Development of a Liquid Catalyst for Diesel Soot Oxidation

From Powder to Prototype

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Stellingen behorende bij het proefschrift

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From Powder to Prototype

door B.A.A.L. van Setten

1. Loon naar willekeurige wetenschappelijke publicatie leidt tot opportunisme.

2. Het Fischer-Tropsch proces verspilt veel energie doordat het thermodynamisch niet koppelbaar is.

3. De zoektocht naar uitlaatgasreinigingsmiddelen neemt soms mystieke 1 proporties aan.


4. Het idee om het brocikaseffect aan te pakken door 100% uitlaatgasrecirculatie toe te passen 2 moet niet serieus genomen worden.


5. De desinteresse van jongeren voor een baan in het onderwijs komt grotendeels doordat dit beroep in de media een negatief imago gekregen heeft.

6. Het patenteren van een techniek waarmee dieselroet en kadavers verbrand kunnen worden, getuigt van veel creativiteit 3.

3 U.S. patent 5,928,618.

7. Er zit een luchtje aan restaurants die eten overmatig kruiden.

8. Indien katalyse wordt geïnterpreteerd als het teweeg brengen van een verlaging van de activeringsenergie, dan werkt niet elk katalytisch filter katalytisch 4.


10. Daar de effecten van een slechte hygiëne in een laboratorium zich meestal niet op de korte termijn openbaren, wordt toegepast beleid soms op de lange baan geschoven.
Development of a Liquid Catalyst for Diesel Soot Oxidation

From powder to prototype

Proefschrift

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Preface

Combustion of fossil fuels for the purpose of transport and heating contributes significantly to the global warming problem. In order to lower the contribution of the latter governments should stimulate what is the most efficient internal-combustion engine: the diesel engine. However, diesel engines emit, besides CO and hydrocarbons, soot particles and NO\textsubscript{x}. These compounds cannot be substantially converted by using a traditional three-way monolith catalyst, because the exhaust gas is oxygen-rich which makes straightforward NO\textsubscript{x} reduction difficult, and the residence time of the particles in the channels of monolith would be too short for complete oxidation.

Delft University of Technology investigates solutions for particle and NO\textsubscript{x} abatement since the early 1990s. The investigation has been divided into two task forces. The Chemical Reactor Engineering group of Prof. Van den Bleek investigates the selective catalytic reduction of NO\textsubscript{x}. The Industrial Catalysis group of Prof. Moulijn studies the catalytic oxidation of diesel soot. The investigation of catalytic diesel soot oxidation was started with a study of the fundamentals by John Neef, who wrote in 1995 the Ph.D. thesis "Catalytic Oxidation of Soot. Potential for the Reduction of Diesel Particulate Emissions", and a reaction mechanism study by Guido Mul, who wrote in 1997 the Ph.D. thesis "Catalytic Diesel Exhaust Purification. A DRIFT Spectroscopic and Mechanistic Study of Soot Oxidation". Recently, the research focused on two possible practical solutions. First, Sytse Jelles investigated the use and mechanism of different catalytic fuel additives, and wrote in 1999 the Ph.D. thesis "Diesel Exhaust Aftertreatment. Development of Catalytic Systems for Diesel Particulate Oxidation". Second, a filter that is coated with a catalyst, i.e. a catalytic filter, might provide a practical solution. The development of a catalytic filter has been divided in three different Ph.D. studies: (1) the development of the catalyst coating, (2) the development of an optimal filter geometry, and (3) the role and utilization of diesel exhaust gas components.

The research is financed by the Netherlands Organization for Scientific Research, with as industrial partner Wärtsilä Diesel, a producer of large diesel electricity-generators. In addition catalytic filters have been evaluated for automotive applications. This part was financed by the European Community Brite-Euram III program, projects CATATRAP and CERFIL, with some major European car manufacturers and car-component suppliers as industrial partners.

The current Ph.D. thesis presents the results of the development of the catalytic coating. The general goal was formulated as follows: "Development of a stable and reliable catalytic soot oxidation filter that regenerates continuously at exhaust gas temperatures; aimed tem-
perature range (325-375°C) without fuel penalty." The innovative part of the research is to apply a liquid catalyst as catalytic coating. Such a catalyst is interesting for two reasons. The first, more practical reason is that it might provide a feasible way towards reliable soot filter regeneration. The second, more scientific reason is that the investigation of its behavior might elucidate the role of the degree of physical contact between the soot and the catalyst during catalytic oxidation. The two main questions to be answered are:

- Does a liquid soot-oxidation catalyst establish tight contact? Or more general: What is the mechanism of a liquid soot-oxidation catalyst?

- Can a liquid oxidation catalyst be applied in a practical catalytic filter?

Chapter 1 gives an overview of the science and technology of catalytic diesel particle filters. Chapter 2 describes the used chemicals, equipment, and procedures. In Chapter 3 different catalysts are tested and the role of the liquid state is discussed. In Chapter 4 different ceramic materials are tested as support for the liquid catalyst. In Chapter 5 catalytic filters are tested under simplified laboratory conditions, a model equation will be formulated in order to predict the 'real world' performance of the catalyst, and the mechanism of the catalyst will be discussed. In Chapter 6 prototype catalytic filters are exposed to extreme conditions in order to predict their long-term stability. In Chapter 7 catalytic filters are tested with the aid of an engine bench, and their mechanism is discussed. In Chapter 8 the presented work is evaluated.
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Chapter 1

Science and Technology of Catalytic Filters

During the last few decades concerns have grown on the negative effects that diesel particulate matter has on health. Because of this, particulate emissions were subjected to restrictions and various emission reduction technologies were developed. It is ironic that some of these technologies led to reductions in the legislated total particulate mass, while neglecting the number of particles. Focusing on the mass is not necessarily correct, because it might well be that not the mass, but the number of particles and the characteristics of them (size, composition) have a higher impact on health. To eliminate the threat of diesel particulate matter, essentially absolute filtration in combination with the oxidation of all emitted hydrocarbons is what will be required.

After two decades of development the first filters will soon be introduced on a large scale. Many different problems had to be overcome, it was especially important for the filter to be robust and its regeneration to be controllable. The key technology to controllable regeneration is oxidation catalysis, which is the main area of focus in this review. Catalytic filter regeneration is very complex, something which is apparent in the main aspects of catalysis: i.e. activity, stability, and selectivity. A complication is that the process conditions can be very transient, and the temperatures are usually low. It is shown that the oxidation catalyst cannot be examined isolated from the total system. Within the margins of size restrictions and an engine’s service life essentially all particulate matter should be trapped; the filter should be regenerated safely; no toxic by-products should be formed; and the catalyst should not alter the filtration characteristics, and vice versa.

The exhaust conditions of passenger cars are not favorable for continuous regeneration strategies, because of which the best strategy seems to be periodical regeneration with the aid of a catalytic fuel additive. This concept is not passive, which makes it complex and expensive. The best technology for filter regeneration with trucks and busses seems to be continuous regeneration. Using the NOx present in the exhaust gas for soot oxidation amounts to a simple and robust concept. A future limitation might be the minimal required NOx:soot ratio: it is not sure if this will be met in future engines. Alternatively, a low-temperature

catalyst may be developed that does not require NO\textsubscript{2}. Developing such an advanced catalytic trap will be one of the major challenges of catalytic filter engineering.

1.1 Introduction

The air we breathe contains numerous particles, originating from natural materials, such as dust from space, skin tissue, plant materials, and wildfires; and human-made materials, e.g. particles derived from construction sites, process wear, and combustion processes. The human body has protective measures against larger particles, but it cannot protect itself against particles roughly smaller than 10 μm, also known as PM-10. In the last decade governments all over the world started to evaluate the effects on health that these particles have, especially diesel particulate matter. Diesel particulate matter is a complex multi-component material. It consists of carbonaceous soot particles, which carry many compounds, which are sometimes toxic. The formation process of diesel particulate matter will be reviewed to give a better understanding of the complexity of the material. The negative aspects will be briefly examined to explain why governments feel that the emission of diesel particulate matter requires legislation. The way that legislation is carried out will be reviewed in order to show how governments deal with this complex compound.

Particles can be trapped with acceptable efficiency from diesel exhaust gas by means of filtration. The filter can be regenerated by combusting the deposited soot fraction of the particulate matter. However, filter regeneration in conjunction with combustion is difficult, since it is very unpredictable. The key to control combustion is catalytic oxidation. The best way to view diesel oxidation catalysis is as a part of the integrated exhaust purification system that is intimately coupled to engine development. Catalytic diesel particulate traps will be discussed in detail: the mechanisms of catalytic and non-catalytic oxidation, the soot trapping methods, soot ignition methods, process conditions, stability requirements, the selectivity of the catalyst, and the technology of commercially available systems.

1.2 The characteristics of diesel particulate matter and exhaust gas

1.2.1 Soot formation

Smith [1] reviewed the different fundamental steps involved in the formation of the soot core of diesel particles. Figure 1.1 summarizes the main results. As a part of the fuel combustion process, diesel is sprayed into the cylinder at high pressure. The sprayed diesel fuel droplets do not mix completely with the abundant oxygen at a molecular level, which results in incomplete combustion [2]. The mechanism of the reacting species is extremely complex, and many pathways lead to the polycyclic structures which are the building blocks of the soot particles. One of the main pathways is the following. Certain molecules are pyrolyzed into small unsaturated molecules where the main constituent is ethyne. The ethyne polymerizes to
Figure 1.1: Schematic mechanism of the formation of soot particles.
polyethylene and, eventually, polycyclic structures are formed by ring closure. These polycyclic structures are called platelets and are in fact small graphite-like sheets that could be seen as the primary building blocks of the soot particle. The platelets stack together to form crystallites, which subsequently stack together to form turbostratic particles \(^2\), as seen in Figure 1.1. The size of the particles increases due to particle coagulation and surface growth instigated by the addition of precursor gas-phase molecules. The surface growth fills the space between the coagulated particles, and because of this the coagulated particles remain spherical. Ishiguro et al. [4] showed that surface growth platelets do not orient themselves in a turbostratic manner, instead they are oriented perpendicular to the radius of the particle, which gives the soot particles a rigid outer shell, which is thermodynamically more stable than the turbostratic inner core. When surface growth stops, the growth of the spherical particles stops. These particles are then called primary soot particles. Those primary soot particles continue to coagulate and form chain-like aggregates. Different aggregates can even clot to form large agglomerates.

### 1.2.2 Diesel particulate matter composition

**Particle size distribution** According to Kittelson's review [5] on nanoparticles, the composition of diesel particulate matter depends on where and how they are collected. In the tailpipe, where the temperatures are high, most of the volatile materials (hydrocarbons, sulfuric acid) are in the gas phase. As the exhaust gas cools down and is diluted by the ambient air, nucleation, condensation, and adsorption transform the volatile materials to solid and liquid particulate matter. During engine emission testing this process is simulated in a dilution tunnel in order to take realistic samples for particle measurements [6]. The details of the collection and cooling processes will determine the relative amounts of material that will adsorb, or condense onto existing particles and nucleate to form new particles. When emitted into the environment the particle properties continue to change due to condensation, and solar radiation [7]. Figure 1.2 shows what a typical particle size distribution in diesel exhaust gas is like. Condensed hydrocarbon and sulfuric acid droplets can be found in the nuclei mode; chain-like aggregates of primary soot particles and associated hydrocarbons in the accumulation mode; and reentrained agglomerates of chain-like aggregates in the coarse mode [5]. Figure 1.3 gives a schematic structure of a diesel particle. Because the measured properties of the diesel particles depend on how, when, and where they are measured, unexpected effects can be encountered. For instance, it is possible to measure a negative filtration efficiency when it is defined according to Equation 1.1.

\[
\text{filtration efficiency} = \frac{\text{particles downstream trap}}{\text{particles upstream trap}} \times 100\% \tag{1.1}
\]

This was reported by Baumgard and Johnson [7] who found negative values for the particle number filtration efficiency of -30 to -460% when using a trap, which was caused by

\(^2\)The definition for turbostratic is a particle where the building blocks (i.e. platelets) are concentrated in a random orientation around the center of the particle [3].
Figure 1.2: Scheme of engine exhaust particle size distribution, both mass and number based concentrations are shown. After [5].

Figure 1.3: Schematic structure of a chain-like aggregate of primary soot particles and associated compounds. After [8].
CHAPTER 1. SCIENCE AND TECHNOLOGY OF CATALYTIC FILTERS

particle formation downstream of the trap during the dilution of the exhaust gas. A counter-productive effect is that it is possible to increase the number of particles while reducing the total particulate mass. This effect relates to the hydrocarbons which are present in the exhaust gas [5]. As the exhaust gas cools down hydrocarbons condense along two pathways: there is nucleation which leads to the formation of new particles and there is adsorption on existing particles. When an engine is optimized and designed to emit fewer particles in the accumulation mode, there is less surface area present in the exhaust gas for adsorption of the hydrocarbons, thus favoring the nucleation of droplets in the nuclei mode, which can result in a major increase in the total number of particles. Figure 1.4 shows the two pathways for condensation of hydrocarbons. A lower diesel particulate mass can thus lead to an increase in the number of nanoparticles!

![Diagram showing two pathways for condensation of hydrocarbons](image)

**Figure 1.4**: Illustration of the condensation mechanisms that can operate in diesel exhaust gas: a, nucleation; b, adsorption.

**Sulfates and metal ash** The sulfates in diesel exhaust gas originate from organic sulfur compounds in diesel fuel. The sulfur is combusted in the engine to form SO\(_2\), approximately 2% of which is oxidized to SO\(_3\) [9]. The SO\(_3\) quickly reacts with water to form sulfuric acid droplets (bp 330°C [10]). A small mass fraction of diesel particulate matter consists of inorganic ash originating from the fuel, lubricating oil, and deriving from engine wear. Van Doorn [11] analyzed the composition of diesel particulate matter produced by a diesel fuel burner. The particulate matter contained 1 wt % inorganic ash. The composition of the ash is given in Table 1.1.

With small modern diesel engines the ash contribution to the diesel particulate matter will be low. With large diesel engines used for powering ships and generating electricity (MW-engines) this will not be the case since such engines often run on heavy fuel oil (HFO).
1.2. PARTICULATE MATTER AND EXHAUST GAS

Table 1.1: Chemical composition of the inorganic ash in diesel particulate matter produced by a diesel fuel burner. After [11]. The aluminum, silicon, and magnesium contents were not included, because the particulate matter was collected on a cordierite (2MgO·2Al₂O₃·5SiO₂) filter.

