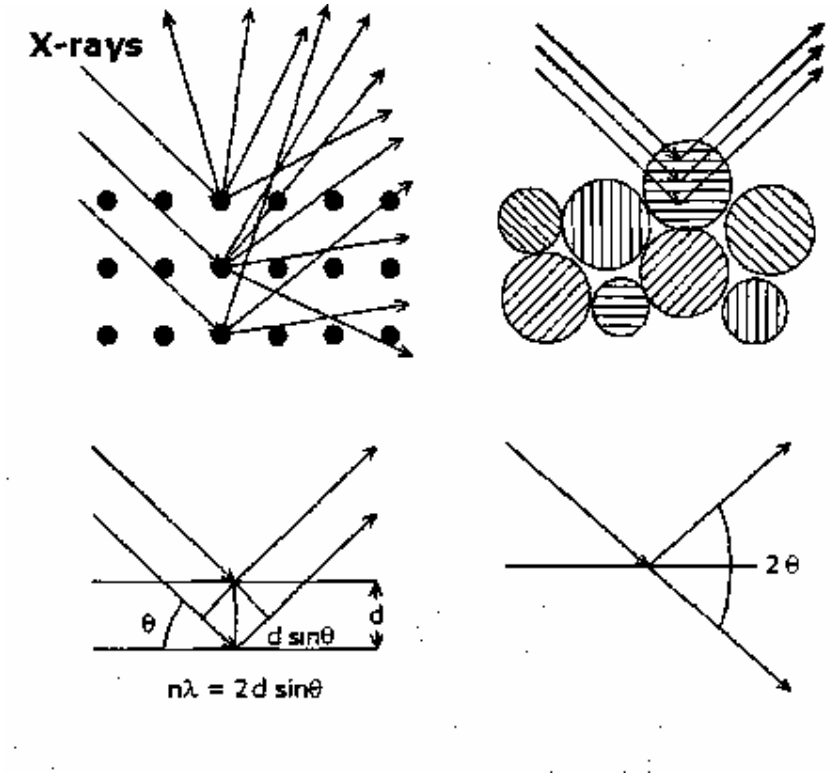
Figure 4.2 Laboratory bench for TPO analysis.

4.6 X-Ray Diffraction (XRD)

X-rays have wavelengths in the angstrom range, are sufficiently energetic to penetrate solids, and are well suited to probe their internal structure. XRD is used to identify bulk phases, to monitor the kinetics of bulk transformations, and to estimate particle sizes. An attractive feature is that the technique can be applied in situ.

A conventional X-ray source consists of a target that is bombarded with high energy electrons. The emitted X-rays arise from two processes. Electrons slowed down by the target emit a continuous background spectrum of bremsstrahlung. Superimposed on this are characteristic, narrow lines. The Cu Kα line, with an energy of 8.04 keV and a wavelength of 0.154 nm, arises because a primary electron under emission of an X-ray quantum. Kβ radiation is emitted when the K-hole is is filled from the M-shell, and so on. This creates a core hole in the K-shell, which

filled by an electron from the L-shell process is called X-ray fluorescence. It is the basis for X-ray sources and it is also encountered in electron microscopy, EXAFS and XPS. X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered monochromatic X-rays that are in phase give constructive interference. Figure 4.3 illustrates how diffraction of X-rays by crystal planes allows one to derive lattice spacings by using the Bragg relation. If one measures the angles under which constructively interfering X-rays leave the crystal, the Bragg relation gives the corresponding lattice spacings, which are characteristic of a given compound.



$n\lambda = 2d \sin\theta$; n= 1,2,…
where

λ	is the wavelength of the X-rays
d	is the distance between two lattice planes
θ	is the angle between the incoming X-rays and the normal to the reflecting lattice plane
n	is an integer called the order of the reflection

Figure 4.3 Diffraction of X-rays

The XRD pattern of a powdered sample is measured with a stationary X-ray source (usually Cu Kα) and a movable detector, which scans the intensity of the diffracted radiation as a function of the angle 26 between the incoming and the diffracted beams. When working with powdered samples, an image of diffraction lines occurs because a small fraction of the powder particles will be oriented such that by chance a certain crystal plane is at the right angle with the incident beam for constructive interference.

X-ray diffraction has an important limitation: clear diffraction peaks are only observed when the sample possesses sufficient long-range order. The advantage of this limitation is that the width (or rather the shape) of diffraction peaks carries information on the dimensions of the reflecting planes. Diffraction lines from perfect crystals are very narrow. For crystallite sizes below 100 nm, however, line broadening occurs due to incomplete destructive interference in scattering directions where the X-rays are out of phase.

XRD identifies crystallographic phases, if desired under in situ conditions, and can be used to monitor the kinetics of solid state reactions such as reduction, oxidation, sulfidation, carburization or nitridation that are used in the activation of catalysts. In addition, careful analysis of diffraction line shapes or - more common but less accurate simple determination of the line broadening gives information on particle size. XRD has serious disadvantages as well. Because it rests on interference between reflecting X-rays from lattice planes, the technique requires samples that possess sufficient long-range order. Amorphous phases and small particles give either broad and weak diffraction lines or no diffraction at all, with the consequence that if catalysts contain particles with a size distribution, XRD may only detect the larger ones. XRD at synchrotrons greatly improves the possibilities for studies of small particles. Finally, the surface region is where catalytic activity resides, but this part of the catalyst is virtually invisible to XRD. (Niemantsverdriet, 2000)

In our experiments we have used the XRD (D501, Siemens). Each sample was analysed after and before any TPO or TG experiment. Also XRD analysis was

crucial in determining the types of materials we produced. Figure 4.4 gives an example of our results. Since the dopants could not be detected (because of their relatively small concentrations at 0,1 and 0,01 molar ratios) XRD analysis was only used in characterizing our catalysts.

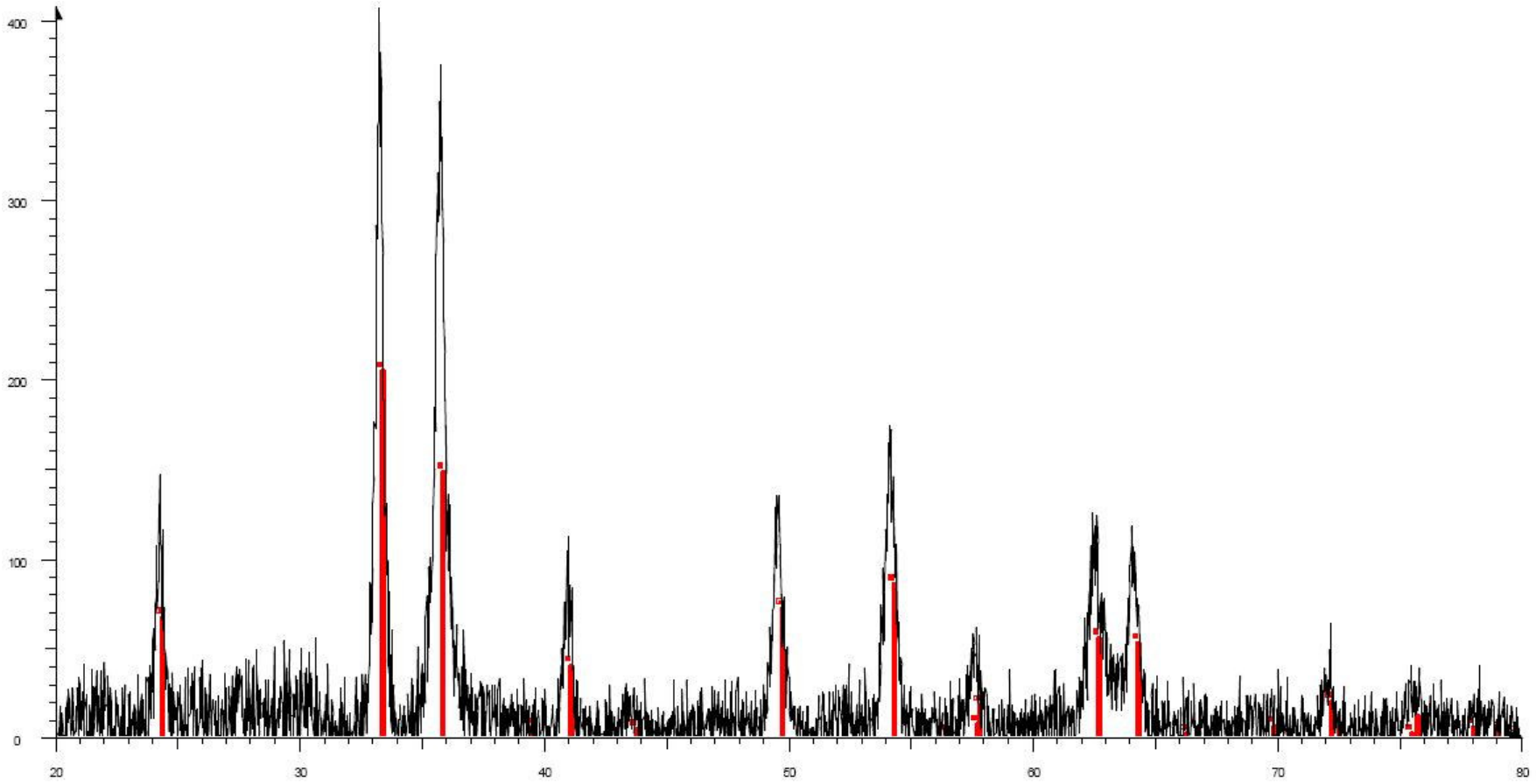


Figure 4.4 XRD analysis of nano-sized Fe_2O_3

CHAPTER FIVE
PRODUCTION OF MATERIALS

This study focuses on the oxidation of soot in diesel exhaust gases using Fe_2O_3 as a model catalyst. The purpose is to establish a usable nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions. Throughout the study so called bulk-Fe_2O_3 and its nano-sized variation was used. Where as various dopants were added in order to determine their effects on activity and thermal stability. This section describes the experimental methods used to produce the catalysts as well as the soot used.

5.1 Production of bulk α-Fe_2O_3

The synthesis of bulk α-Fe_2O_3 was carried out by polyvinyl alcohol (PVA) technique. This technique was found useful in the synthesis of several other substances as well (Kuila et al., 2007, Apostolescu et al., 2006, Hizbullah et al., 2004, Kureti et al., 2003). An aqueous PVA solution with 9 wt. % PVA was mixed with the appropriate amount of metal nitrate solution, where the molar ratio of metal cation/VA monomer was 2. The solution was slowly heated and evaporated leaving a fluffy mass that was dried at 250 $^{\circ}$C and subsequently grinded to powder. The powdered material were then calcinated at 750 $^{\circ}$C in air for 5 h (Apostolescu et al., 2006).

After calcination the catalyst was analyzed by XRD (D501, Siemens) to ensure the formation of the desired crystalline structure. It was previously shown that the specific surface area of α-Fe_2O_3 is 10 m^2 g^{-1}. This value was obtained by BET surface area measurement with multi-point Sorptomatic 1990 (Porotec) using nitrogen as adsorbate (Kureti et al., 2003).

5.2 Production of nano-sized α-Fe_2O_3

There are many established procedures to produce nano-scaled materials in the laboratory, finding an appropriate method has proven one of the most of challenging tasks of this research. Polyol method (Feldmann, 2005, Jungk et al., 2000, Feldmann, 2001) was largely unsuccessful as only γ-Fe_2O_3 was obtained, and thus we had to use nano-sized α-Fe_2O_3 particles produced by the combustion method (Dörr et al., 2007). However, while the experimental work was in progress, we succeeded in producing nano-sized α-Fe_2O_3 particles using the sol-gel method (Sugimoto et al., 1992, Sugimoto et al., 1993).

First of all an outline of each procedure would be helpful for ease of understanding.

5.2.1 Polyol Method

Submicron Fe_2O_3 particles were prepared with the polyol method. 3.9 g iron(II)-acetate dihydrate (99.9%, Aldrich) was suspended in 50 ml diethylene glycol (99.9%, Aldrich) and stirred for 15 min. 1.0 ml demineralized water was added. The whole mixture was heated for 1 h at 140 °C. The components were then dissolved and the liquid became clear. Afterwards, the solution was heated for 4h at 180 °C. The mixture became turbid again. When the suspension had been cooled to room temperature, it was diluted with 50 ml absolute ethanol (99%, Merck). As a result, a brownish red colored suspension containing 1.5 g Fe_2O_3 was obtained. Such suspensions are stable for weeks. Solids content can be increased up to about 20 wt. %. From suspensions the solid material was separated by centrifugation. (Jungk et al., 2000)

5.2.2 Combustion Method

The experimental setup is schematically depicted in Figure 5.1. It consists of a low pressure flat flame burner in an optically accessible chamber for the laser diagnostic measurements and a particle mass spectrometer (PMS) adapted on the top of the burning chamber. The burner is adjustable in height relative to the probing nozzle of the PMS and the optical axes. Iron pentacarbonyl ($Fe(CO)_5$) is delivered at widely variable concentrations from a pressure and temperature controlled bubbler unit as saturated vapor in Ar and introduced after a small mixing chamber below the burner matrix into the flame. In the lean premixed H_2/O_2/Ar low pressure flame $Fe(CO)_5$ is oxidized to iron oxide. Gas flows were controlled by calibrated thermal mass flow controllers and the pressure of the burner chamber is held constant at 30 ± 1 hPa.

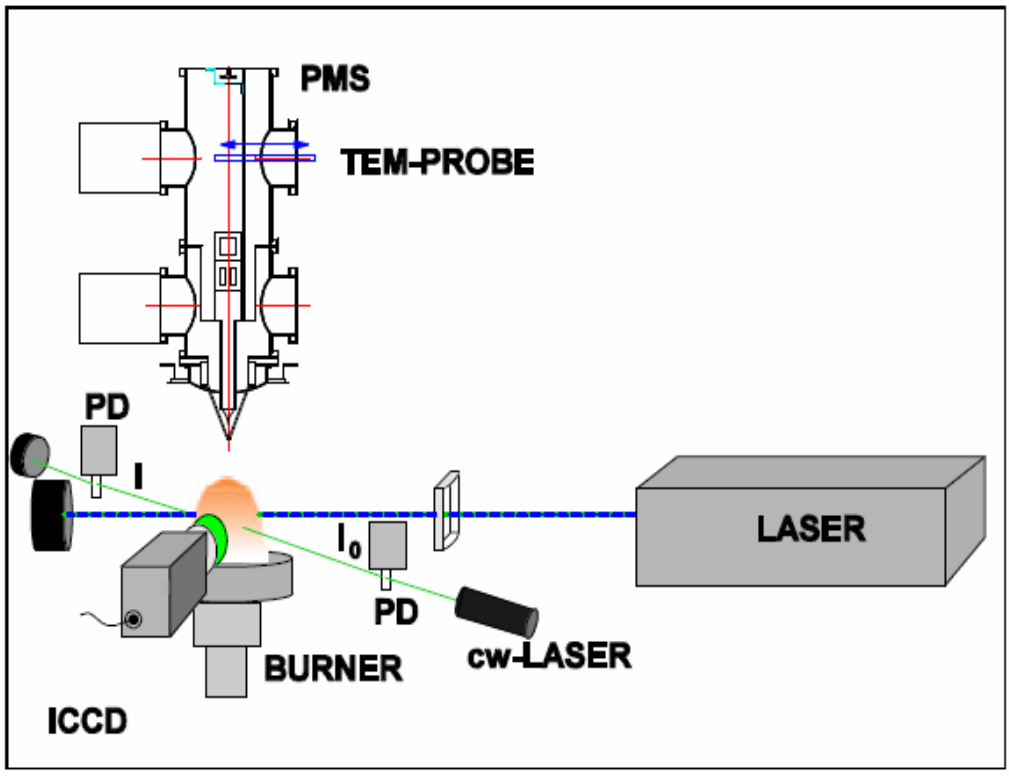


Figure 5.1 Experimental setup with PMS set above burner, laser diagnostics

The PMS samples particles from flame gases into a two-stage molecular beam by a platinum coated quartz nozzle with an inner diameter of 1 mm. A skimmer extracts the central part of the supersonic free jet for the second stage with pressures kept to approx. 10-4 hPa. The molecular beam passes through a variable and symmetrical electrical field, where particle ions are deflected respective to their kinetic energy and charge. The charged particles are detected by a Faraday cup electrometer in conjunction with an ultra-sensitive amplifier with excellent S/N ratio. The particle size of the produced α-Fe_2O_3 particles was reported to be 10 nm. (Dörr et al., 2007)

5.2.3 Sol-Gel Method

NaOH solution (100 ml of 5.4 N) was slowly added to 100 ml of well-stirred 2.0 M $FeCl_3$ solution in a 200 ml bottle at room temperature and the agitation was continued for an additional 10 min. Then, the tightly stoppered bottle containing the highly viscous gel nominally consisting of 0.90 mol dm^{-3} $Fe(OH)_3$ and 0.10 mol dm^{-3} Fe^{3+} was immediately put into a laboratory oven preheated at 100 ± 1°C and aged for 8 days. (Sugimoto et al., 1992)

5.2.4 Producing nano-α- Fe_2O_3

Our first approach was using the polyol method (Jungk et al., 2000), however our effort have repeatedly met with failure. In our first trial we used iron(II)-acetate dihydrate (95%, Aldrich), stirring was done by a magnetic stirrer, temperature was raised using a heating mushroom, and controlled with thermo-couples. After proceeding with the recipe step by step, we have produced a black powder, γ-Fe_2O_3. It should also be noted that, the suspension never became “clear liquid” as was designated by the original recipe. So our general decision was something was amiss with the experimental setup or the starting conditions.

In our proceeding experiments we have tried many different approaches, with little or no success. The magnetic stirrer was replaced with a glass-stick, the heating mushroom and the glass was isolated in order to gain better temperature

displacement, The iron amount was halved, we even experimented with different heating ramps and longer heating periods. Each and every trial produced a brown or black powder, which was not α- Fe_2O_3. For one thing the samples were magnetic which is not the case with α-Fe_2O_3. Some of the samples were analyzed with XRD in order to prove our theory and no trace of α- Fe_2O_3 was found.

To obtain α-Fe_2O_3 some parameters were changed in the synthesis. We have added a regenerator to the experimental setup, but that addition made it impossible to heat the system to 180 °C because diethylene glycol evaporated below that temperature. We also tried increasing the water amount, adding the iron solution drop by drop and heating it in a longer period. Even using the originally advised iron(II)-acetate dihydrate (99%, Aldrich) was not helpful.

Feldmann (Jungk et al., 2000) also states that a brief treatment (15 min, at 250 °C) was sufficient to transform remaining α- Fe_2O_3 to α- Fe_2O_3. It is not clear if the said treatment should be conducted after the powder was produced or during the initial preparation. However in our experiment both cases proved to be ineffective.

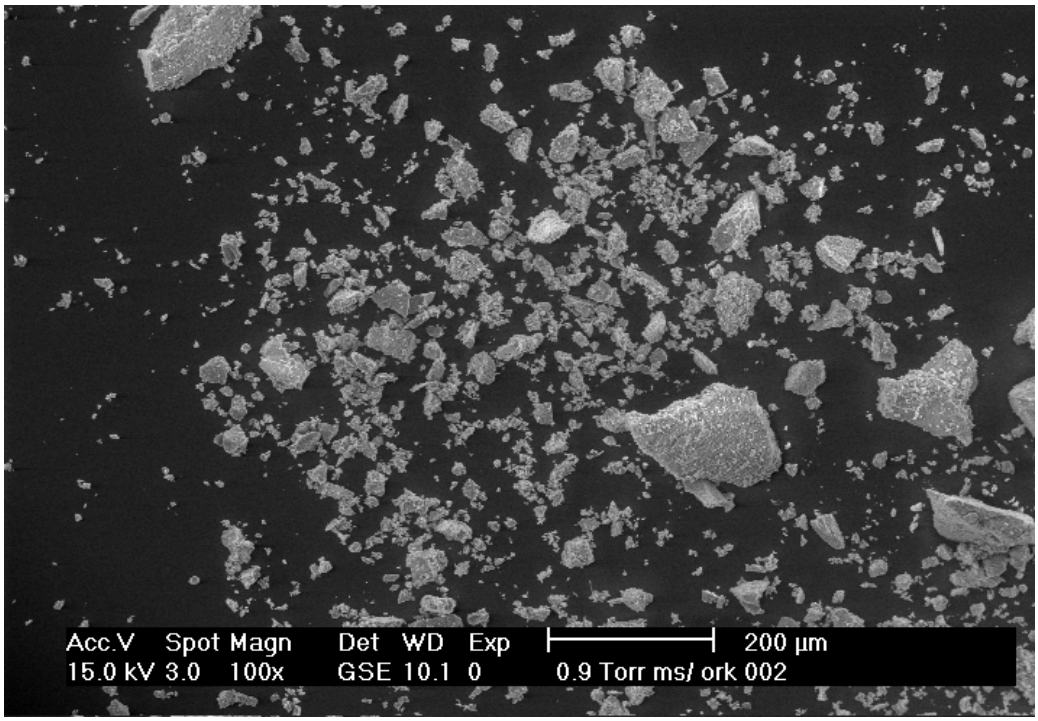
As no fundamental progress was achived nano-α-Fe_2O_3 samples which was cold produced by the combustion method (Dörr et al., 2007) described above was taken. All the experimental work was conducted using those samples.

However in parallel to that, sol-gel method was started based on literature data. Such a wet senthesis route is more advantageous to produce α- Fe_2O_3 in the n-scale as necessary for catalytic studies. It is clearly stated that two prime factors affecting the final product of the sol-gel method is pH and the mixing time. In order to receive the smallest particle size, it is advised that a 2.0 M $FeCl_3$ solution should be mixed with 100 ml of 6 N NaOH solution in 3 seconds. It should be specially noted that NaOH is added to $FeCl_3$ thus a higher pH is received in the initial process. Also the aging time is reduced up to two days by the increased NaOH concentration. (Sugimoto et al., 1992, Sugimoto et al., 1993)

After the aging process, it was found that centrifugation was not a very effective way to separate the α- Fe_2O_3 particles from the liquid phase. However even after repeatedly washing the solution with distilled water, the final product was not pure. It was suggested that use of freeze-drying instead of centrifugation and use of a diffusion bag in order to remove the remaining ions is the correct way to deal with this problem.