<table>
<thead>
<tr>
<th>element</th>
<th>ash (wt %)</th>
<th>element</th>
<th>ash (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-</td>
<td>Ni</td>
<td>1.6</td>
</tr>
<tr>
<td>Ca</td>
<td>14.2</td>
<td>Zn</td>
<td>2.2</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>Cu</td>
<td>2.3</td>
</tr>
<tr>
<td>V</td>
<td>2.2</td>
<td>Mn</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
<td>Pb</td>
<td>14.2</td>
</tr>
<tr>
<td>Ti</td>
<td>2.0</td>
<td>Si</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>27.9</td>
<td>S(inorganic)</td>
<td>9.1</td>
</tr>
<tr>
<td>K</td>
<td>11.0</td>
<td>P</td>
<td>1.9</td>
</tr>
<tr>
<td>Na</td>
<td>9.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.04</td>
<td>total:</td>
<td>100</td>
</tr>
</tbody>
</table>

In Table 1.2 the concentration of vanadium, sodium, and sulfur in HFO has been given together with the amounts that pass a large, typical MW-engine.

Table 1.2: Vanadium, sodium, and sulfur concentrations in heavy fuel oil (HFO), and the fuel consumption at the maximum power output of a typical MW-engine [12] (see also Table 1.3).

<table>
<thead>
<tr>
<th>compound</th>
<th>concentration</th>
<th>consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO</td>
<td>-</td>
<td>847 kg/h</td>
</tr>
<tr>
<td>S</td>
<td>34 g/kg_fuel</td>
<td>28.8 kg/h</td>
</tr>
<tr>
<td>V</td>
<td>102 mg/kg_fuel</td>
<td>86.4 g/h</td>
</tr>
<tr>
<td>Na</td>
<td>24 mg/kg_fuel</td>
<td>20.3 g/h</td>
</tr>
</tbody>
</table>

It is clear from Table 1.2 that enormous amounts of metals and sulfur are fed into a MW-engine. Because these engines are designed to run continuously, one can calculate that in an extreme case 250,000 kg sulfur, 750 kg vanadium, and 177 kg sodium will pass through such an engine on a yearly basis. If we assume that 2% of the sulfur is converted to SO₄ [9] and hydrated, then approximately 15,500 kg/y sulfuric acid will pass through the exhaust pipe.

**Definition of diesel particulate matter** Various terms are used to describe the particles emitted by diesel engines.

**diesel particles or particulates** The individual particles present in diesel exhaust gas.

**diesel particulate matter** 'Particulate' means made up of particles [13]. Diesel particulate matter is the generic term for the solid material that originates from diesel exhaust gas. Because the composition depends on the sampling method the US EPA defined the term 'diesel particulate' as the material collected from diesel exhaust gas on a PTFE-coated glass fiber filter at 45 to 52°C [14].

**diesel soot** Diesel soot is the carbonaceous part of diesel particulate matter. It is the fraction that is oxidized during regeneration of a diesel particle filter.

Often this leads to confusion. In order to come to unambiguous legislation simplification was unavoidable. It is not surprising that all over the world up to now the emission has been
defined as the total particulate mass (TPM) deposited on a filter under controlled conditions (see above, definition 'diesel particulate'). The definition includes both solids and condensed liquids. The EPA divided the total particulate mass in the following fractions [14]:

solvent extractable fraction (SEF) The fraction that can be extracted from the TPM by various solvents and includes both organic and inorganic solvent extracts.

 soluble organic fraction (SOF) The fraction of the TPM that is removed by soxhlet extraction with dichloromethane.

total organic extract fraction (TOE) The fraction of the TPM that is removed by soxhlet extraction using a binary mixture of 32:68 wt/wt of toluene:ethanol.

water soluble sulfates The major extractable inorganic fraction in the particulate sample.

combined water Water that is chemically combined with sulfuric acid and any hydrophilic metallic sulfates that may be present in the TPM.

residual carbon particulate (RCP) The calculated particulate mass remaining after the removal of the total organic fraction, the sulfate fraction, and the combined water fraction.

1.2.3 Exhaust gas conditions

Diesel exhaust gas conditions can vary from application to application, which means that in each case a catalytic trap has to be selected and fine-tuned. In Table 1.3 typical data for stationary conditions of a passenger car, heavy-duty truck, and large diesel engine for electricity generation has been listed. Just measuring engine characteristics under stationary conditions will not be adequate for predicting the performance of a catalytic particle trap. Diesel engines, especially those adapted for road applications, are used in a transient way, as represented by various drive cycles (Section 1.3.2). Figure 1.5 shows typical exhaust temperature ranges and median temperatures close to the exhaust manifold of some light-duty vehicles during transient use [18]. The median temperatures close to the exhaust manifold are in the range of 140 to 250°C. A particle trap will, however, not be placed directly behind the manifold but downstream of the turbocharger, and because of this it will experience even lower temperatures. These lower temperatures present a serious threat to filter regeneration. To avoid problems associated with low exhaust temperatures, e.g. city driving, a passenger car trap should be constantly monitored, and an independent regeneration strategy should be incorporated.

Trade-off effects The preferred method for diesel particulate matter abatement is that of reducing its formation. However, if engine adjustments are made to reduce the soot formation this will have an impact on other processes taking place in the cylinders, and will thus only be acceptable if it offsets the other accompanying changes in the fuel combustion process. These considerations are referred to as trade-off effects. Figure 1.6 shows schematic
Table 1.3: List of exhaust conditions in a typical 1998 passenger car diesel engine, a typical heavy-duty truck, and a typical large diesel electricity generator [12, 15, 16].

<table>
<thead>
<tr>
<th>engine</th>
<th>BMEP&lt;sup&gt;a&lt;/sup&gt;</th>
<th>rpm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>output</th>
<th>$q_m$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$T_{up}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$T_{down}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TPM</th>
<th>Bosch&lt;sup&gt;b&lt;/sup&gt;</th>
<th>NO&lt;sub&gt;x&lt;/sub&gt;</th>
<th>HC</th>
<th>CO</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
</tr>
</thead>
<tbody>
<tr>
<td>passenger car</td>
<td>1 bar</td>
<td>2000 n.q.&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.08 n.q.</td>
<td>190</td>
<td>0.1</td>
<td>0.2</td>
<td>70</td>
<td>100</td>
<td>1500</td>
<td>4.5</td>
<td>14.4</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>4000 n.q.</td>
<td>0.26 n.q.</td>
<td>500</td>
<td>1.7</td>
<td>0.5</td>
<td>1400</td>
<td>20</td>
<td>150</td>
<td>10.8</td>
<td>5.1</td>
<td>10.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2000 n.q.</td>
<td>0.19 n.q.</td>
<td>250</td>
<td>0.7</td>
<td>0.2</td>
<td>250</td>
<td>10</td>
<td>150</td>
<td>3.3</td>
<td>16.1</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>4000 n.q.</td>
<td>0.24 n.q.</td>
<td>640</td>
<td>27</td>
<td>1.9</td>
<td>1000</td>
<td>10</td>
<td>150</td>
<td>10.2</td>
<td>6.1</td>
<td>9.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>truck</td>
<td>n.q.</td>
<td>2000 210</td>
<td>0.39 580</td>
<td>530</td>
<td>16.8</td>
<td>0.7</td>
<td>1100</td>
<td>40</td>
<td>170</td>
<td>8</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>generator</td>
<td>24.5 (=max)</td>
<td>599 3956</td>
<td>8.3 530</td>
<td>340</td>
<td>n.q. 0.8</td>
<td>n.q. 31</td>
<td>40</td>
<td>3.6</td>
<td>11.9</td>
<td>n.q.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>12</td>
<td>599 1935</td>
<td>4.8 448</td>
<td>322</td>
<td>n.q. 1</td>
<td>830</td>
<td>39</td>
<td>51</td>
<td>4.2</td>
<td>13.8</td>
<td>n.q.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>599 966</td>
<td>2.9 392</td>
<td>309</td>
<td>n.q. 1.3</td>
<td>764</td>
<td>47</td>
<td>75</td>
<td>4.1</td>
<td>14.4</td>
<td>n.q.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>BMEP, brake mean effective pressure; $q_m$, exhaust gas mass flow rate; rpm, rotational speed; TPM, total particulate mass; $T_{up}$, temperature upstream turbocharger; $T_{down}$, temperature downstream turbocharger; n.q., not quoted.

<sup>b</sup>Bosch smoke number. The Bosch smoke meter is a filter-soiling spot meter: exhaust is passed through a white filter paper, and the darkening of the paper can be taken as a gauge of the 'black' smoke density. The Bosch smoke number is a measure of the darkening of the filter paper, it is scaled arbitrarily from 0 to 10 [17].
Figure 1.5: Exhaust temperature ranges and median temperatures close to the manifold for different light-duty diesel vehicles, as measured during different test procedures. After [18]. DI, direct injection; IDI, indirect injection; TDI, turbo direct injection; EDC, European driving cycle; FTP, federal test procedure (US).

trade-off curves for the emissions of NO\textsubscript{x} and particulate matter. Starting with an engine without EGR at standard injection timing, NO\textsubscript{x} emissions can be decreased by increasing the EGR rate or retarding the injection timing. However, these measures increase particulate mass emissions. Other measures, like reduced oil consumption, higher injection pressures and cooled EGR, shift the curve to a lower one, but the trade-off remains present [19].

Figure 1.6: Schematic trade-off curves for NO\textsubscript{x} and particulate matter: 0, base case; 1, trade-off curve by increasing EGR and retarding injection timing; 2, shifted trade-off curve by combining higher injection pressures and cooled EGR. After [19].
1.3 Environmental impact of diesel particulate matter and legislation

1.3.1 Negative aspects of diesel particulate matter

Atmospheric particles give rise to concerns for many reasons: they diminish visibility; they change the heat balance of the atmosphere; they settle on plants and interfere with photosynthesis; and they penetrate the lungs, blocking and irritating the air passage ways [20,21]. It is especially diesel particulate matter what, because of its composition and size distribution, poses serious problems. Diesel exhaust gas consists of at least 450 substances [22], several of which are known to be toxic (Table 1.4).

Table 1.4: Diesel exhaust gas compounds and their derivatives listed by the Californian Environmental Agency as toxic air contaminants. After [23].

<table>
<thead>
<tr>
<th>Acetaldehyde</th>
<th>Dibenzofurans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>Inorganic lead</td>
</tr>
<tr>
<td>Aniline</td>
<td>Manganese compounds</td>
</tr>
<tr>
<td>Antimony compounds</td>
<td>Mercury compounds</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Methanol</td>
</tr>
<tr>
<td>Benzene</td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>Beryllium compounds</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Nickel</td>
</tr>
<tr>
<td>Bis[2-ethylhexyl]phthalate</td>
<td>4-nitrophenyl</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>Phenol</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Polycyclic HC</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Propionaldehyde</td>
</tr>
<tr>
<td>Chromium compounds</td>
<td>Selenium compounds</td>
</tr>
<tr>
<td>Cobalt compounds</td>
<td>Styrene</td>
</tr>
<tr>
<td>Creosol isomers</td>
<td>Toluene</td>
</tr>
<tr>
<td>Cyanide compounds</td>
<td>Xylene isomers</td>
</tr>
<tr>
<td>Dibutylphthalate</td>
<td>Ethyl benzene</td>
</tr>
<tr>
<td>Dioxins</td>
<td>Formaldehyde</td>
</tr>
</tbody>
</table>

The human body would normally eliminate many of these compounds, but when they are transported deeply into the lungs by soot particles, it takes a long time for the body to eliminate them. Diesel particulate matter is suspected to cause all kinds of health problems, like asthma, persistent bronchitis, and lung cancer. Several agencies have reviewed the relevant scientific aspects, including the epidemiologic, toxicologic, and experimental sides of diesel exhaust, and have classified (or proposed to classify) that diesel exhaust, or its particulate fraction, is a potential, probable, or definite human carcinogen [24]. There is, however, a lack of reliable data linking lung cancer to diesel exhaust, because of which the
EPA in the US is considering characterizing diesel exhaust as being "likely" to cause lung cancer rather than "very likely" [25]. For more detailed information on the physico-chemical properties of airborne (nano)particles and their health effects is referred to [26].

1.3.2 Legislation and compliance

A detailed description of the various diesel emission standards and vehicle certification tests is beyond the scope of the present review. Up-to-date information can be found on the Internet [27]. The technology of exhaust emission tests has been comprehensively documented by Klingenberg [6].

**Legislation** In Europe emission standards are given in g/km for light-duty vehicles (passenger cars, < 1305 kg; and vans, gross weight < 3500 kg); and in g/kWh for heavy-duty vehicles (trucks and busses, speed > 25 km/h, gross weight > 3500 kg), and off-road engines. Step-wise reduction is demanded for the total particulate mass and toxic gas components. In the EU the steps are referred to as Euro standards. They are given in Table 1.5 for passenger cars, and in Table 1.6 for heavy-duty vehicles. It can be seen that in 2005 only new light-duty vehicles which produce at most 0.025 g particulate/km and new heavy-duty vehicles which produce 0.02 g particulate/kWh will be certified for driving in the EU.

| Table 1.5: European emission standards (in g/km) for new passenger cars. |
|---|---|---|---|---|
| phase | year | HC + NOₓ | NOₓ | CO | TPM |
| Euro I | 1992 | 0.97 | - | 2.72 | 0.14 |
| Euro II - IDI | 1996 | 0.7 | - | 1.0 | 0.08 |
| Euro II - DI | 1999 | 0.9 | - | 1.0 | 0.10 |
| Euro III | 2000 | 0.56 | 0.50 | 0.64 | 0.05 |
| Euro IV | 2005 | 0.30 | 0.25 | 0.50 | 0.025 |

| Table 1.6: European emission standards (in g/kWh) for new heavy-duty vehicles. |
|---|---|---|---|---|---|
| phase | year, category | test cycle | HC | NOₓ | CO | TPM |
| Euro I | 1992, <85 kW | ECE R-49* | 1.1 | 8.0 | 4.5 | 0.612 |
| | 1992, >85 kW | | 1.1 | 8.0 | 4.5 | 0.36 |
| Euro II | 1996 | ECE R-49 | 1.1 | 7.0 | 4.0 | 0.25 |
| | 1998 | | 1.1 | 7.0 | 4.0 | 0.15 |
| Euro III | 2000 | ESC and ELR* | 0.66 | 5.0 | 2.1 | 0.10 |
| Euro IV | 2005 | ESC and ELR | 0.46 | 3.5 | 1.5 | 0.02 |
| Euro V | 2008 | ESC and ELR | 0.46 | 2.0 | 1.5 | 0.02 |

*ECE R-49, steady-state cycle for heavy-duty truck engines; ESC, European stationary cycle (replaces the R-49 test); ELR, European load response test.
1.3. ENVIRONMENT AND LEGISLATION

Legislation of fuel sulfur level  Sulfur is an important constituent of diesel particulate matter. Lowering the fuel sulfur level will be beneficial for the emitted total particulate mass (see also Section 1.5.3); and for the implementation of certain aftertreatment technologies, since sulfur can inhibit catalysts (Section 1.5.4). The currently permitted fuel sulfur level is 500 ppm, but this will change in the near future. In the EU it will be lowered to 50 ppm by 2005, and in the United States to 5 to 30 ppm by 2007 [25].