The following SEM pictures are from two different experiments. In the first experiment 100 ml 2.0 M $FeCl_3$ solution was slowly added to NaOH solution (100 ml of 6 N) in a 200 ml bottle at room temperature and the agitation was continued for additional 10 min. Then, the tightly stoppered bottle containing the highly viscous gel was immediately put into a laboratory oven preheated at 100 ± 1°C and aged for 2 days. The resulting solution was repeatedly washed with distilled water and then centrifuged. The final product was α- Fe_2O_3 with some leftover NaCl particles. The particle size is around 20 nm. Both XRD analysis and SEM pictures confirm these results.(Fig. 5.2)

In the second experiment 2.0 M 100 ml $FeCl_3$ solution was slowly added to NaOH solution (100 ml of 5.4 N) in a 200-ml bottle at room temperature and the agitation was continued for an additional 10 min. Then, the tightly stoppered bottle containing the highly viscous gel was immediately put into a laboratory oven preheated at 100 ± 1°C and aged for 8 days. The resulting solution was repeatedly washed with distilled water and put in to a diffusion bag in order to remove the remaining ions. The bag which works based on diffusion principles, is placed inside demineralized water. It works like a dialysis machine, and the sodium ions inside the solution are passed to the water, leaving the aqueous solution with only water and Fe_2O_3. After that the water was removed from the solution by freeze-drying. The final product was α-Fe_2O_3 with no leftover particles. The particle size is around 300 nm. Both XRD analysis and SEM pictures confirm these results. (Fig. 5.3)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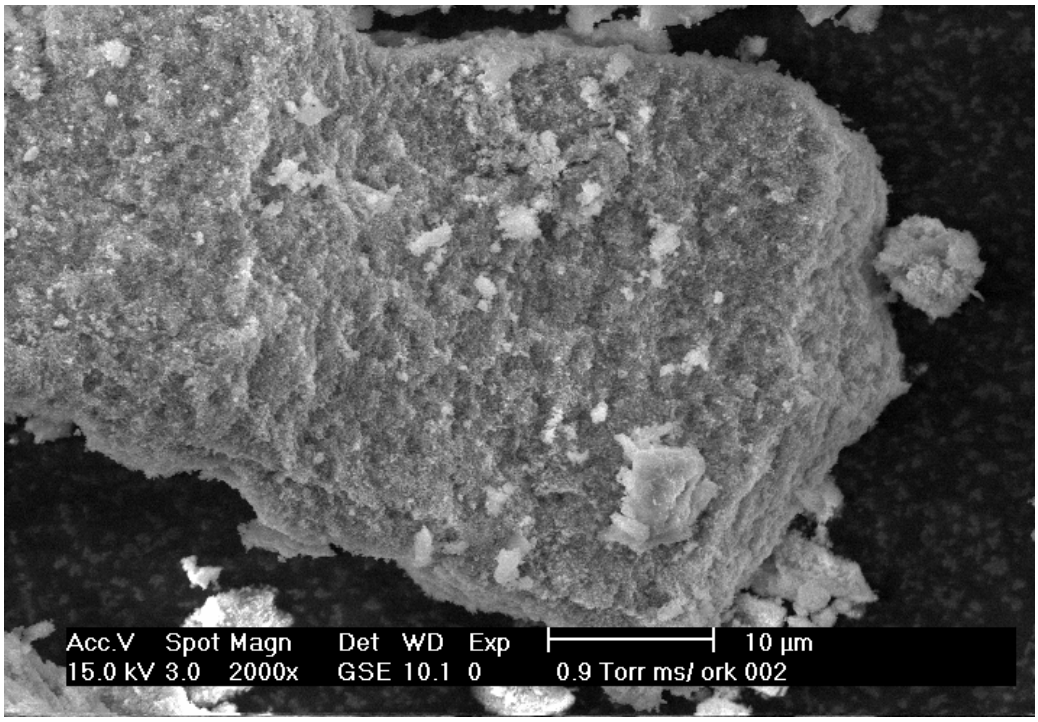
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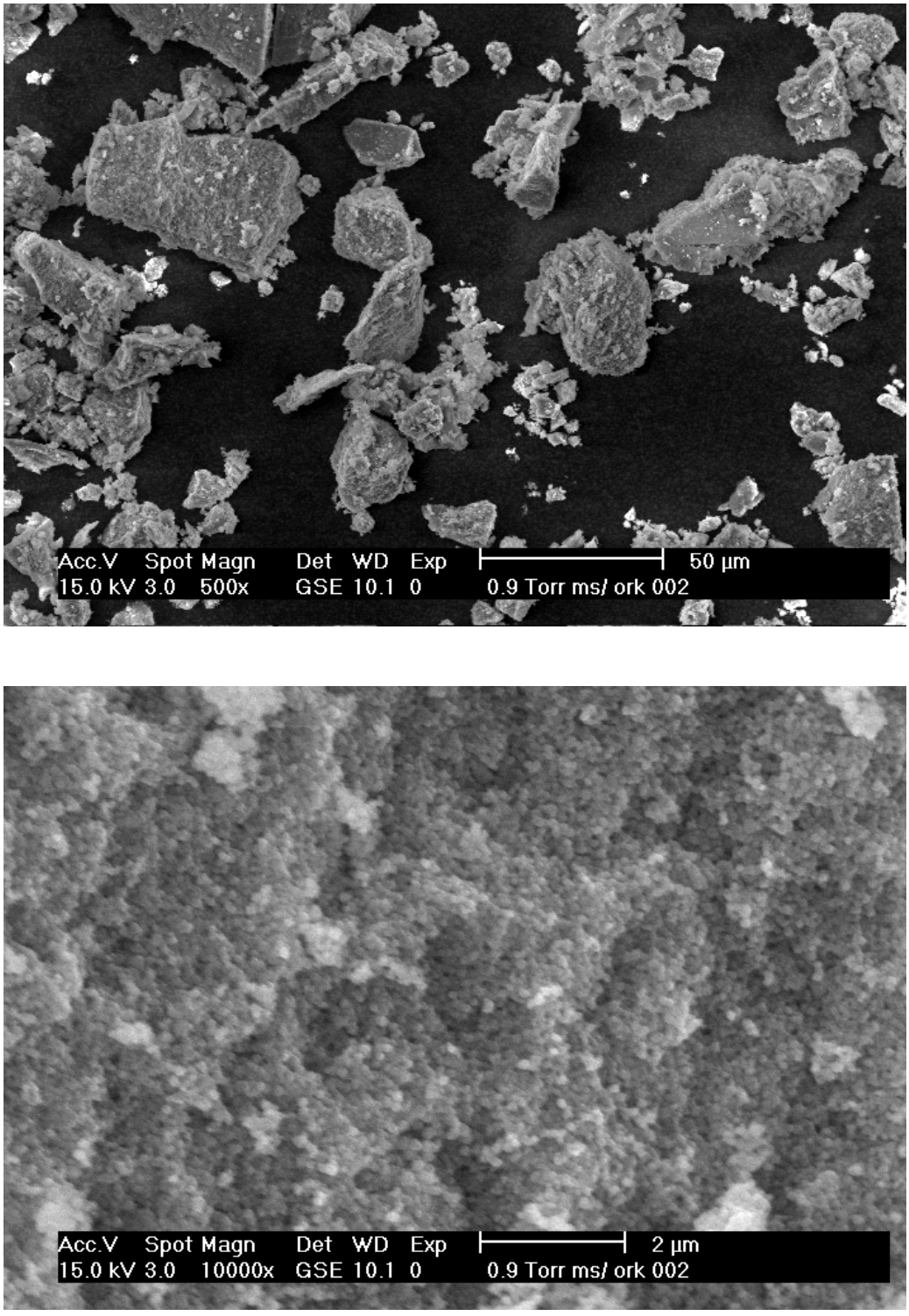
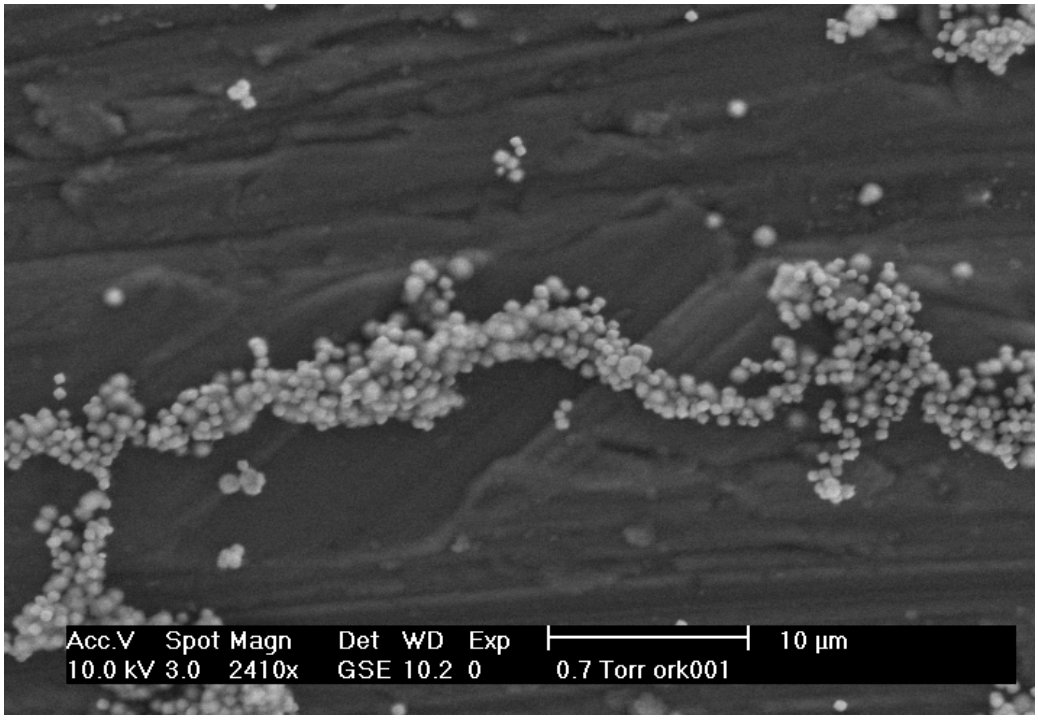
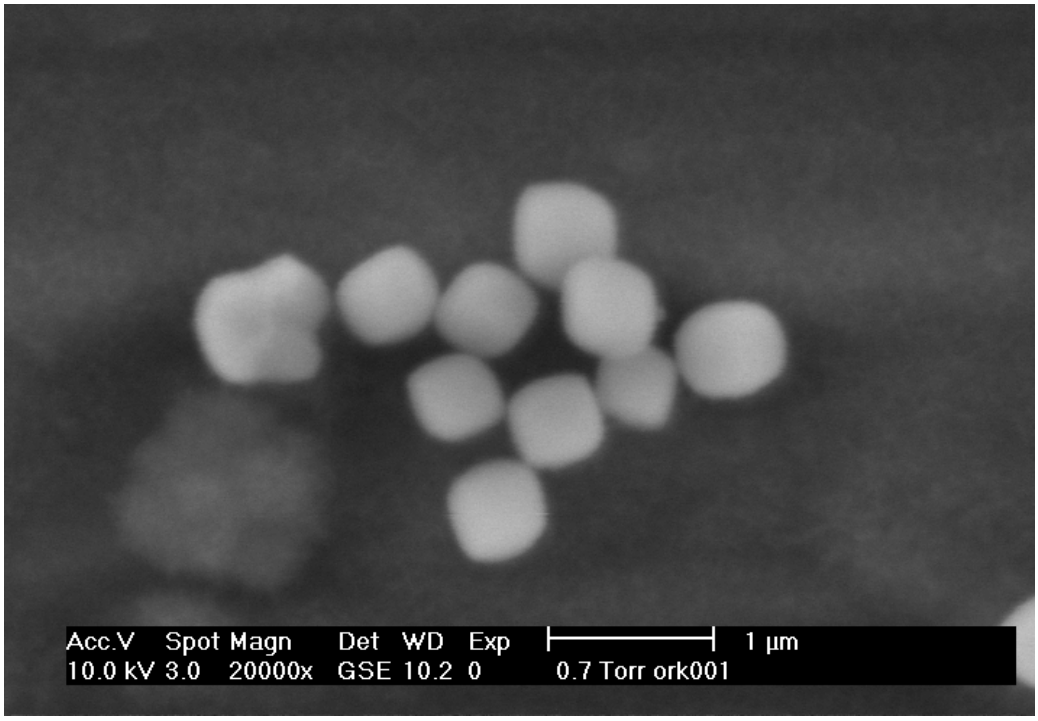


Figure 5.2 SEM pictures of the first sample


Acc.V Spot Magn Det WD Exp 10 µm
10.0 kV 3.0 2410x GSE 10.2 0 0.7 Torr ork001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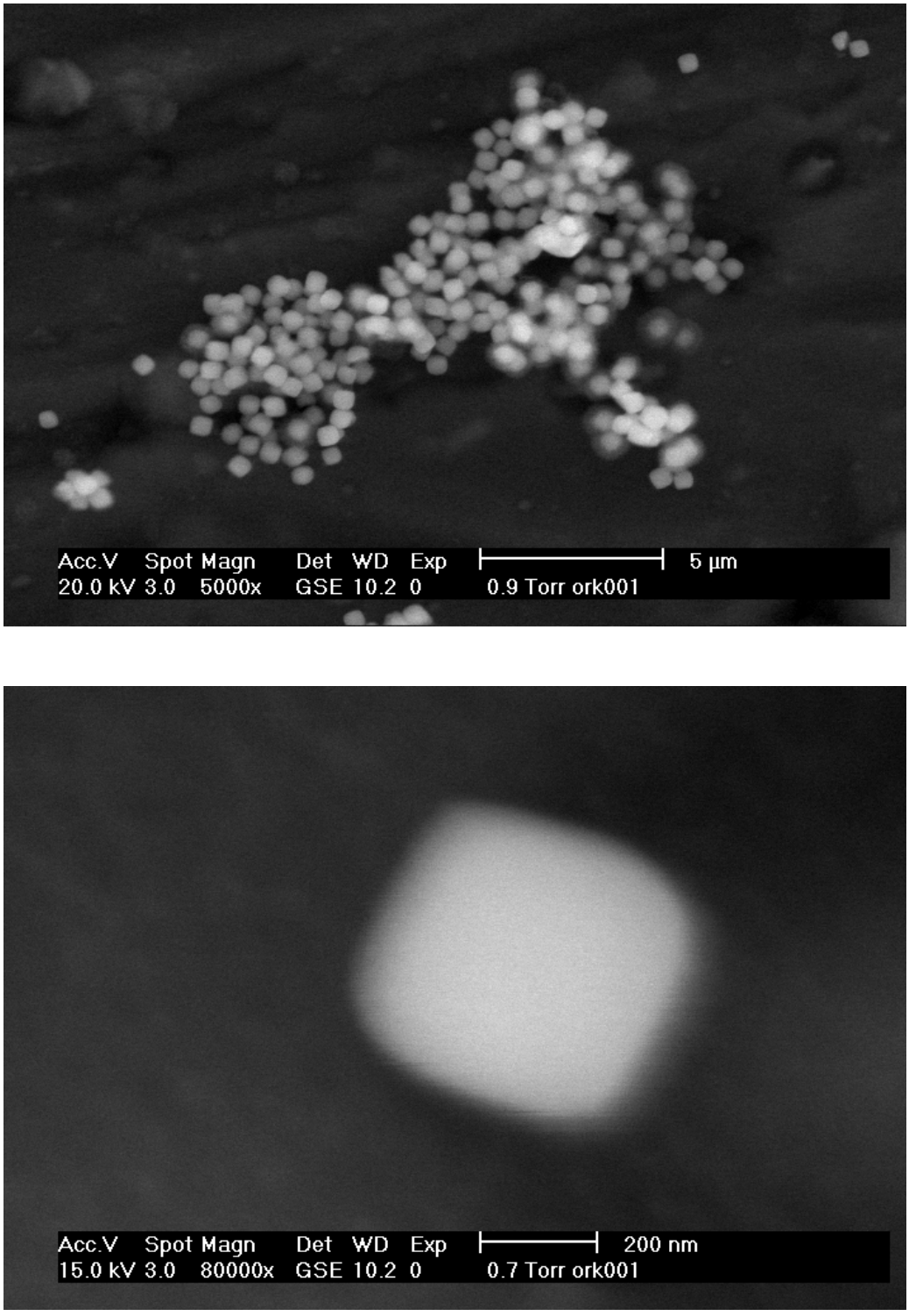

Figure 5.3 SEM pictures of the second sample

5.3 Soot Production

Soot was produced using the laboratory bench, owned by Institut für Technische Chemie und Polymerchemie, Karlsruhe University. The following information describes the laboratory bench (Balle et al., 2006) used in particular and soot production in general.

5.3.1 The Laboratory Bench

The purpose behind the design of the bench has been to evaluate the performance of catalysts for direct NO_x/soot conversion under practical conditions (Balle et al., 2006). For this purpose, the soot containing model exhaust which uses a diffusion burner that is adapted to a reactor and analytical system have been produced. The advantage of this laboratory tool is the possibility of varying only one parameter without affecting other operation parameters. The scheme of the developed laboratory bench is illustrated in Fig. 5.4.

The key part of the set-up is the diffusion burner, in which the soot containing exhaust is produced. The burner is shown in Fig. 5.5. Propene (99.4%, 120 ml/min) is employed as fuel gas that is premixed with nitrogen (99.999%, 500 ml/min) in the inner chamber of the burner, while in the outer one oxygen (99.996%, 600 ml/min) is blended with nitrogen (600 ml/min). The combustible mixture is ignited with a small gas burner that is introduced by an inspection window placed on the level of the burner nozzle. To avoid soot deposits the inspection window zone is additionally flushed with nitrogen (800 ml/min). The adjusted flows result in a soot production of 0.30 mg/min.

The produced burner gas first passes a commercial Pt oxidation catalyst (Pt load = 60 g/ft^3) that is heated to 230 ºC. Hereby, unwanted by-products of the combustion process, i.e. H_2, CO and hydrocarbons, are completely removed from the gas stream. After passing the Pt catalyst the tail gas is conditioned by dosing a mixture of NO (1.5 ml/min), O_2 (100 ml/min) and N_2 (400 ml/min). This is done to obtain

concentrations that are typical for diesel exhaust. All gases used (Air Liquide) are fed from independent flow controllers (MKS Instruments).

For the catalytic NO_x/soot conversion the feed flows into a quartz glass tube (i.d. 22 mm) that contains the DPF system and a Pt pre-catalyst that reveals a diameter of 20 mm, a length of 30 mm, a cell density of 400 cpsi and a Pt load of 60 g/ft^3. The pre-catalyst is used to produce NO_2 which is reported to enhance the N_2 formation in NO_x/soot reaction. The inlet and outlet temperatures are monitored by K-type thermocouples (TC), while the corresponding pressure is measured by recorders from Burster. The TC and pressure sensors are directly placed in front of the pre-catalyst and behind the DPF, respectively. At a total gas flow of 3.1 l/min the outlet pressure is 40 mbar that is mainly referred to the back pressure of the gas analysers. After leaving the DPF system, the exhaust stream passes a back-up filter that avoids a possible breakthrough of soot. The back-up filter represents a bare DPF with 300 cpsi. Optionally, the water can be removed from the gas flow by a condenser unit (4 ºC). With the exception of CO_2 and N_2O, the gaseous components are recorded by Chemical Ionization Mass Spectrometry (CIMS, Airsense 500, V&F). By using the CIMS analyser the adjusted high concentration of CO_2 (7.5 vol.%) cannot be measured reliably and it leads to drastic interference with the N_2O signal, even when Xe is employed for ionization. Thus, N_2O and CO_2 are monitored by means of non-dispersive infrared spectroscopy (NDIR, Uras 10E, Hartmann & Braun). Since the used NDIR is cold measuring, water is separated as described above before the tail gas passes into the CIMS and NDIR analysers.

Instead of flowing into the DPF containing reactor the exhaust stream can be passed into a cylinder that contains a sinter metal filter to collect the soot.