Certification and compliance  Engine certification for light-duty vehicles is performed on a chassis dynamometer, which is used to simulate driving behavior. The European driving cycle is shown in Figure 1.7. Before the test, the vehicle is kept for at least 6 hours at 20 to 30°C. The cycle is started with four times the ECE15 (urban driving cycle) segment to imitate city driving conditions after which it is followed by the EUDC (Extra Urban Driving Cycle) segment to imitate highway driving conditions.

Figure 1.7: ECE15+EUDC driving cycle adhered to by the EU for certification of light-duty vehicles.

Figure 1.8 shows certification data measured during the ECE15 + EUDC cycle for European passenger cars. The data is presented as a scattergram in which the sum of NO\textsubscript{x} and hydrocarbons has been plotted as a function of total particulate mass. None of the currently licensed light-duty vehicles comply with the Euro IV total particulate mass standard, but it can be seen in Figure 1.8 that there are prototypes that do. It is expected that car producers will be able to fulfill the Euro IV standards without there being a need for filters. In the United States this might not be the case. Figure 1.8 shows the Super Ultra Low Emission Vehicle II (SULEV II) standard for NO\textsubscript{x}, hydrocarbons, and total particulate mass. The SULEV II standard is the most strict standard to date and it will eliminate light-duty diesel
car sales in California when it is phased in between 2004 and 2007, unless a significant technological breakthrough takes place before then [30].

After the $1 billion settlement of the charges brought by the US EPA against several heavy-duty engine producers, it became clear that the producers of heavy-duty engines have major problems when it comes to meeting emission standards and keeping fuel efficiency levels high. To get trucks certified, in some cases a defeat device has been incorporated [31]. The truck engine would switch to a less fuel efficient but cleaner mode during laboratory testing, while during real highway driving it would switch to a fuel-efficient but more polluting mode. In the near future emission standards for heavy-duty vehicles will become very stringent in the EU and the US; filter technology will become inevitable.

1.3.3 Concerns about the effects of legislation

Nanoparticles Whether the legislation introduced in the last few years has pushed the emission reduction technology in the right direction remains debatable. To meet the standards cars were developed which emit less particulate mass. Unfortunately, the reduction of particulate mass may be accompanied by a dramatic increase in the number of nanoparticles [7]. A possible mechanism for this was shown in Section 1.2.2. Nanoparticles are thought to be the most dangerous diesel particulate fraction [32–34], although they only make a small contribution to the total particulate mass, as illustrated in Figure 1.2. Legislating particle numbers will pose many practical problems because it is difficult to carry out particle number measurements. If, in future legislation, particle numbers would replace total particulate mass, gasoline engines might become involved in the particle problem, because some gasoline cars, even those equipped with three-way catalysts, have been reported to emit particle numbers which are similar to those emitted by diesel engines [35]. Figure 1.9 shows real data of particle numbers emitted by diesel and gasoline engines.
Unregulated compounds The notion of regulating particle numbers might also be too 'simpistic'. Bagley et al. [36] found regardless of the engine and exhaust aftertreatment device implemented that the use of a low sulfur fuel led to a 90% reduction of particle numbers. However, the mutagenicity of the particle phase was significantly increased, because other fuel composition changes accompanied the change to low sulfur fuel. The best way of legislation will be to express the toxicity of diesel particulate matter. This point was also mentioned in the VERT (Vermindung der Emissionen von Realmaschinen im Tunnelbau) program [37–41]. This program did a very comprehensive study of particle traps for construction site engines. Total particulate mass filtration efficiency was examined; efficiency for 20 to 500 nm particles; creation of new particles in traps; modification of the nature of particles; aging effects; and the influence of conditioning, particulate matter buildup, and regeneration. It was reported that gravimetric analysis is nonspecific with respect to the chemical composition and particle properties (such as size and surface) and, hence, delivers no toxically relevant information [40]. Whether developing methods to measure the toxicity of diesel particulate matter in a relatively simple standardized way will go faster than developing improved particle abatement methods is doubtful. Probably, the best policy is to demand essentially zero particle emissions. Filtration is the most promising way, since for particles in the range of 20 to 500 nm filtration efficiencies higher than 99% have already been reported [37].

1.4 Non-catalytic diesel soot oxidation

In the early 1980s great advances were made with diesel particle trapping techniques. The wall-flow monolith was developed and it was found that particulate emissions could be controlled without having to make engine adjustments. It was thought that a method for oxidizing the trapped soot fraction of diesel particulate matter would quickly be discovered. A catalytic device like the three-way catalyst for gasoline engines was seen as unreliable, since the onset temperature of 400 to 450°C of the soot combustion catalysts of those days
was too high for *spontaneous* regeneration [42]. The general regeneration strategy followed has been to substantially load the trap with soot, ignite the soot by raising the temperature, and then switch the heating off. The required high temperature for completion of the regeneration is maintained by the energy released during the *exothermic* soot combustion. The mechanism is known as *self-supporting flame propagation* [43]. This type of regeneration can easily get out of control and damage the filter, due to chaotic thermal runaways. Higuchi et al. [44] recognized early on that it is influenced by many variables like temperature, oxygen concentration, deposited soot amounts, and gas flow rate; and that these conditions should remain within certain limits to guarantee safe regeneration. This is in conflict with the demand that a trap should be able to regenerate during *all* driving conditions [42] *without* the intervention of the driver [45]. Another problem that Higuchi et al. found was an inadequate regeneration efficiency: up to 35% of the soot can remain on the filter. This is undesirable because it will create a soot gradient buildup, which can lead, when finally ignited, to extremely high temperature-gradients within the filter.

### 1.4.1 The non-catalytic oxidation mechanism

**Unified mechanism** The reactivity of different carbon materials is a function of such properties as crystallite size, crystallite orientation, vacancy concentration; and impurity concentration, type and location [46]. These properties control the fraction of the carbon material that is susceptible for the carbon-oxygen reaction, also known as the *active surface area*. Moulijn and coworkers [47–50] proposed a reaction mechanism for the carbon-oxygen reaction. The mechanism does not account for all observations made during the combustion of carbonaceous materials but it is considered by the authors to be a step further towards a *unified* carbon oxidation mechanism. The mechanism containing simplified oxygen complexes and graphite structures is shown in Figure 1.10. Graphite that contains a ketone *surface oxygen complex*, reacts with oxygen to form a surface semiquinone group and a physically adsorbed oxygen atom (step a). The C-C bond strength in the semiquinone complex is only slightly weaker than the C-C bond strength in graphite. It is unlikely that the semiquinone complex will decompose, which is why this complex is called a *stable surface-oxygen complex*. Due to the electronegativity of the oxygen atoms in the semiquinone complex, the C atom between the CO groups becomes a target for bonding with oxygen. A semiquinone complex with off-plane oxygen is formed (step b), and this results in the lowering of the C-C bond strength of the neighboring C atoms. The complex decomposes (step c) and graphite with a carbonyl group is formed. The C atom next to the carbonyl group becomes a target for bonding with oxygen due to the electronegativity of the oxygen atom in the carbonyl group. A carbonyl complex with off-plane oxygen is formed (step d), and this results in the lowering of the C-C bond strength of the neighboring C atom. CO is released (step e) and the reaction cycle can start again with step a. In steady-state the reaction rate is not influenced by the rate-constant values of the individual steps, but by the amount of carbon complexes formed on the active surface area.
Figure 1.10: Reaction mechanism of the non-catalytic oxidation of carbon. Reaction mechanism constructed after [48].
**CHAPTER 1. SCIENCE AND TECHNOLOGY OF CATALYTIC FILTERS**

**Kinetics** The oxidation rate of carbonaceous materials can be described using a general kinetic model equation:

$$ r = N_T \cdot k(T) \cdot f(p_{O_2}, p_{H_2O}, p_{NO_2}, \ldots) \quad (1.2) $$

in which $r$ is the reaction rate, $N_T$ the total number of active carbon sites, $k(T)$ a temperature dependent reaction rate constant, and $f(p_{O_2}, p_{H_2O}, p_{NO_2}, \ldots)$ a function which describes the dependency of the reaction rate on the partial pressures of various gas components.

The temperature dependent rate constant $k(T)$ can be described referring to the Arrhenius equation:

$$ k(T) = k_0 \cdot e^{-\frac{E_a}{RT}} \quad (1.3) $$

in which $T$ is the absolute temperature, $k_0$ the pre-exponential factor, $R$ the gas constant, and $E_a$ the activation energy. The influence of the gas partial pressures is often limited to the influence of the oxygen partial pressure, described by an $n^{th}$ order:

$$ f(p_{O_2}, p_{H_2O}, p_{NO_2}, \ldots) = p_{O_2}^{n_{O_2}} \quad (1.4) $$

This leads to the following equation for the oxidation rate $r$:

$$ r = N_T \cdot k_0 \cdot e^{-\frac{E_a}{RT}} \cdot p_{O_2}^{n_{O_2}} \quad (1.5) $$

The total number of active carbon sites $N_T$ can be described by:

$$ N_T = \lambda \cdot \frac{S_a}{S_{a,0}} \quad (1.6) $$

in which $\lambda$ is the surface concentration of active sites and $S_a$ the actual surface area, in this context known also as total surface area (TSA), and $S_{a,0}$ the initial surface area. The dependency of $N_T$ can be described as a function of conversion. A simple approach is to use an empirical $n^{th}$ order model. The relation between the surface area and the conversion is then:

$$ \frac{S_a}{S_{a,0}} = (1 - \xi)^{n_{\xi}} \quad (1.7) $$

in which $\xi$ is the conversion and $n_{\xi}$ the reaction order in carbon. For $n_{\xi}$ is 2/3 the $n^{th}$ order model is also known as the shrinking core model: the surface area is directly proportional to the outer surface area of the carbon particle, which is assumed to be spherical.

The $n^{th}$ order model does not predict the reaction of many porous solids with gases accurately. For highly porous carbons, like soot and activated carbon, $S_a$ is created by a complex network of pores. Soot pores consist of the space between the primary soot particles: 3 nm pore openings can be found between 20 nm primary soot particles [51]. Due to pore growth and opening of closed pore space, $S_a$ and with that the reaction rate can increase during the reaction. Several pore models have been put forward to allow for pores in reacting solids. Pore models exist that idealize the complex internal structure by geometric assumptions of cylinders and spheres, as illustrated in Figure 1.11 a; or by a network model of pore topology, as illustrated in Figure 1.11 b.
The random pore model of Bhatia and Perlmutter [52] describes the pores as overlapping cylindrical surfaces. Important features of the model are: $S_a$ is described at any given conversion as a function of an initial pore structure parameter $\psi$, and reactions are represented which show a maximum in the reaction rate (i.e. $\psi > 2$) as well as ones that do not (i.e. $\psi < 2$). The conversion dependence of the surface area is described as follows:

$$\frac{S_a}{S_{a,0}} = (1 - \xi) \cdot \sqrt{1 - \psi \ln(1 - \xi)}$$

(1.8)

The random pore model can successfully predict experimental observations, but the effect of the pore topology is included in an average sense. Because of this it is not possible to evaluate $S_a$ in a fundamental fashion. Reyes and Jensen [53] used a Bethe network to describe the pore structure of a solid. With this model the conversion dependence of the surface area is described as follows:

$$\frac{S_a}{S_{a,0}} = (1 - \xi) \cdot \left(1 + \xi \frac{1 - \epsilon_0}{\epsilon_0}\right)$$

(1.9)

where $\epsilon_0$ is the initial porosity of the material.

Discrepancies between model predictions and experimental observations should not only be attributed to assumptions made in the description of the evolution of physical and transport properties with conversion, but also to catalytic effects by inorganic impurities present in the solid material [53]. The surface concentration in active sites ($\lambda$) is also known to cause discrepancies, because it can change during the ongoing reaction according to Laine et al. [46] and is probably a function of the temperature according to Kapteijn et al. [49].

The above mentioned observations are mainly based on kinetic considerations. Ishiguro et al. [54] performed a microstructural analysis of diesel soot oxidation and proposed the following steps:
1. To release or oxidize occluded species.

2. To allow graphitic layers to grow in primary soot particles.

3. To induce fine particle formation by flaking off crystallites from the outermost shell of the primary particles.

It is likely that oxidation models can be further refined, but it will be very difficult to attain a unified model to account for the reaction kinetics of the complete class of carbon materials, because the class of materials is very large and there are many parameters to include.

1.4.2 Non-catalytic filter regeneration

Induced periodical regeneration

Basically there are two ways for igniting trapped diesel soot. The soot can be indirectly ignited by raising the temperature of the exhaust gas or filter, or directly by selectively raising the temperature of the soot itself.

External heating  Placing an electrical heater or fuel burner upstream of a filter seems like an obvious method, since fuel and electricity are easily available in a vehicle. Fuel burners are favored because they are up to five time more energy efficient than electrical heaters [55]. On the other hand a fuel burner is more complex and less reliable, because its flame has to be ignited. If that fails the filter could be soaked with fuel, which can lead to a disastrous thermal runaway [56]. In general pre-heaters are not attractive, because they must heat up all the exhaust gas, something which is not very energy efficient. Further, the conditions in the exhaust pipe are transient which makes regeneration with a burner problematic [18]. One way of lowering fuel usage is by using a by-pass system [57], where the full exhaust flow does not pass through the filter during regeneration. These types of systems are, however, rather difficult to apply. A niche market for such technology could be vehicles with known operation patterns, like forklifts [58].