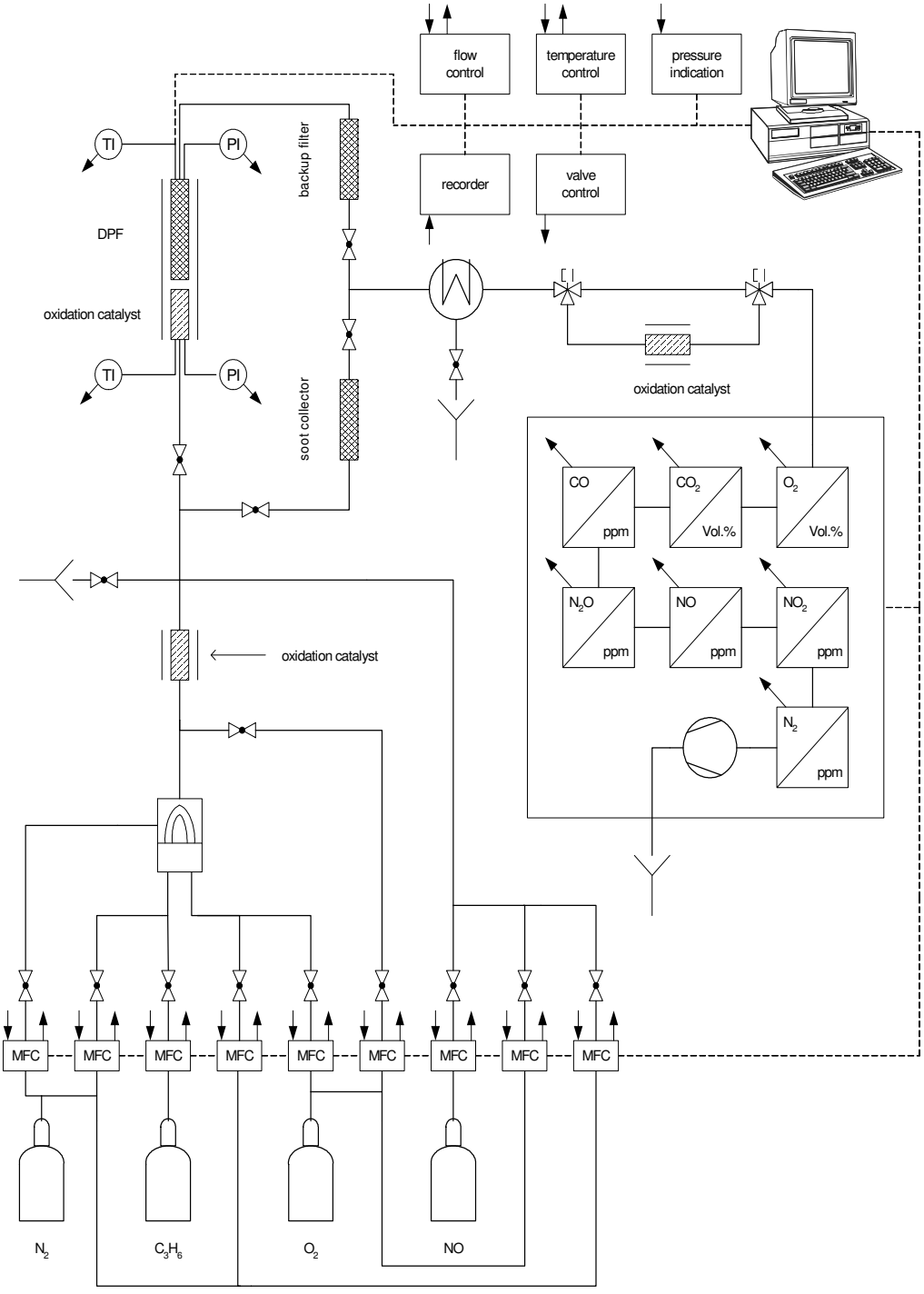

Figure 5.4 Developed laboratory bench for practical investigation of catalytic NO_x/soot conversion.

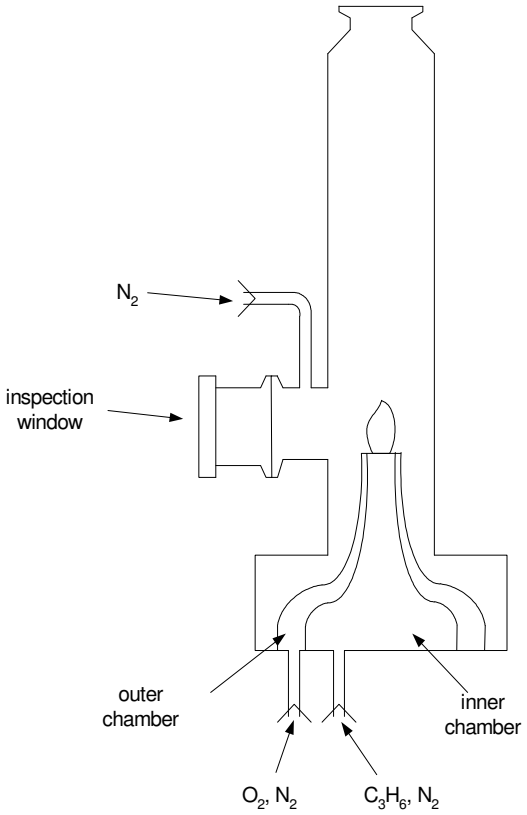

Figure 5.5 Diffusion burner

5.3.2 Characterization of Soot

The chemical composition of the soot taken from the collectors unit is examined by the use of thermogravimetry (TG), temperature programmed desorption (TPD) and temperature programmed oxidation (TPO). Additionally, the soot is characterized with transmission electron microscopy (TEM).

5.3.2.1 Thermogravimetry(TG)

The TG analysis is performed on a STA 409 balance from Netzsch; a mass of 32 mg soot is heated in N2 flow (1000 ml/min) from ambient temperature to 750 C at a rate of 10 K/min. The TG data of the collected soot show a small amount of adsorbed species only (2.6 wt. %). This is useful for the intended examination of the catalytic reaction between NO_x and soot, as parallel reactions and unwanted secondary effects

that both might be caused by pronounced presence of adsorbed hydrocarbons, are to be neglected.

5.3.2.2 Temperature Programmed Desorption (TPD)

For TPD analyses 120 mg soot is taken. is conducted by heating the soot in N_2 (500 ml/min) from ambient temperature to 1000 .C at a rate of 10 K/min, while the desorption of CO and CO_2 is monitored by NDIR (Uras 10E, Hartmann & Braun). The oxygen content of the soot is deduced from the TPD pattern that indicates the desorption of CO (9.2 mg/g soot) and CO_2 (3.3 mg/g soot).

5.3.2.3 Temperature Programmed Oxidation (TPO)

For TPO analyses 120 mg soot is taken. In TPO, the sample is first heated in N_2 flow to 400 C to remove adsorbed compounds. Then, a mixture of 6 vol.% O_2 and 94 vol.% N_2 (500 ml/min) is added and the temperature is increased to 720 C at a heating ramp of 5 K/min. H_2O and NOx evolved in TPO are measured with CIMS. The content of H is determined by TPO, in which the hydrogen is detected in the form of H_2O (43 mg/g soot). Furthermore, neither the evolution of NO_x nor ash residues are observed in temperature programmed oxidation.

5.3.2.4 Transmission Electron Microscopy (TEM)

TEM micrographs (912 omega, Zeiss) are taken to determine shape as well as size of the soot primary particles. The pictures clearly show the spherical shape of the primary particles that are condensed to form chains. It is obvious that the most probable diameter is at 45 nm being in fair agreement with diesel soot. the experimental data are well fitted by a Gaussian distribution with $y_0 = 0.916$, $A = 879$ and $w = 28.2$.

CHAPTER SIX
THERMOGRAVIMETRIC ANALYSIS

This study focuses on the oxidation of soot in diesel exhaust gases using Fe_2O_3 as catalyst. The purpose is to establish a thermally stable nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions.

In the first step of the experimental study, thermogravimetric analysis was conducted using Netzsch STA 409. We have used a heat ramp of 10 K /min and a maximum temperature of 800 °C. The flow rate was decided to be 500 ml/min (STP) with an O_2 concentration of 6.0 vol. % using N_2 as balance.

For reference purposes pure soot (40mg) was tested. However in all the experiments performed complete soot oxidation was not achieved with these initial conditions. Thus the oxygen amount in the flow was increased to 20 vol. % which is the amount of oxygen in air. At this flow, complete oxidation of soot was observed. This experiment was repeated three times in order to check for consistency (Figure 6.1). Thus all thermogravimetric studies were conducted using synthetic air, at a ramp of 10 K / min.

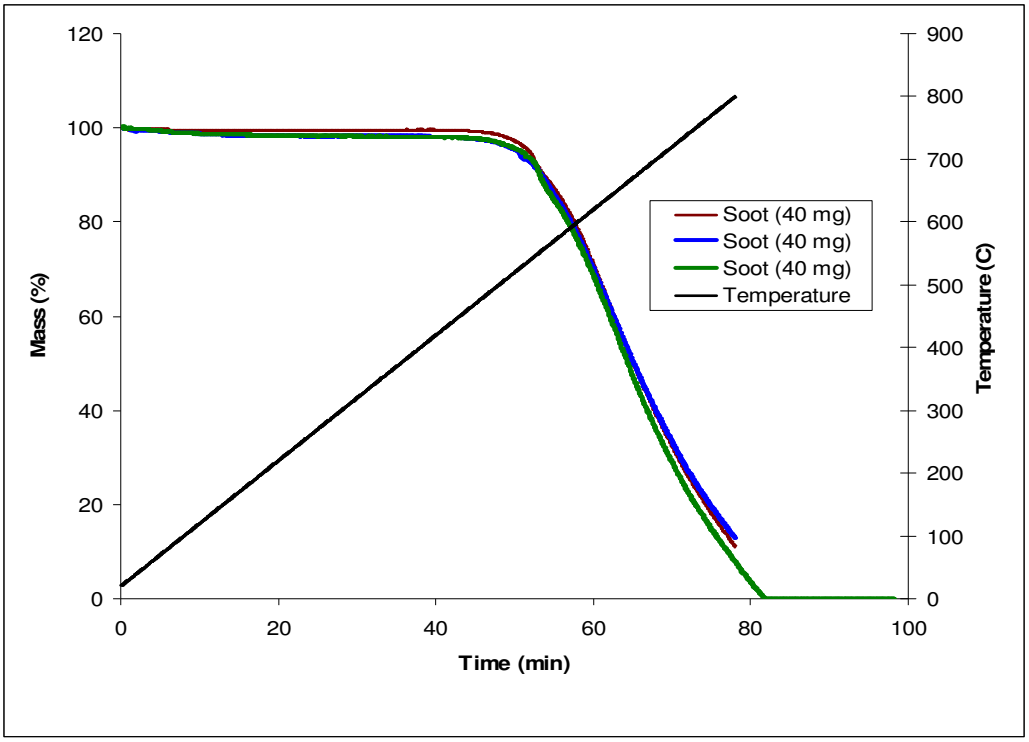

Figure 6.1 Thermogravimetric analysis of pure soot samples, 500 ml/min air flow, 10 K/min, up to 800 °C.

Since it is known that nano sized Fe_2O_3 looses its particle size when subjected to high temperature treatments we added various dopants into our catalyst. The selected dopants were Fe, Zr and Ce. In order to better investigate the effect of dopants three different molar ratios were chosen, 1/1, 1/0,1 and 1/0,001. After the addition of the dopants, the catalyst was calcinated in flow and at 350 °C. For each run of the experiment 5 mg of soot was mixed with 95 mg of catalyst. Catalytic studies were stopped at 700 °C as soot is already consumed at this temperature.

One other measure was taken at this point, which was to reduce the maximum temperature to 700 °C. Based on the previous studies and taking into account the mass ratio of the catalyst and the soot, at this temperature the oxidation of soot should already be completed.

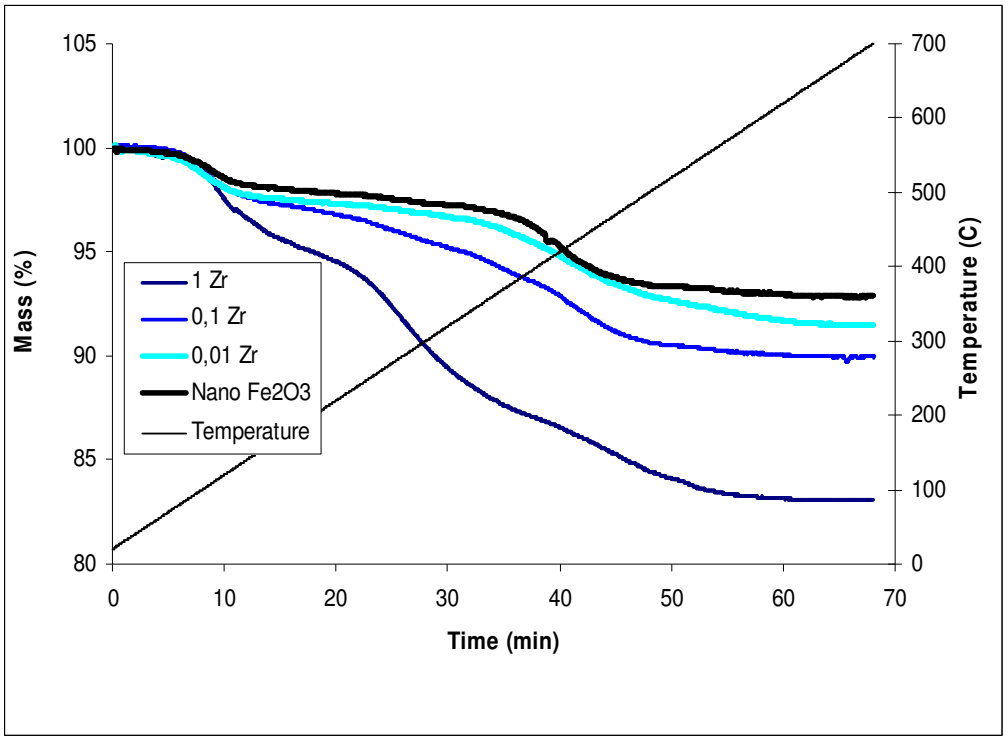

Figure 6.2.a The thermogravimetric analysis relative to Zr dopant

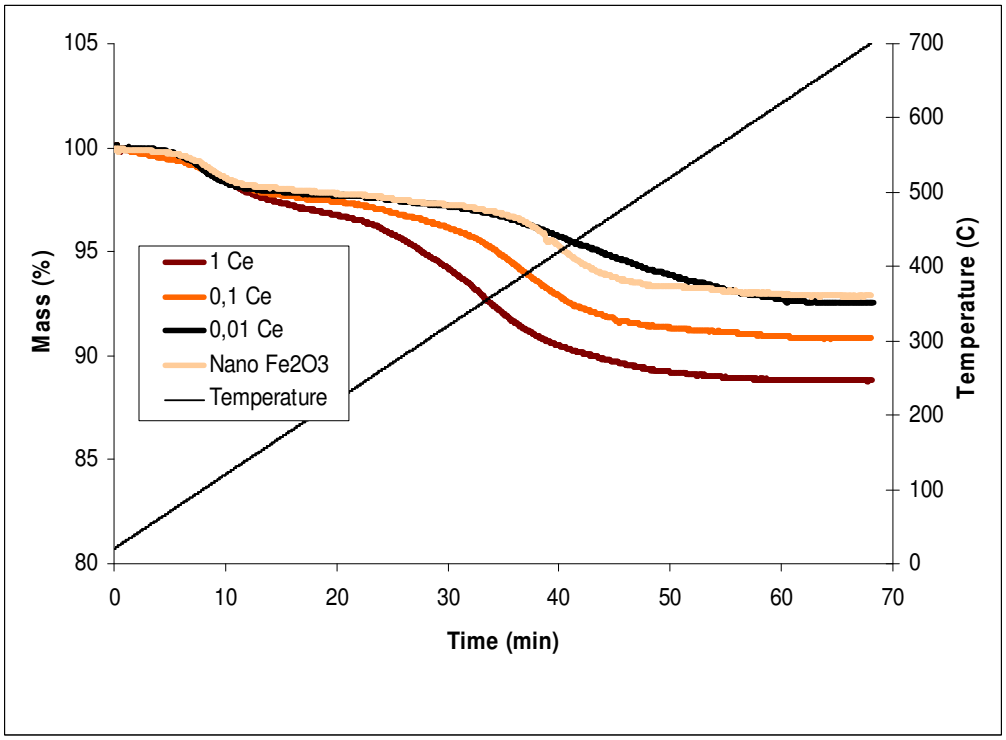

Figure 6.2.b The thermogravimetric analysis relative to Ce dopant

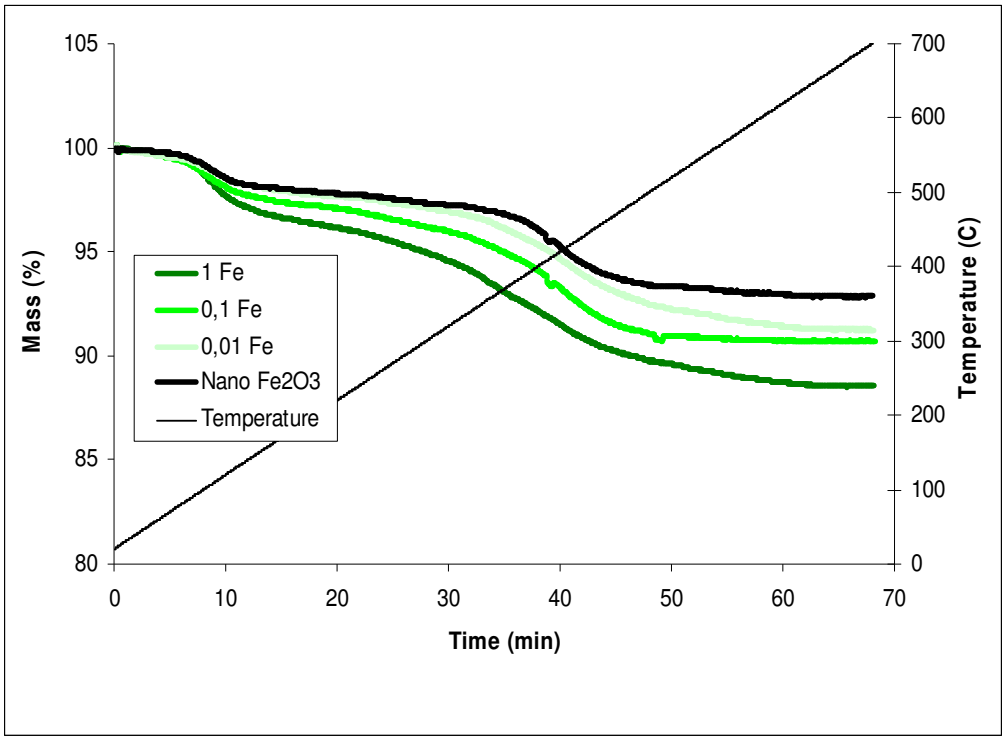

Figure 6.2.c The thermogravimetric analysis relative to Fe dopant

Figure 6.2.a, b and c shows the results relative to dopants. All samples show an increasing mass reduction, with the increase in dopant concentration. Other than this obvious result it is quite hard to comment on the results. Reduction of carbon monoxide is the prime factor we are investigating, however since each sample shows two or three different slopes, it is hard to determine the start and the end points of the process. The first slope is probably the desorption of water (molecular) present on the catalyst and the second step is dehydroxidation of surface OH groups. The remainder of the slopes could be related to different materials that has been present inside the nano sized Fe_2O_3 or they could be the result of remaining nitrate particles that has not been completely calcinated.

Figure 6.3 shows blank TG analysis of the Zr-doped samples without soot addition. As can be seen a 3-15 % reduction in mass is observable in here also. Since curves are close and strongly overlapped, it is not possible to differentiate OH dehydroxidation and soot oxidation.

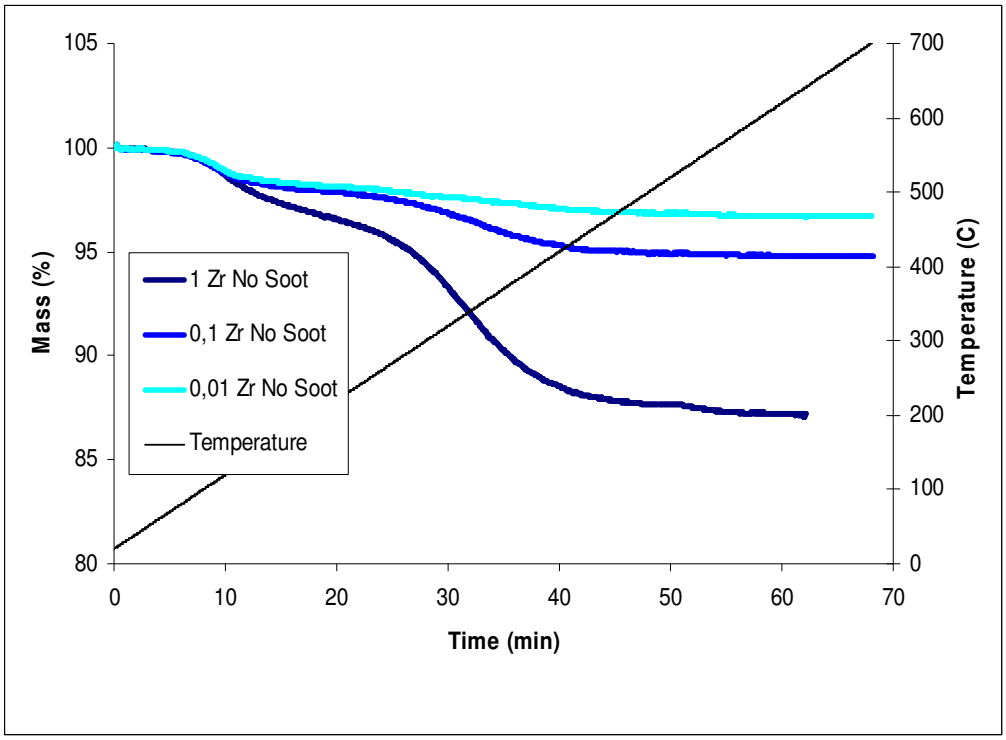

Figure 6.3 The thermogravimetric analysis of zirconium without soot.

To sum up we concluded that thermogravimetric study was not an appropriate approach in determining the ability of nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions. The results show various mass reductions which can not be separated from each other clearly. Which leads to uncertainty in determining where the important soot oxidation occurs.

CHAPTER SEVEN
TEMPERATURE PROGRAMMED OXIDATION ANALYSIS

This study focuses on the oxidation of soot in diesel exhaust gases using Fe_2O_3 as catalyst. The purpose is to establish a thermally stable nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions.

Since thermogravimetry did not provide conclusive data, we have conducted Temperature Programmed Oxidation Analysis (TPO). With the use of gas analysers to follow the soot oxidation TPO analysis will provide the exact place of the soot oxidation.