Engine controlled heating  Modern diesel engines can have flexible fuel injection and control systems that can be used to produce the required additional heat in the engine. Several options exist:

- The exhaust gas can be heated by throttling the gas stream. This is not a favored method because engine power is decreased during throttling, making regeneration control difficult because of the reduced oxygen content [59]. On the other hand if the filter is highly loaded with soot it could be a distinct advantage since the reduced oxygen content would lead to a reduced exotherm, which could provide a means of control to prevent filter damage.
By *varying* fuel injection timing the combustion process can occasionally be adjusted to achieve exhaust temperatures which are high enough to induce regeneration. The four demands that have to be met when regeneration is to be induced in an acceptable manner with this approach are these [60]: (1) maximum temperature increase at minimum fuel expense; (2) the driver should not be involved; (3) there should be no additional noise; and (4) no additional by-products should be formed like CO, unburned hydrocarbons, and soot. To fulfill these demands fuel is injected during different phases of the cylinder cycle to produce the required amount of work and heat [60]. Basically, it means that when regeneration is initiated the engine is operated in the usual way, with additional fuel injection at the top-end of the cylinder's expansion stroke. There no additional work can be done and the energy is released as heat.

Gantawar et al. [61] raised the temperature by temporarily ramping the engine to *full load* in order to initiate self-supporting regeneration and then subsequently reducing the engine to idle. Such kind of regeneration strategy is not favored in practice since it cannot be initiated independently by a management system: the driver is forced to drive at high speed once in a while.

**Microwave heating** Garner and Dent [59] reported *regeneration efficiencies* of 40 to 80% with *microwave* regeneration. They attributed these low values to uneven heating of the soot.

\[
\text{regeneration efficiency} = \frac{\text{soot combusted during regeneration}}{\text{soot present at start regeneration}} \times 100\% \quad (1.10)
\]

During their experiments the soot was ignited for 7 minutes, while the complete regeneration needed 23 minutes to complete. The reason why regeneration failed was probably not because the soot ignition failed, but because the regeneration reactions were not fully self-supporting. Walton et al. [62] improved the regeneration efficiency by incorporating ferrite in the filter. Ferrite heats equally well in the electric and magnetic field components of microwave radiation and it provides uniform energy input into the soot-loaded filter. Microwave regeneration is not considered to be practical and it will most probably not be applied [18].

**Internal filter heating** The temperature in a filter can be raised *internally*, by incorporating electrical heating elements into the filter structure. Hüthwohl et al. [43] developed a wall-flow monolith containing electrical heating filaments. In this way the soot could be ignited *directly*, without the need to heat all exhaust gas. The system was further optimized with catalysts to achieve a maximum regeneration efficiency during self-supporting regeneration. Figure 1.12 shows a monolith with internal electrical heating wires.

Sekhar et al. [63] developed a foam filter based on a *metal-ceramic composite*. When an electric current is applied to the composite filter, it will heat up like a heating element. No results relating to improved regeneration were reported for this composite trap. Simon et al. [42] developed a rotating mini-burner which could heat a wall-flow monolith locally to achieve a regeneration efficiency of 100% with a fuel efficiency loss of only 1%, without the need for all exhaust gas to be heated.
Aerodynamical regeneration  Since the early 1990s Levendis and coworkers [64,65] have been developing an aerodynamical regeneration system. Their latest prototype consist of a normally operated wall-flow monolith where the exhaust flow is switched off every 13 minutes and a 7.3 bar back pulse is given for 3 seconds. During these three seconds the exhaust gas and the filtered particulate matter is made to flow into a nylon filter bag or in an electrical incinerator. For practical applications the system is rather complex and impractical [18].

Induced continuous regeneration

Certain induced regeneration methods do not rely on high temperatures. They might be applied in a continuous manner at an acceptable energy expense.

Non-thermal plasma reactors  A plasma is a highly reactive gas that consists of ions and radicals. In the plasma electrons are usually accelerated by voltages of 20 to 30 kV. The high-energy electrons collide with gas molecules and transfer their energy by two pathways: dissociation of molecules; or by raising the vibrational energy of molecules, thereby raising the temperature. A plasma which is very efficient in the first pathway but not in the second one is called a non-thermal plasma. Its energy might be applied to convert low-concentration pollutants rather than to raise the temperature of the total exhaust gas volume. However, due to the low contamination concentrations in exhaust gas it is unlikely that the contaminants will be directly dissociated. In exhaust gas the electrons deposit their kinetic energy primarily into the major exhaust gas components, N₂ and O₂ [66].

\[ e + N₂ \rightarrow e + N + N \]  \hspace{1cm} (1.11)  
\[ e + O₂ \rightarrow e + O + O \]  \hspace{1cm} (1.12)

The N and O radicals can cause various reactions, the reduction of NO being the desired one [66]:

\[ N + NO \rightarrow N₂ + O \]  \hspace{1cm} (1.13)

There are two reasons why plasma reactors were not instantaneously a success. Firstly, the highest electric field that can be applied while maintaining a nonthermal plasma (the electric breakdown threshold) coincides with the optimal electron mean energy for dissociation of high amounts of oxygen molecules, and not for dissociation of nitrogen molecules [66].
1.4. NON-CATALYTIC DIESEL SOOT OXIDATION

Figure 1.13 illustrates this. It are mainly oxygen radicals that are produced, while the number of nitrogen radicals which are needed for Reaction 1.13 are quite low. The production of each nitrogen radical costs 310 eV at the electric breakdown threshold. If we assume that only nitrogen molecules are dissociated and that all the produced nitrogen atoms are used for Reaction 1.13 in order convert the 1100 ppm NO\textsubscript{x} present in the exhaust gas of the truck given in Table 1.3, then 460 kW (!) would be required to achieve 100% NO\textsubscript{x} reduction (the truck engine produces 210 kW at the given conditions). Even if the electric breakdown threshold could be raised to a higher value, then the energy requirement would still be very high. For an electron mean energy of 20 eV a power of 74 kW would be required.

Secondly, the combination of highly reactive radicals and a wide range of diesel exhaust components makes for a wide range of products which can be formed such as: a net NO\textsubscript{x} production [67, 68]; organic nitrates [69]; N\textsubscript{2}O [67–70]; acetaldehydes and alcohols [69–71]; CO from CO\textsubscript{2} [72]; particulate matter [72]; and unknown byproducts [72, 73]. This gives rise to two additional problems. Firstly, it complicates the analysis of the part played by the plasma in reducing NO\textsubscript{x}; and secondly, whether the formation of these byproducts is desirable remains doubtful. Hoard and coworkers [69, 73] showed clearly how the formation of unknown compounds complicates exhaust analysis. Using different analysis techniques they analyzed the composition of exhaust treated with a plasma with or without a DENOX catalyst. They could measure 67% NO\textsubscript{x} reduction using the commonly used NO\textsubscript{x} chemiluminescence analyzer, and they found by means of N\textsubscript{2} GC analysis that only 27% NO\textsubscript{x} was converted to N\textsubscript{2}. The 'missing' 40% was converted to unknown products that could not even be detected using FTIR analysis. By placing a Cu-ZSM zeolite catalyst downstream of the plasma reactor they could convert the 'missing' fraction back to NO\textsubscript{x}. 
**Possible applications** Because O$_2$ is easily dissociated at the electric breakdown threshold it will be mainly O radicals that are produced in exhaust gas. Most research currently focuses on the utilization of these O radicals for NO$_2$ production. NO$_2$ is more reactive than NO, because of which plasma generated NO$_2$ enhances catalytic reduction with NO$_x$ [72, 74–76] and, like with NO$_x$-aided CRT, oxidation of soot [71]. Figure 1.14 gives a diagram of a plasma CRT.

\[
\begin{align*}
O_2 + e & \rightarrow O + O + e \\
O + O_2 & \rightarrow O_3 \\
O_3 + NO & \rightarrow NO_2 + O_2 \\
NO_2 + C & \rightarrow CO + NO
\end{align*}
\]

**Figure 1.14:** Simplified diagram of a continuously regenerated plasma trap.

Winterbottom and coworkers [77] developed a more practical design for a nonthermal plasma reactor (Figure 1.15) and claimed that it is "the holy grail" of diesel emission purification. They claimed a promising performance both for removing NO$_x$ and particles at an acceptable energy consumption. In a more recent publication [78] the system is no longer
"the holy grail", because the claim of NO\textsubscript{x} reduction is not mentioned anymore and only the soot removal claim remains. The findings are based on short-term experiments because of which it is difficult at present to determine what is the real potential of the system.

**Thermal plasma** Levendis and Larsen [79] investigated soot oxidation in air that had been ionized with a thermal plasma. They conducted experiments in the range of 200 to 450°C, and occasionally found oxidation rate increases of more than 100%. They attributed this to the generation of O radicals and NO\textsubscript{2}. The applicability of the system is questionable, because it generates NO\textsubscript{x}.

**Electrochemical regeneration** Christensen et al. [80, 81] reported having developed an electrochemical reactor (Figure 1.16) which can remove 90% particulate mass, 50% CO, 50% hydrocarbons, and 10% NO\textsubscript{x} at temperatures above 250°C with a fuel penalty of only 1%. The system consists of porous ceramic filter tubes, covered with a catalytic electrode, to which a voltage of 20 to 60 V DC is applied. Particulate matter that has been deposited on the filter tubes is oxidized electrochemically. This system looks interesting but until now only very short time-scale experiments have been reported.

![Illustration of the electrochemical diesel particle filter](image)

**Figure 1.16:** Illustration of the electrochemical diesel particle filter. Courtesy of DINEX.

### 1.5 Catalytic diesel soot oxidation

In general the catalytic oxidation of soot is slow, since the solid particles are large and when deposited immobile. Because of this they do not penetrate into the catalyst's micro or mesopores where catalytic processes usually take place. Soot oxidation takes place on the filter walls of the particle filter where the catalyst has been deposited. Table 1.7 gives some of the characteristic physical properties of a monolith, ceramic foam, and a typical γ alumina
catalyst pellet bed; for reference the size of a typical soot particle and a benzene molecule are indicated.

Table 1.7: Physical properties of a monolith, ceramic foam, and γ alumina pellet. After [82]. By way of comparison the diameter of an average soot particle and a benzene molecule are given.

<table>
<thead>
<tr>
<th>property</th>
<th>monolith</th>
<th>foam</th>
<th>pellet</th>
<th>soot</th>
<th>benzene$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>channel opening</td>
<td>mm</td>
<td>1.5</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>size of pellet</td>
<td>mm</td>
<td>-</td>
<td>-</td>
<td>Ø1.42 × 5</td>
<td>-</td>
</tr>
<tr>
<td>bulk density</td>
<td>g/ml</td>
<td>0.68</td>
<td>0.36</td>
<td>0.60$^b$</td>
<td>-</td>
</tr>
<tr>
<td>void</td>
<td>vol %</td>
<td>63</td>
<td>79.3</td>
<td>42.1$^b$</td>
<td>-</td>
</tr>
<tr>
<td>pore volume</td>
<td>vol %</td>
<td>18.6</td>
<td>3.0</td>
<td>15.1$^b$</td>
<td>-</td>
</tr>
<tr>
<td>solid part</td>
<td>vol %</td>
<td>18.4</td>
<td>17.7</td>
<td>42.8$^b$</td>
<td>-</td>
</tr>
<tr>
<td>surface area</td>
<td>m$^2$/g</td>
<td>0.53</td>
<td>0.10</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>outer surface area</td>
<td>cm$^2$/g</td>
<td>25$^c$</td>
<td>31</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>cm$^2$/ml</td>
<td>17$^c$</td>
<td>11</td>
<td>46</td>
<td>-</td>
</tr>
<tr>
<td>diameter reactant</td>
<td>nm</td>
<td>-</td>
<td>-</td>
<td>500$^d$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$^a$Benzene was chosen to represent a typical hydrocarbon.

$^b$Values on a basis of dense packing in a reactor of 8.5 mm inner diameter.

$^c$It was only the inner wall surfaces of straight channels that were considered.

$^d$Average particle on mass basis, as seen in Figure 1.2.

It is clear that there are enormous size differences, when there is a soot to benzene diameter ratio of 1000:1 and a monolith to pellet-bed surface-area ratio of 1:340.

### 1.5.1 The catalytic oxidation mechanism

The mechanism underlying catalytic oxidation of carbonaceous materials is difficult to study, because of the complexity of the processes taking place at different size scales.

**Atomic processes** Two general ways have been proposed for the catalytic action on an atomic scale. Either they can be classified as electron-transfer mechanisms or as oxygen-transfer mechanisms:

- **electron transfer** The electron transfer mechanism was originally proposed by Long and Sykes [83]. The mechanism (for which no firm proof exists) is thought to act by altering the distribution of π electrons in the graphite sheets, thereby making the carbon substrate more susceptible to oxidation.

- **oxygen transfer** The oxygen transfer mechanism, originally proposed in general outline by Neumann et al. [84], is thought to be the general mechanism for the catalytic oxidation [85]. Amariglio and Duval [86] suggested that only metals which can "oscillate" between two oxidation states can catalyze the oxidation of graphite sheets. An illustration of such oscillation or redox cycle is given in Figure 1.17.
Processes on a meso and macroscopic level

Pioneering analysis techniques  The surface of cleaved graphite crystals is ideal for the analysis of carbon oxidation by means of microscopy. Microscopy made it possible to see the effect of crystallographic orientation and introduced irregularities on oxidation. The pioneering work of Hennig [88] in the 1960s with transmission electron microscopy (TEM) made clear that the catalyzed reaction of graphite is dominated by catalyst droplets that physically come into contact with edges, steps or vacancies in the graphite sheets. Irregularities were introduced by etching, for instance, with an oxygen-chlorine mixture, and they were made visible (even in the case of monolayer graphite sheets) to ex-situ TEM analysis by decorating them with gold nuclei (i.e. etch-decoration, ex-situ TEM). It was recognized early on that catalysts that have an improved physical contact with the graphite will show high reaction rates. For instance, $V_2O_5$ was found to be "abnormally" active due to the molten state of the catalyst during the reaction. The development of the controlled atmosphere electron microscope by Baker [89] made it possible to directly observe the catalytic action in-situ on a scale of more than 30 graphite sheets [90]. This method, in combination with etch-decoration TEM, provided a reasonably good understanding of the catalytic processes taking place on graphite surface layers.