The same heating ramp and maximum temperature, 10 K/min and 700 °C respectively, was used in order to be able to have comparable data. The flow, as was established before, was 500 ml/min and synthetic air (20% O_2 80% N_2). Experiments were conducted using 95 mg of catalyst and 5 mg of soot. Figure 7.1 shows the catalytic activity of nano-sized Fe_2O_3 under these conditions. As can be seen Fe_2O_3 is a good catalyst and nearly complete CO reduction occurs. In each of the experiments conducted similar results were observed. Since our investigation focuses on establishing a usable nano-sized Fe_2O_3 catalyst, CO level will not be discussed rather CO_2 levels will be our compass.

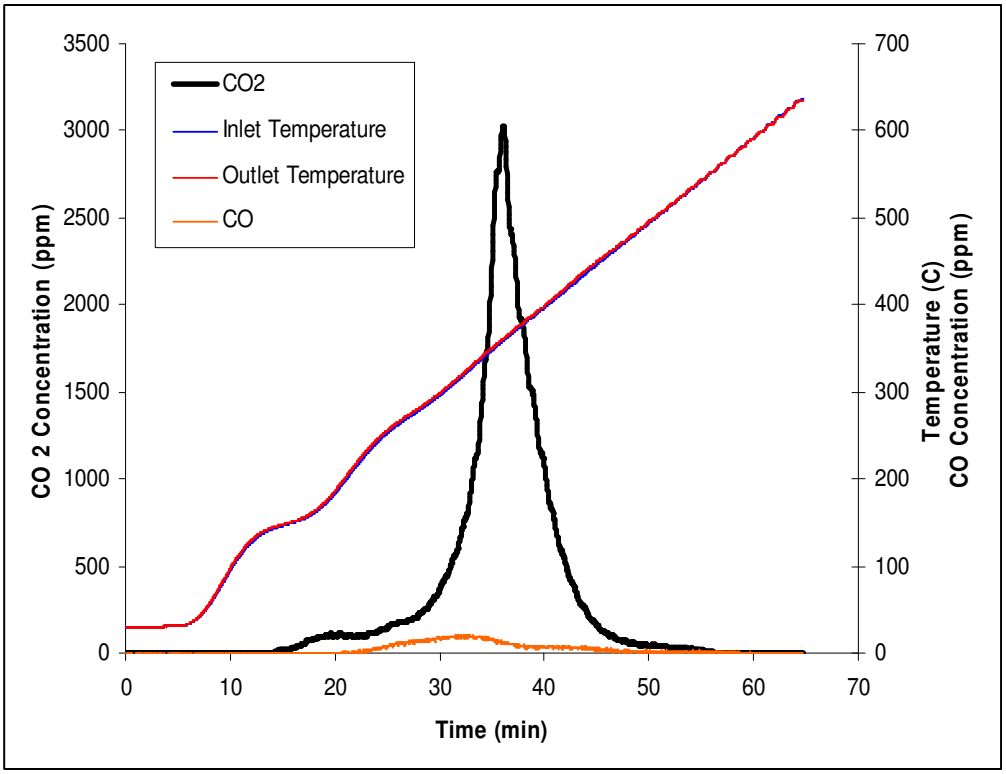

Figure 7.1 TPO Analysis of nano-sized Fe_2O_3

Now that we have established that we can receive conclusive results with TPO analysis, we first start to investigate the effectiveness of nano-sized Fe_2O_3. Figure 7.2 shows TPO analysis of bulk Fe_2O_3 and nano-sized Fe_2O_3. Using nano sized Fe_2O_3 as a catalyst, no CO potentially formed in soot oxidation.. The results show that using the nano-sized catalyst grants us nearly 100 °C advantage in peak values. The clear advantage was already expected and is the result of increased surface area of the Fe_2O_3.

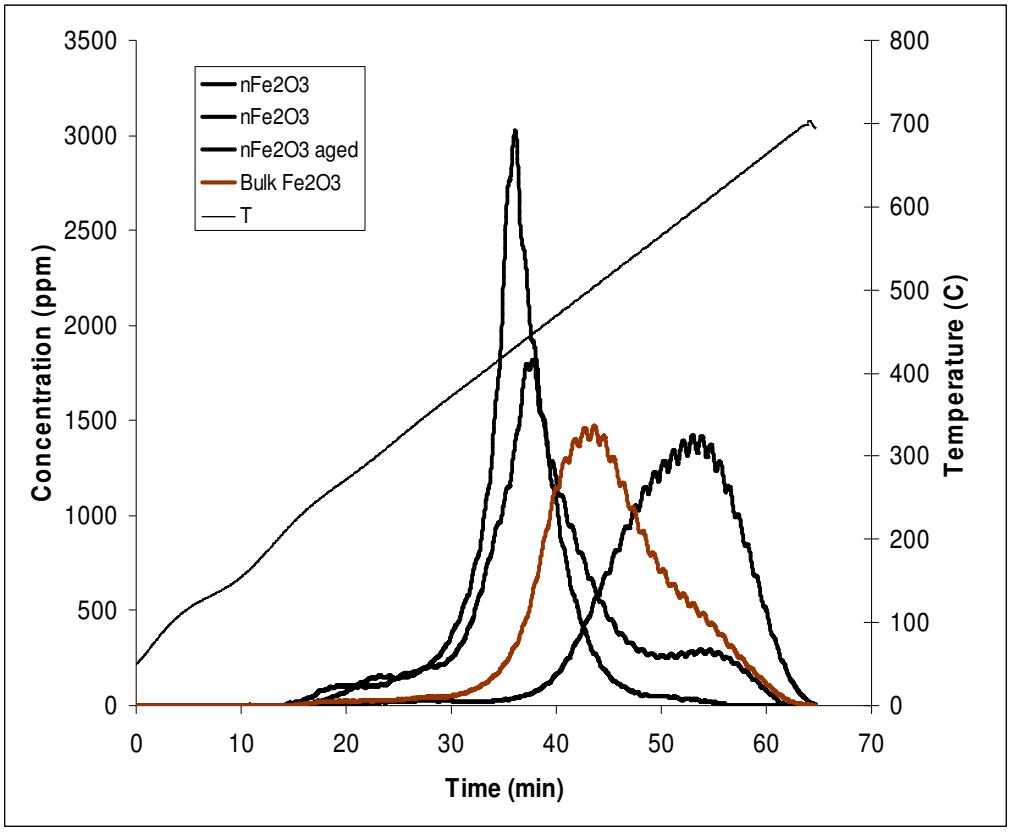

Figure 7.2 TPO Analysis of Fe_2O_3

The effects of the selected dopants and their different loadings were investigated. (Figure 7.3.a, b, c). Addition of Zirconium (ZrO_2) had given a slight decrease in catalytic activity. However equal amounts of zirconium and nano-sized Fe_2O_3 has proven to be an ineffective catalyst. The peak catalytic activity of the sample has been reduced above the bulk Fe_2O_3. This drastic change in catalytic activity is probably the result of Zr ions which surround the Fe_2O_3 particles, and decrease the contact surface between soot and Fe_2O_3 to a minimal value.

Addition of Cerium (CeO_2) which is a catalytic agent itself, has increased catalytic activity. The increase is directly proportional to the increase in Ce load. Equal amounts of Ce and nano-sized Fe_2O_3 give us a 50 °C decrease in starting temperature. Even a slight concentration of Ce seems to be very effective way to increase the effectiveness of the catalyst.

The last dopant Iron (Fe_2O_3) nearly does not show any effect on the catalytic process. A slight loading of Fe decreases the starting temperature somewhat, but as the concentration increases even this small improvement is nullified.

If we order these results we find that, nano-sized Fe_2O_3 interacts with each dopant in a different way. Iron has a slight positive effect that decreases with concentration, Zirconium has a negative effect, which at high concentration renders the catalyst ineffective and Cerium reveals a strong positive effect that stimulates catalytic activity, and this effect increases with the addition of more cerium.

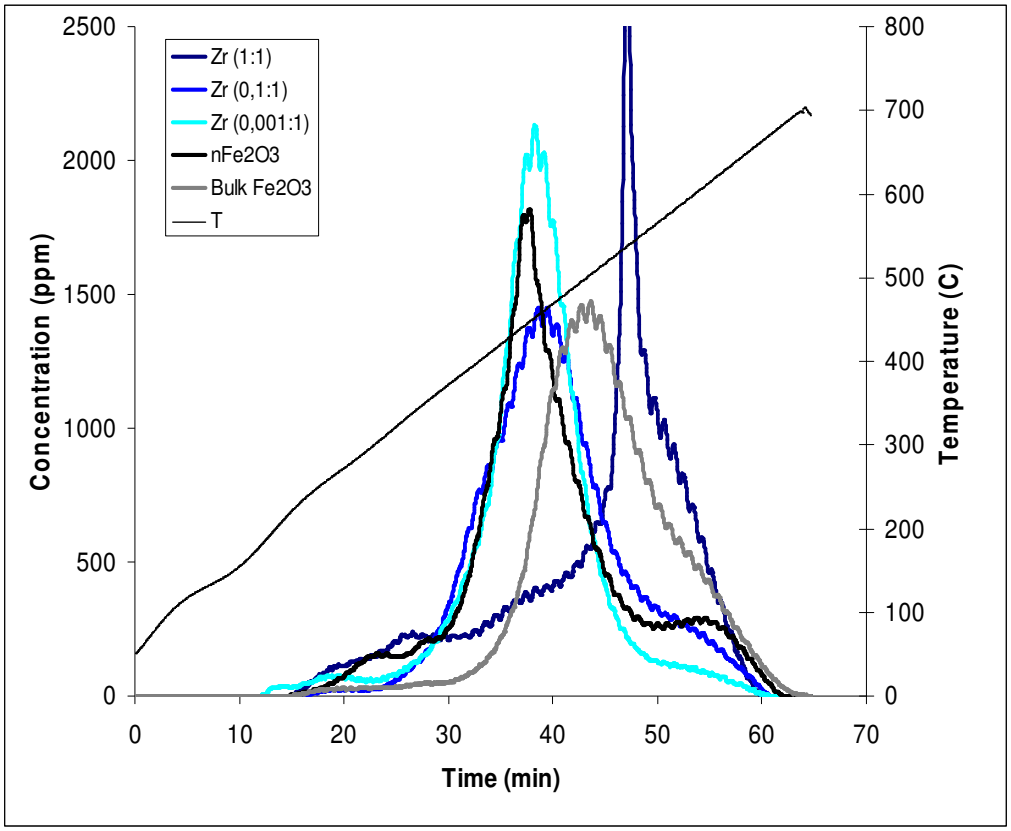

Figure 7.3.a TPO Analysis of Fe_2O_3 relative to Zr dopant

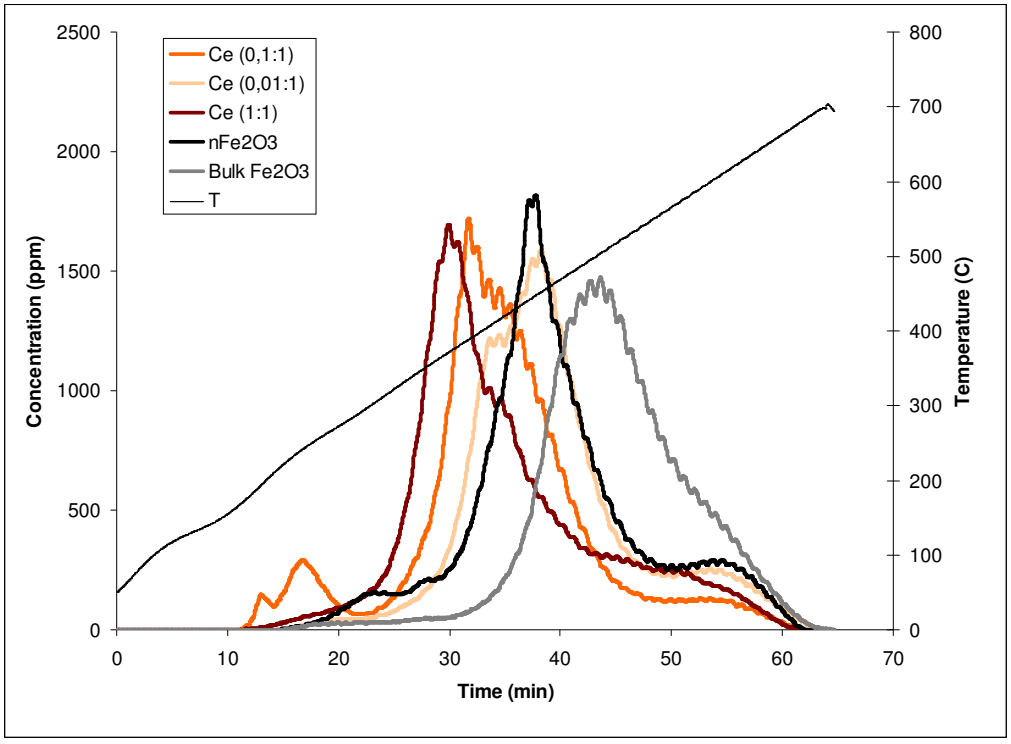

Figure 7.3.b TPO Analysis of Fe_2O_3 relative to Ce dopant

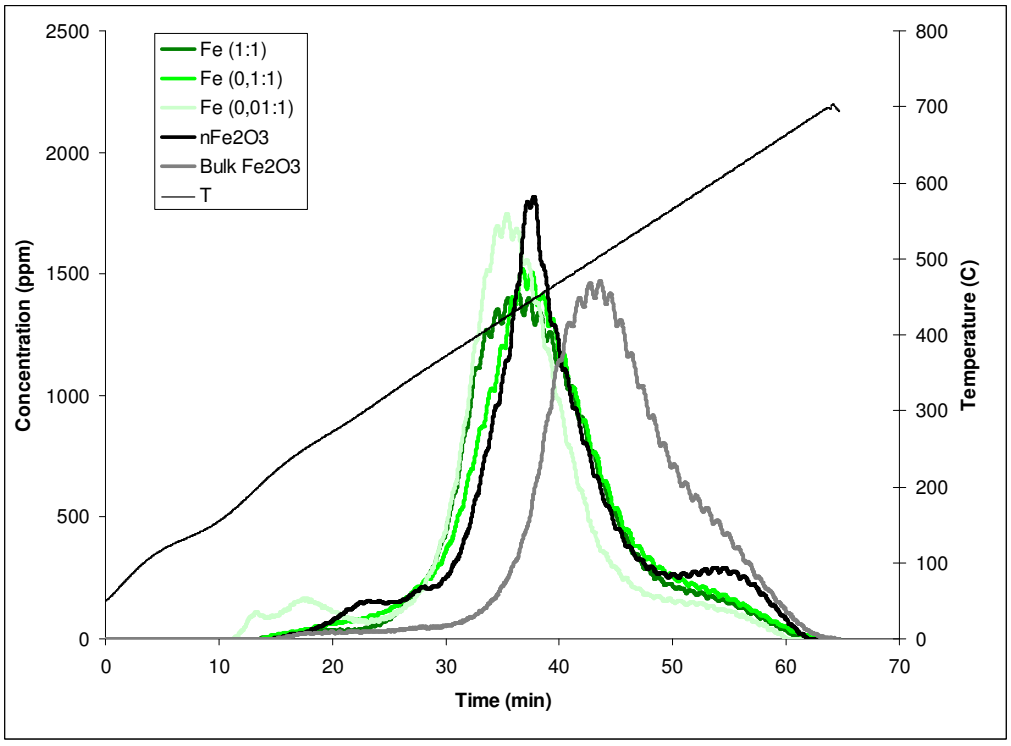

Figure 7.3.c TPO Analysis of Fe_2O_3 relative to Fe dopant

Since cerium is clearly the most promising dopant, the thermal stability of the Ce/ Fe_2O_3 system is investigated. For this purpose three new samples were prepared and doped with the different loads of Ce. These samples and a sample of undoped nano-sized Fe_2O_3 were aged in an oven at 750 °C for 12 h. This temperature is typical for diesel particulate matter filter systems. The samples were than mixed with 5 mg of soot and a TPO was performed using the same initial values explained before. The recorded data are shown in Figure 7.4.

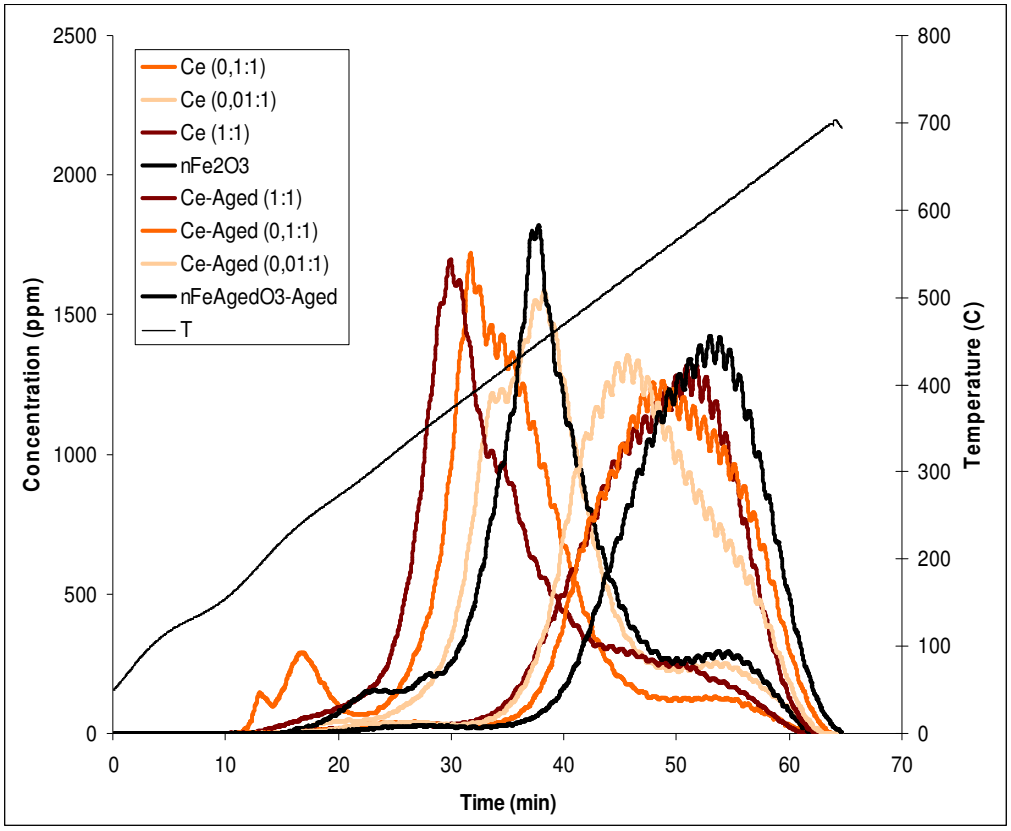

Figure 7.4 TPO Analysis of aged Fe_2O_3 samples

Each aged sample shows considerable decrease in catalytic activity. The aged nano-sized Fe_2O_3 starts the catalytic activity around 500 °C and reaches peak values at around 600 °C. If we consider peak temperatures as the quantifier like (Aneggi et al., 2006) did, our catalyst is better fresh or aged. (Aneggi et al., 2006) has experimented with CeO_2 and ZrO_2 as catalysts. Their results show a peak temperature between 660-690 °C with fresh catalysts and 680-720 °C with aged

samples. As can be seen Fe_2O_3 doped with cerium proves to be a better catalyst under both conditions.

The interesting result here is not the decrease in catalytic activity in each sample with the aging but rather its relationship with concentration. A low weight % of cerium shows the most positive effect, while the highly doped sample has just a slight positive effect. Overall aged cerium samples show an increase in catalytic activity inversely proportional to their cerium concentration.

CHAPTER EIGHT
CONCLUSION

This study focuses on the oxidation of soot in diesel exhaust gases using Fe_2O_3 as catalyst. The purpose is to establish a thermally stable nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions. In the first step of the experimental study, thermogravimetric analysis was conducted using Netzsch STA 409. We have used a heat ramp of 10 K/min and a maximum temperature of 800 °C. The flow rate was decided to be 500 ml/min (STP) with an O_2 concentration of 6.0 vol. % using N_2 as balance. It was found that thermogravimetric study was not an appropriate approach in determining the ability of nano-sized Fe_2O_3 catalyst for use in diesel exhaust emissions. The results show various mass reductions which can not be separated from each other clearly. Which leads to uncertainty in determining where the important soot oxidation occurs.

Since thermogravimetry did not provide conclusive data, we have conducted Temperature Programmed Oxidation Analysis (TPO). With the use of gas analysers to follow the soot oxidation TPO analysis will provide the exact place of the soot oxidation.

The same heating ramp and maximum temperature, 10 K/min and 700 °C respectively, was used in order to be able to have comparable data. The flow, as was established before, was 500 ml/min and synthetic air (20% O_2 80% N_2).

Using nano sized Fe_2O_3 as a catalyst, no CO potentially formed in soot oxidation.. The results show that using the nano-sized catalyst grants us nearly 100 °C advantage in peak values. The clear advantage was already expected and is the result of increased surface area of the Fe_2O_3. Using nano sized Fe_2O_3 as a catalyst, complete reduction of CO to CO_2 was achieved in the temperature range of 350 °C – 450 °C. The results show that using the nano-sized catalyst grants us nearly 100 °C advantage. The clear advantage was already expected and is the result of increased surface area of the Fe_2O_3.

It has been observed that nano-sized Fe_2O_3 interacts with each dopant in a different way. Iron has a slight positive effect that decreases with concentration, Zirconium has a negative effect, which at high concentration renders the catalyst ineffective and Cerium reveals a strong positive effect that stimulates catalytic activity, and this effect increases with the addition of more cerium.

To sum up our results show that nano-sized Fe_2O_3 doped with cerium is the most promising catalyst investigated. It has been tested under both ideal and heavy load conditions and it does prove beneficial in the oxidation of soot in diesel exhaust gases under both circumstances.

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