Direct contact catalysts  Most catalysts require direct physical contact with carbonaceous materials if oxidation is to be accelerated. The catalyst may activate the carbon atoms, or it may act itself as a renewable, activated oxygen donor. The physical contact requirement places restrictions on the development of such catalysts, because the catalyst should not only be intrinsically active, but should also be able to establish intimate physical contact with the carbon by means of a meso or macroscopic mechanism:
**channeling** Channeling has been observed during the catalytic oxidation of graphite. The process commences on the edge or in a step of a graphite sheet. Catalysts operating according to this mechanism are, therefore, known as *edge specific*. The catalyst particles catalyze the oxidation of high-coordination edge carbon atom sites, thereby creating new high-coordination sites, etc. and leaving a channel behind them which is of the same width as the diameter of the catalyst particle [91]. The process is called *deep channeling* when it involves multiple graphite layers, and *monolayer channeling* when it involves single graphite sheets. The channeling mode that occurs depends on the rate-limiting step evident during oxidation, and it can differ from one catalyst to another [90]. Figure 1.18 a gives a schematic representation of catalytic channeling.

![Illustration of different macroscopic oxidation mechanisms on graphite sheets: a, deep channeling; b, edge recession. After [92].](image)

**edge recession** Edge recession starts on the edge of a graphite flake, at a step between different graphite layers, or in a vacancy on a graphite layer. The catalyst catalyzes the oxidation of the high-coordination edge carbon atom sites, thereby creating new high-coordination carbon sites etc. The catalyst moves like a front, as shown in Figure 1.18 b. The catalyst gradually penetrates each graphite layer at vacancies released by removal of the layers on top [88].

The way in which the catalyst operates is governed, to a large degree, by the strength of the interaction between the metal and the graphite edge atoms [93]. Figure 1.19 shows the extremes of catalyst-graphite interaction. In a nonwetting situation no reaction occurs. In the intermediate wetting state the catalyst is present as a cap-shaped particle and the mode of attack is channeling. In a complete wetting situation edge recession occurs which leads to the most efficient catalyst use [93]. The actual mechanism depends on the chosen reaction conditions and catalyst [88,90,94]. Table 1.8 shows how different metals can operate according to different mechanisms. Baker [93] found for ruthenium, rhodium, and iridium, that they can operate according to both mechanisms, depending on the reaction temperature.
Figure 1.19: Illustration of the influence of the metal-graphite interaction on the mode of catalytic attack. After [93].

Table 1.8: Classification of the modes of catalyzed oxidation of graphite by various metals. Compilation of experimental data obtained with controlled atmosphere electron microscopy. After [93].

channeling
channeling and edge recession
edge recession
no wetting
no wetting
Indirect contact catalysts  Some catalysts can oxidize soot without having intimate physical contact. They catalyze the formation of a mobile compound (NO$_2$, O$_{ads}$, ...) that is more reactive than O$_2$. In the absence of physical contact the formation of those mobile species is the main advantageous property of this type of catalyst. For indirect contact catalysts two main reaction mechanisms are known:

**NO$_x$ aided gas-phase mechanism** Cooper and Thoss [9] discovered a way of using gas-phase NO$_2$ as an activated mobile species for soot oxidation. They proposed that the NO:NO$_2$ combustion cycle accelerates soot combustion:

\[
2\text{NO} + O_2 \rightarrow 2\text{NO}_2
\]

(1.14)

\[
\text{NO}_2 + C \rightarrow \text{NO} + \text{CO}
\]

(1.15)

**spillover mechanism** Some catalysts can dissociate oxygen and transfer it to the soot particle where it reacts as it was in a non-catalytic reaction. This mechanism is known as the spillover mechanism (Figure 1.20). There exist some examples that show that contact is not prerequisite for the catalytic reaction. For instance, Baumgarten and Schuck [95] showed that the rate of catalytic coke oxidation can be accelerated while there is no direct contact between the catalyst and the coke, which they explained by oxygen spillover. Baker and Chludzinski [96] showed that Cr$_2$O$_3$ can accelerate edge recession of graphite while being motionless. Mul et al. [97] showed with a labeled oxygen study that spillover and redox oxidation can occur simultaneously. They discussed that the dominating mechanism will depend on the degree of physical between the catalysts and the soot.

![Figure 1.20: Illustration of spillover soot oxidation mechanism on a catalyst surface.](image-url)
1.5. CATALYTIC DIESEL SOOT OXIDATION

1.5.2 Catalysts for regeneration

Various soot oxidation catalyst technologies have been developed. Indirect catalytic soot oxidation based on the NO:NO\textsubscript{2} combustion cycle has been commercialized by Johnson Matthey and will be discussed in Section 1.7.2. In the current section the different catalysts which require direct physical contact with soot will be examined.

Catalytic fuel additives for induced regeneration

A good way of improving the quality of induced self-supporting regeneration of a particle filter is that of increasing the reactivity of the soot with a built-in metal catalyst. The catalyst can be incorporated during the soot formation process. Blending a stable organometallic additive into the fuel (typically 10 to 100 ppm) is the most convenient method. These catalytic fuel additives are also known as fuel-born catalysts, and the type of regeneration as quasi-continuous regeneration [98], or passive-active regeneration [99].

Types of fuel additives

Hüthwohl et al. [43] were among the first to investigate the mechanism of induced regeneration with fuel additives. They investigated the role of manganese (240 ppm) and iron (60 ppm) additives. In the case of manganese, they witnessed that flowing, glowing catalyst particles were igniting local combustion reactions in the monolith channels, after which a self-supporting flame propagated through the channels. Gantawar et al. [61] investigated the effect of copper (60 ppm) on induced regeneration and found that there was up to a sevenfold increase in regeneration efficiency due to the fuel additive. Bloom et al. [45] compared copper (30 ppm), iron (30 ppm), and cerium (50 ppm) additives with each other during consecutive induced regenerations, and found that only copper could regenerate a filter efficiently, while the regeneration remained partial with cerium and iron additives which caused the pressure drop in the filter to constantly increase, as shown in Figure 1.21. The activity order was: copper >> cerium > iron.

Some fuel additives are so active that they spontaneously initiate self-supporting regeneration reactions at low temperatures. Richards et al. [100] tested mixed fuel additives based on strontium and iron for passive periodical regeneration without additional heating. They reported successful road tests of 5,000 km for certain passenger cars with mixed driving patterns. Spontaneous self-supporting regeneration was found every 100 to 600 km at exhaust temperatures higher than 225 to 400°C. Lepperhoff et al. [98] found that copper and iron can spontaneously initiate complete regeneration at temperatures even below 200°C! They considered such a high activity not a blessing. It could lead to extremely high local temperatures, and to filter damage. With cerium this behavior was not found: the regeneration reactions it initiated spontaneously at low temperatures remained local. This means that cerium activated soot can be reliably ignited by employing on-board diagnostics, while undesired spontaneous regeneration does not occur.

Hardenberg et al. [101,102] tested a dissolved copper catalyst that was injected upstream of the filter into the exhaust prior to regeneration. They used 0.07 g/km, which is a high amount. Even if this amount might be cut down to more acceptable levels, other limitations remain: the spray nozzle can be plugged with deposits, the catalyst should be distributed
evenly over the soot surface, and the amount of catalyst used should be proportional to the amount of soot. In this respect fuel additives are superior.

Catalytic fuel additives for passive regeneration

Catalytic fuel additives have often been investigated for passive regeneration. During passive regeneration a trap regenerates itself, without the intervention of on-board diagnostic and control systems. Passive regeneration is often a continuous process, because of which it is sometimes referred to as continuous regeneration. During continuous passive regeneration catalytic fuel additives bring the rate of soot oxidation in equilibrium with the rate of soot deposition, which causes a constant pressure drop over the filter. Oser and Thoms [103] defined the temperature at which equilibrium occurs as the balance temperature. Figure 1.22 shows the results of a typical balance temperature determination experiment with a Corning EX80 wall-flow monolith, where the lowest balance temperature for 100 ppm cerium additive was found to be between 430 and 440°C [104].

Types of fuel additives  Lepperhoff et al. [98] compared cerium, iron, and copper additives. They found the lowest balance temperatures for iron and copper, which were 350°C. Jelles et al. [104] measured balance temperatures for different mixed additives to discover whether synergetic effects play a role, as was tried before with little success for a copper-manganese combination by Daly et al. [105]. Jelles et al. found that after some time of running on low-concentration fuel additive combinations there was a dramatic balance temperature reduction. The reduced balance temperature was explained as follows. Platinum which was deposited on the monolith started to catalyze the oxidation of NO to NO₂. NO₂ subsequently reacted with the fuel additive catalyzed soot. The enhanced activity was explained by assuming that each NOₓ molecule is used many times, as is illustrated in Figure
1.5. CATALYTIC DIESEL SOOT OXIDATION

1.40. Figure 1.23 shows a reaction scheme of the proposed mechanism of the oxidation of soot by using platinum:cerium fuel additive. Road trials of the mixed catalysts showed that not only the regeneration of the filter is altered but also the fuel combustion: the fuel efficiency increased by 5 to 7% with at the same time a decrease of the produced particulate mass of 10 to 25% [106].

The results of the studies of Lepperhoff et al. and Jelles et al. have been summarized in Table 1.9. It should be noted that the listed balance temperatures are only valid for the conditions under which they were measured. As Daly et al. [105] indicated, they depend on several factors: particulate matter loading, trap volume, trap materials, trap pore size, additive concentration, oxygen concentration, engine type, and engine load.

**Supported catalysts**

Simple metal oxides can be supported on a trap for soot oxidation, but they only operate satisfactorily at high temperatures (> 450°C). During the last decade several research groups...
have tried to develop catalysts that can oxidize diesel soot at lower temperatures, preferably below 300°C. In all the studies the catalysts were tested under simulated model conditions. The powder catalysts (< 250 μm) were mixed with synthetic soot, and tested with temperature programmed oxidation (TPO) experiments (except for Inui et al. [82, 107] who used isothermal conditions). The reaction carried out is a batch reaction, since no additional soot is fed to the reactor. It is difficult to compare the results published by different researchers, because the reaction rate is a function of the degree of physical contact between the catalyst and the soot, and samples with varying physical contact have been reported.

**Table 1.9: List of measured balance temperatures for different catalytic fuel additives [98,104].**

<table>
<thead>
<tr>
<th>wall-flow monolith producer: Corning</th>
<th>additive</th>
<th>c ppm</th>
<th>T_{bal.} °C</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX47</td>
<td>Ce</td>
<td>100</td>
<td>400</td>
<td>[98]</td>
</tr>
<tr>
<td>EX47</td>
<td>Fe</td>
<td>100</td>
<td>350</td>
<td>[98]</td>
</tr>
<tr>
<td>EX47</td>
<td>Cu</td>
<td>100</td>
<td>350</td>
<td>[98]</td>
</tr>
<tr>
<td>EX80</td>
<td>none</td>
<td>–</td>
<td>537-557</td>
<td>[104]</td>
</tr>
<tr>
<td>EX80/Pt</td>
<td>none</td>
<td>–</td>
<td>417-427</td>
<td>[104]</td>
</tr>
<tr>
<td>EX80/Pt</td>
<td>Pt/Ce</td>
<td>0.5/5</td>
<td>327</td>
<td>[104]</td>
</tr>
<tr>
<td>EX80/Pt</td>
<td>Pt/Cu</td>
<td>0.5/5</td>
<td>347</td>
<td>[104]</td>
</tr>
<tr>
<td>EX80/Pt</td>
<td>Pt/Fe</td>
<td>0.5/22</td>
<td>357</td>
<td>[104]</td>
</tr>
<tr>
<td>EX80</td>
<td>Ce</td>
<td>100</td>
<td>432</td>
<td>[104]</td>
</tr>
</tbody>
</table>

C, additive concentration; T_{bal.}, balance temperature.

**Type of contact** Inui and Otowa [82] and Löwe and Mendoza-Frohn [108] were among the first to realize that the contact of deposited soot on a catalytic filter is poor. Neef et al. [109,110] systematically investigated the effect that the degree of physical contact has on catalytic soot combustion: they mixed soot and catalyst powders with a spatula and defined that as loose contact, they did the same with a mechanical mill and defined that as tight contact, and they filtered diesel soot from an exhaust stream on a bed of catalyst particles and defined that as in-situ contact. Figure 1.24 shows the results of the investigation. T_{max. rate} is the temperature at which the maximum oxidation rate is observed. Combustion temperature differences as large as 200°C can be found between loose and tight contact samples of one catalyst. It is clear that Neef et al. measured apparent activities which were a function of the intrinsic activity and the degree of physical interaction. They found with the in-situ samples combustion temperatures similar to the combustion temperatures of the loose contact samples and concluded that the contact that arises during practical conditions is similar to loose contact. This is of course unfortunate. Various reasons exist why tight contact mixtures are more reactive: (1) the catalyst will have more contact points with the soot; (2) the catalyst particles will be smaller and better dispersed; and (3) Mul et al. [97] found that the type of contact controls the mechanism that is occurring: they found for V_2O_5 and MoO_3 that a redox and spillover mechanism occurs simultaneously in tight contact, and discussed that in loose contact only the spillover mechanism occurs. They expected for soot oxidation in a catalytic filter that oxygen spillover would be the predominant mechanism.
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![Graph showing comparison between $T_{\text{max, rate}}$ of the oxidation of soot deposited on different catalyst powders.](image)

Figure 1.24: Comparison between $T_{\text{max, rate}}$ of the oxidation of soot deposited on different catalyst powders. The samples were prepared according to different methods: loose, tight, and in-situ in exhaust gas. After [110].

**Reported catalysts** Watabe [111] was the first to report a catalyst based on a formulation of Cu/K/M/(Cl), where M is V, Mo, or Nb. For years catalysts based on this formulation were investigated extensively [109,110,112–122] because they exhibited high soot oxidation rates at low temperatures. The high activity was related to the mobility and volatility of the active copper chloride component of the catalyst [123]. Unfortunately, catalyst compounds evaporated during soot oxidation [112,119], because of which the catalyst should be kept below 350°C at all times [119], which makes the feasibility of the catalyst questionable [112].

Various alternatives for the Cu/K/M/(Cl) catalyst have been investigated. What they have in common is that the mobility of the catalytic phase played a major part in the oxidation mechanism. This mobility probably explains why the stability of some of the reported catalysts was low. Querini et al. [124] stated that the high activity of Co/MgO and Co/K/MgO could be caused by enhanced catalyst mobility caused by potassium. Badini et al. [120,125] reported that KCl-KVO$_3$ and KI-KVO$_3$ are active catalysts, but they also reported the emission of volatile components of the catalyst.

**Simultaneous NO$_x$ and soot reduction** Teraoka et al. [126,127] investigated several interesting mixed metal oxides consisting of mixtures of La, Sr, K, Co, Li, Cs, Fe, Mn, Cu, and V for the simultaneous reduction of soot and NO$_x$ (NO$_x$ conversions into N$_2$ as high as 60%). Unfortunately, high N$_2$O yields were possible, which is undesirable because N$_2$O is a strong greenhouse gas [20].
Bench marking  Table 1.10 ranks the performance of several catalysts by their \( T_{\text{max. rate}} \).

Table 1.10: List of experimental conditions and results for different soot oxidation catalysts reported by different authors.

<table>
<thead>
<tr>
<th>Catalytic phase</th>
<th>( T_{\text{max. rate}} ) °C</th>
<th>TPO method</th>
<th>Heating rate °C/min</th>
<th>Sample mixing</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Nb/K(Cl)</td>
<td>300</td>
<td>TGA/DSC</td>
<td>5</td>
<td>ball mill</td>
<td>[128]</td>
</tr>
<tr>
<td>Cu/K/V(Cl)</td>
<td>330</td>
<td>TGA/DSC</td>
<td>1-50</td>
<td>mortar</td>
<td>[115,116]</td>
</tr>
<tr>
<td>Co/K/MgO</td>
<td>340</td>
<td>flow reactor</td>
<td>12</td>
<td>mech. mixed</td>
<td>[124]</td>
</tr>
<tr>
<td>Cu/K/V(Cl)</td>
<td>350</td>
<td>flow reactor</td>
<td>10</td>
<td>mortar</td>
<td>[120]</td>
</tr>
<tr>
<td>Na/CuO</td>
<td>360</td>
<td>TGA/DSC</td>
<td>5</td>
<td>ball mill</td>
<td>[129]</td>
</tr>
<tr>
<td>Cu/K/Mo(Cl)</td>
<td>369</td>
<td>TGA/DSC</td>
<td>10</td>
<td>ball mill</td>
<td>[110,114]</td>
</tr>
<tr>
<td>KI-KVO3</td>
<td>385</td>
<td>flow reactor</td>
<td>10</td>
<td>mortar</td>
<td>[125]</td>
</tr>
<tr>
<td>CuFeO₂</td>
<td>390</td>
<td>flow reactor</td>
<td>1</td>
<td>mortar</td>
<td>[126]</td>
</tr>
<tr>
<td>Cu/K/Mo(Cl)</td>
<td>428</td>
<td>TGA/DSC</td>
<td>10</td>
<td>in-situ</td>
<td>[110,114]</td>
</tr>
<tr>
<td>Cu/K/Mo(Cl)</td>
<td>464</td>
<td>TGA/DSC</td>
<td>10</td>
<td>spatula</td>
<td>[110,114]</td>
</tr>
<tr>
<td>KI-KVO3</td>
<td>585</td>
<td>flow reactor</td>
<td>10</td>
<td>shaking</td>
<td>[125]</td>
</tr>
</tbody>
</table>

The order of \( T_{\text{max. rate}} \) in Table 1.10 is no true bench mark for the performance of the catalysts, because of the different experimental procedures applied. In general, for the loose contact samples prepared with a spatula a high \( T_{\text{max. rate}} \) was found, while for tight-contact samples prepared with ball mills and mortars a low \( T_{\text{max. rate}} \) was found. It should be noted that the performance of samples prepared with tight contact is easily overestimated, since a tight contact starting situation will not occur under practical conditions. Some of the catalysts might be applicable for passive regeneration for some heavy-duty engines, but commercial applications have yet not evolved from this type of catalysts.

1.5.3 Catalyst selectivity

The selectivity of oxidation catalysts applied in diesel exhaust gas is a critical parameter. The preferred reaction products are \( \text{N}_2 \), \( \text{CO}_2 \), and \( \text{H}_2\text{O} \).

Substrate selection selectivity  Diesel oxidation catalysts should oxidize soot, hydrocarbons and \( \text{CO} \), but not \( \text{SO}_2 \). When the latter is converted, reaction with water occurs and sulfuric acid is formed, which adds up to the total particulate mass. For the \( \text{NO}_x \)-aided continuously regenerated trap (CRT), sulfuric acid formation is so critical that it until now slowed down the market introduction of the system (Section 1.7.2). Figure 1.25 shows the emitted total particulate mass as a function of the fuel sulfur level of an engine running with and without \( \text{NO}_x \)-aided CRT. The increase in total particulate mass at higher sulfur levels can be attributed to an increase of the sulfate fraction [130].
Product selectivity

\( \text{N}_2\text{O} \) Shangguan et al. [126] reported that \( \text{CuFe}_2\text{O}_4 \) could be a promising catalyst for the simultaneous removal of soot and \( \text{NO}_x \). They found a reduction in \( \text{NO}_x \), but besides \( \text{N}_2 \) also a conceivable amount of the greenhouse gas \( \text{N}_2\text{O} \) was formed, which is undesirable. \( \text{N}_2\text{O} \) formation has also been reported for plasma reactors (Section 1.4.2.)

\( \text{NO}_2 \) \( \text{NO}_x \)-aided CRT uses \( \text{NO}_2 \) for soot oxidation, without producing additional \( \text{NO}_x \). Thermal and nonthermal plasma reactors can also produce \( \text{NO}_2 \) for soot combustion. In some cases, however, they cause a net \( \text{NO}_x \) production (Section 1.4.2), which is, of course, highly undesirable.

dioxins and dibenzofurans Municipal incinerators and traffic are the main sources of the highly toxic dibenzodioxins and dibenzofurans. In traffic heavy-duty diesel engines have a high share, they contribute 20 times more than passenger cars [131]. The formation of dibenzodioxins is a three-step process [132]. Firstly \( \text{Cl}_2 \) is formed from \( \text{HCl} \) and \( \text{O}_2 \), secondly chlorinated aromatics are formed as a result of substitution reactions with \( \text{Cl}_2 \), and thirdly dioxins are formed due to the condensation of chlorophenols, as shown in Figure 1.26. The presence of \( \text{Cu(II)} \) is highly undesirable because it enhances the condensation reaction [132, 133]. Neeb [134, 135] and Clunies-Ross et al. [136] investigated the effect of copper fuel additives on the composition of diesel exhaust gases. Both discovered a significant increase in the dioxin levels when the copper additive was applied. Neeb compared copper with iron and cerium fuel additives. He found concentration increases by four orders of magnitude in dibenzodioxins and dibenzo furans when the copper additive was applied, while iron and cerium additives had no effect.
hydrocarbons Flow-through diesel oxidation catalysts (Section 1.7.1) have been reported to increase the mutagenic activity of a fraction of the hydrocarbons that are only partially oxidized [137]. Fortunately, the relative increase reported was offset by the absolute reduction in the hydrocarbon concentration.

1.5.4 Durability of the catalytic trap

Legislation demands a minimal distance in which a vehicle should fulfill the emission standards. For instance, the EPA Tier 2 standard demands that passenger cars and light-duty trucks meet the emission standards for 193,000 km [27]. Such a lifetime will not be adequate for a passenger car's filter trap system because an over-aged filter system might influence the safety and overall performance of the car. Depending on the anticipated vehicle life 300,000 to 400,000 km seems more adequate. In a few year's time heavy-duty diesel vehicles emission control devices in the EU and the US should have durabilities of 500,000 and 700,000 km, respectively [138]. Durability is so important that one failure can deter all producers from pursuing a certain route to a solution, as occurred after the introduction of a filter system in 1985 to the Californian market that led to failure. To enhance the temperature for soot oxidation, the filter was placed in front of the turbo-charger, but the system failed because ceramic filter flakes destroyed the turbo-charger's radial turbine [139]. This failure is one of the main reasons why the placement of a filter upstream of the turbocharger is not favored nowadays.

There are basically two types of failures in relation to the durability of the catalytic trap: fouling due to solid deposits, and filter breakage.

Mechanical damage

In time a filter can deteriorate, which may result in emission of particulate matter. Vehicle vibrations in combination with poorly canned filters, mounting pressures that are too high, and temperature influences can all lead to deterioration. The first two processes relate to mechanical stress, and the third to thermal stress.

Mechanical stress Vibrations are caused by road shocks and the internal frequency of the engine. Problems deriving from vibrations were overcome by canning with intumescent fiber mats. The mat is stuffed between the ceramic filter and the can, where it compensates for the
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thermal expansion coefficient differences, which can be as high as 10. A popular mat is based on vermiculite \((M_{53}(Al, Si)_2O_{10}(OH)_2 \cdot (H_2O)_4)\) with alumina silicate fibers: vermiculite has a thermal expansion coefficient higher than that of metal and ceramics, the alumina silicate fibers provide high-temperature resistance and they contain the vermiculite \([140, 141]\). The canning of ceramic filters should be well controlled, since pressures up to 1200 kPa can occur \([141]\). Canning failures occur less frequently than failures during regeneration \([140]\), and are generally caused by improper alignment of the filter prior to can closure, nonuniform mat, inadequate dimensional tolerances, unoptimized mat properties, and high closure rates, leading to localized damage, such as shear failure, as shown in Figure 1.27.

![Facial crack due to tangential thermal stress](image)

![Ring-off crack due to axial thermal stress](image)

Figure 1.27: Scheme of different types of cracks in a cylindrical filter due to mechanical or thermal stress.

![Shear failure arising during canning](image)

**Determining mechanical strength**  A simple test for the determination of the mechanical strength of a filter is the crush test performed with a compression bench, which measures the uniaxial compressive strength. The test is well suited for testing relative differences, but in the case of a cylindrical filter it does not simulate the radial force exerted by the intumescent mat. To measure the radial compressive strength Gulati and Reddy developed the single \([142]\) and double-band \([143]\) fixture test. These tests use a draw bench and a special tourniquet in which the cylindrical filter is wrapped, as shown in Figure 1.28 for the double-band fixture test. A more realistic but rather arbitrary test is the hot vibration test \([144, 145]\) that exposes the filter to high temperatures and vibrations (Figure 1.29).

**Thermal stress**  High temperatures can cause melting of a filter, thermal stress can break filters instantly or decrease their strength by introducing microcracks. In particular high temperature-gradients are damaging. The most severe temperature-gradients are encountered during uncontrolled regeneration. The worst type of uncontrolled regeneration occurs when a car with a highly loaded filter goes up a slope under a high engine-load and then goes into idle \([146]\). When idling, the high oxygen concentration level promotes the reaction of the hot particulate matter, and the lack of adequate flow prevents the combustion heat from being removed from the filter by convective processes \([147]\). Essentially, optimal conditions are created for a serious thermal runaway.
Material properties The thermal properties of a filter should be optimal if high temperatures are to be attenuated. The key thermal properties are: the thermal expansion coefficient ($\alpha$), the specific heat ($C_p$), the thermal conductivity ($\kappa$), and the melting point ($T_{mp}$). Table 1.11 shows the thermal properties of cordierite; silicon carbide; stainless steel AISI 409, which is commonly used for producing cans [141]; and 3M Interam 100, a popular canning mat.

Table 1.11: Structural formulas and properties of cordierite, silicon carbide, stainless steel AISI 409, and 3M Interam 100 vermiculite canning mat [61, 141, 148, 149].

<table>
<thead>
<tr>
<th>material</th>
<th>chemical formula</th>
<th>$T_{mp}$ °C</th>
<th>$C_p$ J/g°C</th>
<th>$\alpha$ μm/m°C</th>
<th>$\kappa$ W/m°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cordierite</td>
<td>2MgO·2Al$_2$O$_3$·5SiO$_2$</td>
<td>1200</td>
<td>0.6</td>
<td>1.0</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>silicon carbide</td>
<td>SiC</td>
<td>1650 (dec)</td>
<td>0.75</td>
<td>4.6</td>
<td>11</td>
</tr>
<tr>
<td>stainless steel</td>
<td>86%Fe 11%Cr (+additives)</td>
<td>1468</td>
<td>0.46</td>
<td>11.7</td>
<td>25</td>
</tr>
<tr>
<td>canning mat</td>
<td>Mg$_3$(Al, Si)$<em>4$O$</em>{10}$(OH)$_2$·(H$_2$O)$_4$ 950 (erosion)</td>
<td>950</td>
<td>1.02</td>
<td>450</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$·SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\alpha$, thermal expansion coefficient; $C$, heat capacity; $\kappa$, thermal conductivity; $T_{mp}$, melting point; dec, decomposition.

Ceramic particle filters are mainly fabricated from cordierite and silicon carbide. Their physical characteristics are very different, which makes them behave differently under demanding conditions. The cordierite crystal has anisotropic expansion behavior $^3$ [150], as shown in Figure 1.30 a. Microcracks caused by local expansion mismatches are avoided by aligning the cordierite crystals during the extrusion of the monolith [150]. Although local

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$^3$Anisotropic, having properties which vary according to the direction which they are measured [13].
1.5. CATALYTIC DIESEL SOOT OXIDATION

stress is avoided, the crystal alignment makes the complete monolith itself expand anisotropically, as shown in Figure 1.30 b, which can lead to high thermal stress [62]. Besides the anisotropic expansion behavior, cordierite cannot attenuate high, local temperatures quickly as it has a low thermal conductivity. It is not surprising that cordierite filters can break easily under certain regeneration conditions [44]. Stroom [140] showed that for homogeneous cordierite filters, axial and radial temperature-gradients lead to axial and tangential stress, which, respectively cause, ring-off and facial cracks, as seen in Figure 1.27. The melting point of 1200°C is on the low side, since such temperatures can be encountered during regeneration [44]. It has been reported that silicon carbide has better thermal properties for regeneration: it has (1) a low thermal expansion coefficient, reducing thermal stress; (2) a high decomposition temperature, giving it a large operating window; (3) a high specific heat, allowing storage of released heat; and (4) a high thermal conductivity, leading to efficient heat distribution. Gantawar et al. [61] and Høv et al. [152] confirmed that during extreme regenerations silicon carbide has better thermal properties. Under similar regeneration conditions, in cordierite wall-flow monoliths maximum temperatures of 1100°C occurred, while for silicon carbide the temperatures did not exceed 700°C. However, the regeneration efficiency of the silicon carbide filter was lower due to the lower maximum temperatures. Ohno et al. [146] measured the tolerance of cordierite and SiC wall-flow monoliths as a function of soot load and gas velocity during uncontrolled regeneration. Figure 1.31 shows their results. For the cordierite wall-flow monolith the soot loading should not exceed 3 to 5 g/lfilter, SiC can tolerate soot loadings that are three times higher.

**Homogeneity** Table 1.12 shows the results of various studies of the effects of inhomogeneities in filters on thermal-mechanical properties. Scardi et al. [153] reported that the
Figure 1.31: Tolerance of cordierite and SiC filters expressed in soot loading as a function of gas velocity. Regeneration conditions: no catalyst, 21 vol % O₂, and start regeneration at 720°C. After [146].

strength of cordierite monoliths with inhomogeneous composition decreased even after homogeneous heating. The inhomogeneous composition led to a mismatch of the thermal expansion coefficients of the present phases, which gave rise to local mechanical stress. Lucchini and Maschio [154] investigated the effect of repeated heating and quenching on cordierite and found that a glass phase was formed which caused cracks. The other authors mentioned in Table 1.12 investigated the effects of ash contaminants on the thermal-mechanical properties. For instance, Dario and Bachiorrini [155] investigated the effect of V₂O₅ and Na₂O on silicon carbide and found that sodium silicates were formed at temperatures as low as 550°C, and that SiO₂ was formed above 750°C. They concluded that silicon carbide had insufficient thermal and chemical resistance for diesel applications. This conclusion may be true in the case of large engines running on heavy fuel oil which contains high vanadium and sodium concentrations (Table 1.2), but silicon carbide filters implemented in light-duty applications will probably have no problems with filter deterioration caused by ash, since these engines use relatively clean fuel.

Fouling

Filter surfaces might be plugged by particulate matter, because of which the pressure drop over the filter will increase, the fuel efficiency will decrease, and ultimately the engine will stop.

Inorganic ashes  Inorganic ashes originate from engine wear, fuel, and lubricating oil components. From Table 1.2 in Section 1.2.2 it can be calculated that in the case of a MW-engine running on heavy-fuel oil, 2.5 kg/day of sodium and vanadium can pass through the exhaust pipe. Fuel additives are also a source of inorganic ash deposition. Current state-of-the-art catalytic fuel additive based systems for passenger cars have to free their filter every
Table 1.12: List of diesel exhaust filter related studies on the effect of contamination on thermal-mechanical properties. In the studies contaminations were deliberately introduced, temperature treatment was given, and the effects were studied.

<table>
<thead>
<tr>
<th>geometry</th>
<th>ceramic</th>
<th>treatment</th>
<th>contamination</th>
<th>phase formed</th>
<th>effect</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>monolith</td>
<td>cordierite</td>
<td>isothermal</td>
<td>Fe₂O₃</td>
<td>(Mg, Fe)₂Al₃Si₂O₁₈</td>
<td>cracks</td>
<td>[153]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>high</td>
<td>ZnO</td>
<td>ZnAl₂O₄, Zn₂SiO₄</td>
<td>glass</td>
<td>[154]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>temperature</td>
<td>V₂O₅</td>
<td>MgV₂O₆, Al₂V₂O₄, SiO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>monolith</td>
<td>cordierite</td>
<td>heating &amp;</td>
<td>none</td>
<td>glass</td>
<td>cracks</td>
<td>[156]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>quenching</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>monolith</td>
<td>cordierite</td>
<td>isothermal</td>
<td>CaO</td>
<td>Ca₂(Al, Mg)(Si)SiO₄</td>
<td>cracks</td>
<td>[155]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>high temp.</td>
<td>ZnO</td>
<td>ZnAl₂O₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>powder</td>
<td>SiC</td>
<td>heating &amp;</td>
<td>Na₂O</td>
<td>Na₂Si₂O₅, Na₂SiO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>quenching</td>
<td>PbO</td>
<td>Pb₂SiO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>V₂O₅</td>
<td>SiO₂</td>
<td></td>
<td>[157]</td>
</tr>
<tr>
<td>powder</td>
<td>cordierite</td>
<td>cyclic heating</td>
<td>Na₂O</td>
<td>amorphous phase</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

80,000 km from cerium deposits. This can be done by flushing them out with high-pressure water and air jets [60]. In the case of copper additives flushing might not be possible, since copper additive deposits have been reported to have a sticky nature [45].

Catalyst deactivation Several mechanisms can lead to catalyst deactivation in catalytic particle traps. There are three variations: a chemical change which leads to a less active phase, a physical change which leads to a less active phase, and catalyst loss.

Poisoning A poison may adsorb on the catalyst sites, thereby inhibiting the reaction. An example of precious metal inhibition in diesel oxidation catalysis is the platinum catalyst in the NOₓ-aided CRT system (Section 1.7.2), where the catalytic NO oxidation is inhibited by SO₂ [9]. Figure 1.32 gives the balance temperature of NOₓ-aided CRT as a function of the fuel sulfur level [130]. It is clear that sulfur is inhibiting the system. The effect was reversible: the catalyst recovered when the fuel was switched to low sulfur fuel again. With metal oxides the sulfur may be incorporated in the catalyst, which in general is irreversible [158]. Van Doorn et al. [11] reported an example of metal oxide deactivation: vanadium oxide reacted with SO₂ to the less active vanadium sulfate. However, the opposite can occur when vanadium oxide is converted to vanadium pyrosulfate, which is a more active compound due to its high mobility [159].

Catalyst-support interaction The catalyst might react with the support material, which will lead to a change in the composition of the catalyst. If this change leads to reduced combustion activity one could view the support as a poison to the catalyst. McKee [160] reported that by forming an alloy alumina can inhibit the catalytic action of copper during graphite oxidation. When a catalytic filter is designed a negative catalyst-support interaction can be predicted by examining phase diagrams.
Catalyst loss  There are three ways for catalyst loss. It can disappear along with the support when support pieces break off from the filter. If the catalyst can dissolve in water it might, in the case of water condensation, leave the exhaust pipe with water droplets. If high temperatures are attained the catalyst might evaporate and leave the catalytic trap. In studies of the very active Cu/K/Mo/(Cl) [112], Cu/K/V/(Cl) [119] and KI-KVO₃ [125] catalysts progressive loss of catalyst components was found due to evaporation which makes the applicability questionable.

Sintering  Sintering is not detrimental for catalytic fuel additives because the catalyst is constantly replenished. NOₓ-aided CRT is a continuous process in which extremely high temperatures do not occur, and ashes, some components of which might be good sintering aids, mainly deposit in the filter downstream of the catalyst.

Stability testing  Long-term on-road tests are the most realistic way of testing the stability of a filter system, but such tests are expensive, hard to interpret, and cost much time. In the early developmental stages accelerated tests under simulated conditions are often used. Such tests could help failure to be avoided in later stages. Table 1.13 summarizes some aging tests where model conditions were used to simulate aging in diesel exhaust.

Overview  Durability studies are complex because of the many processes that can lead to failure. To complicate matter, the different processes can interconnect. For instance, ashes can simultaneously: plug a filter, react with the catalyst to form a new phase, react with the support to form a new phase, catalyze phase transitions, and even catalyze soot oxidation. Figure 1.33 shows an overview of the different processes than can affect the durability of a catalytic filter.
1.5. CATALYTIC DIESEL SOOT OXIDATION

Table 1.13: Laboratory scale aging tests.

<table>
<thead>
<tr>
<th>test</th>
<th>sample</th>
<th>gas</th>
<th>t</th>
<th>$T (^{\circ}C)$</th>
<th>analysis</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>catalyst</td>
<td>100 ppm SO$_2$</td>
<td>6-20h</td>
<td>350-650</td>
<td>TPO</td>
<td>[11]</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>catalyst</td>
<td>200 ppm SO$_2$, or steam</td>
<td>24-96h</td>
<td>380-600</td>
<td>TPO, XRD</td>
<td>[120]</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>catalyst</td>
<td>1000 ppm SO$_2$</td>
<td>8h</td>
<td>300</td>
<td>TPO</td>
<td>[159]</td>
</tr>
<tr>
<td>TS</td>
<td>catalyst</td>
<td>–</td>
<td>3h-15d</td>
<td>400-1000</td>
<td>TPO, XRD</td>
<td>[119]</td>
</tr>
<tr>
<td>TS</td>
<td>monolith</td>
<td>–</td>
<td>3h</td>
<td>800-1200</td>
<td>SEM, XRD</td>
<td>[153]</td>
</tr>
<tr>
<td>TS</td>
<td>monolith</td>
<td>–</td>
<td>3h</td>
<td>800-1200</td>
<td>SEM, XRD, DRM, DM, FT</td>
<td>[156]</td>
</tr>
<tr>
<td>TS</td>
<td>catalyst</td>
<td>–</td>
<td>3h-1y</td>
<td>500-1000</td>
<td>FTIR</td>
<td>[157]</td>
</tr>
<tr>
<td>TSR</td>
<td>monolith</td>
<td>–</td>
<td>60sh</td>
<td>600-900 $\Delta T$</td>
<td>XRD, DM, FT, SEM, MP</td>
<td>[154]</td>
</tr>
<tr>
<td>TSR</td>
<td>monolith</td>
<td>–</td>
<td>100sh</td>
<td>600$\Delta T$</td>
<td>RST</td>
<td>[161]</td>
</tr>
</tbody>
</table>

TS, thermal stability test; TSR, thermal shock resistance test; DRM, digital resonance method; RST, rupture strength test; FT, flexure test; DM, dilatometry; MP, mercury porosimetry; sh, thermal shock.

Figure 1.33: Overview of the processes that can affect the durability of a catalytic trap.
1.6 Diesel particle traps

There are many possible ways of removing particles from a gas stream. Regarding the diesel particle trap application certain minimum conditions need to be fulfilled. With current passenger cars the trapping efficiency for the total particulate mass should be at least 90% in order to meet the Euro IV standards (Figure 1.8). Particle number filtration efficiencies should be 99% for a filter in order to compete with state-of-the-art wall-flow monoliths. The average pressure drop should be low to attain a maximum fuel efficiency. For large electricity generators a maximum average pressure drop of 50 mbar is permitted [162]. With passenger cars a higher average pressure drop might be allowed because customers often consider speed, size, gadgets, and price to be more important. The filter capacity should be sufficient. In a recent application 500 km was stipulated for passenger cars [163]. The filter should be durable and suitable for reliable regeneration. The filter volume should be low. One to two times the engine displacement is usually considered acceptable [164]. The production costs should be reasonable. The filter should require no special attention from the driver of the vehicle [45], and should need no maintenance [18].

1.6.1 Filtration

Surface filtration

The most popular way to trap diesel particles is by means of surface filtration, sometimes known as cake filtration, or sieving. In this process the particles flow through a porous support and are captured to form a layer: the filter cake, which is itself an efficient filter medium, especially for the particles it is composed of. During the process, the thickness of the cake increases continuously, which results in flow restrictions, and increasing pressure drop. In practice, the flow usually abides by Darcy’s law:

\[ v_s = \frac{-1}{\eta} k \delta p \]  

(1.16)

where \( v_s \) is the superficial velocity, \( \delta p \) the pressure drop over the cake, \( \eta \) the viscosity of the gas, and \( k \) the permeability of the cake. Figure 1.34 gives a schematic representation of cake filtration. In commercial applications surface filters of the wall-flow monolith type, originally introduced by Howitt and Montierth [165], are commonly found. They are extruded, ceramic, porous honeycomb structures which have alternately blocked channel openings, as shown in Figure 1.35. The obvious advantage of this structure is the large filter-surface to volume ratio. According to Opir and Johnson [166] the wall-flow monolith filter only acts as cake filter after some initial particle deposition in the pores of the monolith walls. When a steady-state particle loading in the walls has been established a cake layer is formed which becomes the dominant filtration medium. The mechanism gives rise to a high filtration efficiency, which has been reported to be > 90% for total particulate mass, > 97% for elementary carbon, and > 99% for 20 to 500 nm particles [37].
Figure 1.34: Illustration of the flow pattern in a surface filter. The arrows indicate the stream direction of the exhaust gas. The circles represent soot particles which form a cake on the filter surface.

Figure 1.35: Illustration of flow pattern in a wall-flow monolith. The arrows indicate exhaust gas with particles, the grey arrows indicate filtered exhaust gas. Courtesy of Corning.
Deep-bed filtration

It is possible to design filters that have a relatively open structure compared to surface filters. In such filters particulate matter is found throughout the filter structure and not just on one side of the filter surface, as with surface filters. This technology is called *deep-bed filtration*. Particles may deposit in one of three different ways [167], see Figure 1.36:

**inertial interception** On approaching a collecting body a particle carried along a gas stream tends to follow the streamline but it may well strike an obstruction because of its inertia.

**Brownian diffusion** Smaller particles, particularly, those typically below 300 nm, exhibit considerable Brownian movement and do not move uniformly along the gas streamline. These particles diffuse from the gas to the surface of the collecting body and may be collected.

**flow-line interception** If a fluid streamline passes within one particle radius of the collecting body, a particle traveling along a gas streamline will touch the body and may be collected without being influenced by inertia or Brownian diffusion.

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Figure 1.36: Schematic overview of particle deposition mechanisms on collecting bodies. After [167].
1.6. DIESEL PARTICLE TRAPS

Ceramic foams and woven ceramic fibers are often mentioned as diesel particle deep-bed filters. Ceramic foams are positive images of sponges [168] that operate according to the deep-bed filtration mechanism [108,169,170]. Ceramic foams do not qualify as 'absolute' filters, since their filtration efficiency depends on the exhaust gas velocity [171], filter length [172], pore size [171-173], and filter surface roughness [174]. In contrast, when selecting a wall-flow monolith, only its dimensions needs to be considered in design studies. Table 1.14 lists the performance of deep-bed filters revealed in different studies.

Table 1.14: List of diesel engine tests conducted on ceramic foam and fiber filters.

<table>
<thead>
<tr>
<th>filter</th>
<th>pore size</th>
<th>ηf</th>
<th>dp</th>
<th>Vfilter</th>
<th>engine</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>foam</td>
<td>26</td>
<td>71-74</td>
<td>140</td>
<td>n.r.</td>
<td>2.3</td>
<td>[62]</td>
</tr>
<tr>
<td>foam</td>
<td>25-32</td>
<td>40-78</td>
<td>40-110</td>
<td>7</td>
<td>n.r.</td>
<td>[170]</td>
</tr>
<tr>
<td>foam</td>
<td>28</td>
<td>43-82</td>
<td>0-250</td>
<td>2.5</td>
<td>1.6</td>
<td>[171]</td>
</tr>
<tr>
<td>foam</td>
<td>24-39</td>
<td>48-78</td>
<td>90-390</td>
<td>0.5-1.5</td>
<td>4.3</td>
<td>[172]</td>
</tr>
<tr>
<td>foam</td>
<td>16-31</td>
<td>70-75</td>
<td>50-450</td>
<td>n.r.</td>
<td>14.6</td>
<td>[173]</td>
</tr>
<tr>
<td>foam</td>
<td>8-9</td>
<td>35-60</td>
<td>25-40</td>
<td>3.4</td>
<td>2.2</td>
<td>[175]</td>
</tr>
<tr>
<td>fiber</td>
<td></td>
<td>95-99</td>
<td>0-100</td>
<td>20</td>
<td>n.r.</td>
<td>[45]</td>
</tr>
<tr>
<td>fiber</td>
<td></td>
<td>75-99</td>
<td>0-100</td>
<td>n.r.</td>
<td>12</td>
<td>[101]</td>
</tr>
</tbody>
</table>

ηf, filtration efficiency; dp, pressure drop over filter; Vfilter, filter volume; engine, engine displacement; n.r., not reported

The reported efficiencies of the foam filters are reasonable, especially when one considers that more or less standard foam materials were used, made by producers for quite a different application, i.e. molten metal filtration. Higher filtration efficiencies might be expected for tailor-made foams.

The ceramic fiber filter consists of a number of perforated cylindrical metal tubes with ceramic fiber threads (SiO₂ or SiO₂-Al₂O₃) woven in a diamond pattern, as shown in Figure 1.37. The tubes are placed in a container and exhaust gas flows to the outside of the filter tubes and passes through the fibers to the inside. Because of its shape the filter is also known as a candle filter. The main advantage of fiber filters is that they have good filtration efficiencies at low pressure drops, as is shown in Table 1.14. The range of 75 to 99% efficiency is caused by the filtration mechanism. Initially the efficiency is relatively low, but during particle deposition it increases to 99% [101].

**High-temperature resistance of different filter geometries**

During operation the particles are deposited in a tubular formation in the inlet channels of the wall-flow monolith. The tubular deposits are isolated from each other by the filter walls and the air space in the surrounding outlet channels. During self-supporting regeneration the
deposits burn like an array of parallel, independent "wicks" going from the inlet to the outlet [62], as shown in Figure 1.38, which can lead to locally high temperatures, and thermal stress. Foams and other deep-bed filters have three-dimensional connected structures resulting in better transport of heat and particles through the filter than through the wall-flow monolith. During regeneration this leads to nearly isotropic propagation of the combustion front [62] which in turn results in lower temperatures, and less thermal stress. Table 1.15 shows the ignition temperatures and the maximum temperatures which were found during soot combustion in a wall-flow monolith and a foam filter. Maximum temperature differences of 300°C were observed between the two filter types.

Table 1.15: The ignition temperatures and maximum temperatures which were found during soot combustion in a cordierite wall-flow monolith and a foam filter [62, 171].

<table>
<thead>
<tr>
<th>Filter</th>
<th>$T_{\text{ign.}}$</th>
<th>$T_{\text{max.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>monolith</td>
<td>495°C</td>
<td>900-1000°C</td>
</tr>
<tr>
<td>foam</td>
<td>440°C</td>
<td>640-740°C</td>
</tr>
</tbody>
</table>

$T_{\text{ign.}},$ ignition temperature; $T_{\text{max.}},$ maximum temperature during regeneration.

The structure of ceramic fiber filters is optimal for high temperatures [58]. Fiber filters consist of many independent fibers that are not cross-linked, which makes the total structure

---

4The definition of isotropic is having the same properties along all axes [13].
1.6. DIESEL PARTICLE TRAPS

less stiff than the monolith and ceramic foam. If the fibers are bonded to each other, the structure becomes more brittle, and can be damaged by thermal and mechanical stress [45].

Compatibility between filters and regeneration strategies

An important difference between deep-bed filters and the wall-flow monolith surface filter is that the latter has closed ends which causes that the exhaust gas must pass via the soot cake through the filter surface, while the former is 'open' which gives the exhaust gas a free pathway. These differences may give rise to different problems if certain regeneration strategies are applied on the two filter types. For instance, the wall-flow monolith may be less suited as catalyst support; the catalytic coating might obstruct the exhaust gas flow to some degree, and in the case of NO\textsubscript{x}-aided regeneration strategies the Pt catalyst should be located upstream of the filter and not in the filter, as illustrated in Figure 1.39.

Figure 1.39: Formation of NO\textsubscript{2} in a catalytic particle trap: a, NO\textsubscript{2} formation in filter surface; b, NO\textsubscript{2} formation upstream of filter surface.

The US 'Diesel Emission Control Sulfur Effects' Program (DECSE) [130] compared NO\textsubscript{x} aided CRT (catalyst upstream of filter) with a precious metal coated wall-flow monolith (catalyst within filter). Pressure drops, balance temperatures, and CO and hydrocarbon emissions were examined. The 'clean' pressure drops (i.e. no particulate matter present) of the filters were similar; apparently, the precious metal coated wall-flow monolith was not obstructed by the catalyst (the catalyst layer was probably very thin). The balance temperature of the precious metal coated filter was 50 to 70°C higher, which is probably caused by the unoptimized location of the catalyst, as illustrated in Figure 1.39 a, or by the thin catalyst layer (i.e. low catalyst loading).

An oxidation catalyst deposited on a ceramic foam filter would probably hardly affect the pressure drop for such a filter. It is even conceivable that NO\textsubscript{x}-aided CRT would utilize the precious metal catalyst more efficiently when deposited in the foam, because each NO molecule could then undergo multiple NO:NO\textsubscript{2} combustion cycles, as illustrated in Figure 1.40, and, therefore, less precious metal would be needed, or the catalytic filter could be used for engines with less favorable NO\textsubscript{x}:soot ratios.
The very open structure of the ceramic foam filter may make it less suitable for periodical regeneration strategies, because trapped particulate matter (with fuel additive ash) may reentrain into the exhaust gas. For instance, it has been reported that particulate matter can easily be blown-off from foam filters by sudden exhaust-gas speed changes [171].

The fiber filter might not be suited for every continuous regeneration strategy, because it only filters efficiently after some initial particle deposition [45]. If continuous regeneration causes a deposition-oxidation equilibrium at a low particle equilibrium-loading in the filter, then a low filtration efficiency might be the result.

1.6.2 Trapping by means other than filtration

Although most research and applications for particle trapping have concentrated on filtration, there are other ways for separating particles from exhaust gas. In general, the advantage of these methods is that they not only separate the particles from the gas stream, but also transport them away from the gas stream, which causes that not pressure buildup problem can develop. Figure 1.41 shows schematic structures of different traps. Ludecke and Dimick [176] evaluated some of them. In all cases they seemed not applicable for diesel particulate abatement. They found that the gas cyclone required too high gas velocities or volume, the electrostatic precipitator was unreliable and inefficient, and water scrubbers and oil baths were impractical and inefficient.

Despite the problems alternative methods are still being developed. For instance, van Hardeveld et al. [179] reported a turbulent flow precipitator with an oxidation catalyst for soot oxidation that is based on the turbulent flow precipitator developed by Dullien [177]. The precipitator creates stagnant, turbulence-free regions where the particles enter and settle. Maganas and Harrington [178] reported a fluidized bed trap of silica or alumina particles for diesel particulate abatement. At temperatures of 300 to 375°C they removed 98% of the particles from a heavy-duty truck engine with a reactor that contained 775 (!) kg silica particles. It remains to be seen if this type of devices is viable for automotive applications, but they may show some promise for applications which have less stringent size restrictions, like ships and stationary engines.
Figure 1.41: Different particle traps based on trapping mechanisms other than filtration. After [167, 176–178].
1.7 Commercial catalytic diesel particle filters

1.7.1 Flow-through oxidation catalysts

When diesel particulate matter became part of environmental awareness, engines were not optimized for clean combustion and, at that time, traps started to be studied extensively. Advances in diesel fuel combustion technology have, however, greatly reduced the total particulate mass, with the result that initially air standards could be satisfied by using an oxidation catalyst deposited on a flow-through monolith [180]. Of course soot particles are not trapped, but the oxidation catalyst converts CO and hydrocarbons (including the ones that form the soluble organic fraction of the total particulate mass) from temperatures of 200°C [180], with less than 5% oxidation of the soot fraction of the particulate matter [181] at gas hourly space velocities of 50,000 to 300,000 l/h [182].

Sulfuric acid formation The flow-through diesel oxidation catalyst is based on platinum, which is an excellent SO₂ oxidation catalyst [180]. At temperatures above 300 to 350°C the catalyst oxidizes SO₂ to SO₃, which quickly combines with water to form sulfuric acid and contributes significantly to the total particulate mass [183]. A good knowledge of the exhaust gas temperatures and particulate matter composition is required if the catalyst is to be tailored to meet specific requirements [180,184]. In practice, this means that if average temperatures are below 250°C a very active catalyst will not be a problem since the SO₂ oxidation rate is low, but if temperatures are often above 300°C a less active catalyst will be required to minimize SO₂ oxidation. Rhodium and palladium are less active oxidation catalysts, and by alloying them with platinum, a tailored catalyst with compromise activity can be made [180]. Base metals were also found to tailor the activity of platinum [181]. In a special case where only the soluble organic fraction of the total particulate matter needed to be lowered to meet the total particulate mass standard a base-metal-only catalyst sufficed [183].

1.7.2 NOₓ-aided CRT

The NOₓ-aided continuously regenerated trap (NOₓ-aided CRT) for trucks and busses, developed by Johnson Matthey, is an ingenious design. It consists of a wall-flow monolith with an upstream flow-through diesel oxidation catalyst, which is called in this context the pre-oxidizer. Figure 1.42 provides a schematic representation of the system. The oxidation catalyst converts 90% of the CO and hydrocarbons present to CO₂, and 20 to 50% of the NO to NO₂ [185]. Downstream the particles are trapped on a cordierite wall-flow monolith and subsequently oxidized by the NO₂.

Modular design The modular design of the separated and detachable pre-oxidizer and filter facilitates a high flexibility of the system, which is a big advantage for retrofitting of different busses and trucks. In each case the optimal trap and pre-oxidizer can be chosen, which can, in many cases, save space, heat loss, back pressure, and system costs.
1.7. COMMERCIAL CATALYTIC DIESEL PARTICLE FILTERS

The filter should produce a surplus of NO$_2$ in order to compensate for time periods where the temperature is too low for regeneration. The surplus NO$_2$ should not be too high because NO$_2$ is foul-smelling in the vicinity of the vehicle, where it has not yet been diluted sufficiently with ambient air. For the environment the NO$_2$ gives no additional problems, since NO reacts to NO$_2$ anyway in short time-scales [185].

Advantages The NO$_x$-aided CRT system is an effective catalytic filter that oxidizes all carbon components in diesel exhaust gas, including small particles, and unregulated compounds [186]; and it reduces the NO$_x$ concentration by 3 to 8% [185]. It is a simple concept that allows for fit-and-forget usage. The temperature window of 200 to 450°C [185] is very reasonable; 200°C is needed for CO and hydrocarbon oxidation [138], while 450°C relates to the chemical equilibrium between NO and NO$_2$ which is not favorable above 450°C [9]. The balance temperature is actually higher than 200°C and depends on the fuel sulfur level, as was shown in Figure 1.32. Because of continuous regeneration extreme temperatures are avoided, which enhances stability: a satisfactory performance during 600,000 km [138] has been reported.

Limitations The system has not yet been introduced on a wide scale, because it requires the use of low-sulfur fuel (< 50 ppm [138]), since SO$_2$ restricts the performance (Section 1.5.4) and when oxidized by the platinum catalyst it adds up significantly to the total particulate mass (Section 1.5.3). Low sulfur fuel can easily be made available to public transport companies, which often have their own diesel depots, but for many other heavy-duty applications that is not practical. In a few years time this will, however, change, when low sulfur fuel becomes widespread in Europe and the US (Section 1.3.2). Problems may arise for international transport companies that operate in countries that will not introduce low-sulfur fuels on the short term. The dependency of NO$_x$ is another problem for the system, because it is uncertain what the NO$_x$ concentration will be in future engines.
1.7.3 The integrated catalytic trap for passenger cars

The issue of regeneration of filters for light-duty vehicles has provided a major challenge. It took two decades to identify the salient problems and to develop the key components that would lead to satisfactory performance. The key components are:

the silicon carbide wall-flow monolith The obvious reason for choosing a wall-flow monolith filter is its high filtration efficiency (Section 1.6.1). Silicon carbide is the preferred construction material for a periodically regenerated filter because of its superior physical properties (Section 1.5.4).

gasoline controlled heating Engine controlled heating is the most practical way of temporarily raising exhaust temperatures (Section 1.4.2). The preferred method is fuel-injection-timing control because it does not affect drivability.

cerium fuel additive Fuel additives are the best choice for ensuring a high regeneration efficiency (Section 1.5.2). Cerium is the preferred fuel additive, because it is sufficiently active for helping self-supporting regeneration reactions with sustaining themselves, while its activity is too low for spontaneously igniting self-supporting regeneration reactions (Section 1.5.2). It is environment-friendly, since it does not catalyze the formation of unwanted toxic by-products (Section 1.5.3).

pre-oxidizer At low engine loads and speeds additional heat to initiate regeneration cannot be produced in the engine without producing extra engine power [60]. In such cases first some additional engine heat is produced to light-off a pre-oxidizer, then the exhaust gas hydrocarbon concentration is raised to produce heat by oxidation in the pre-oxidizer [60]. Figure 1.43 shows the two critical temperature regions for this method.

Peugeot-Citroën will be the first car manufacturer to commercialize the above components for serial production. Figure 1.44 gives a schematic representation of their system. The system is a good example of clever component selection and technology integration. The strongest point of the system is the way in which it integrates two catalyst technologies, because of which several oxidation mechanisms might become available:

- Cerium aided, periodically induced self-supporting regeneration.
- Cerium catalyzed spontaneous, local regeneration reactions at low temperatures, as was reported by Lepperhoff et al. [98].
- Cerium catalyzed continuous soot oxidation at high temperatures, as was reported by Lepperhoff et al. [98] and Jelles et al. [104].
- Cerium catalyzed reduction of black smoke, after some initial cerium deposition in the combustion chamber and exhaust system [187]. Cerium fuel additive reduces the raw particulate emissions by 20% [98].
- Platinum catalyzed oxidation of volatile hydrocarbons and CO.
Figure 1.43: Plot of the critical pre-oxidizer temperatures of engine controlled exhaust heating in combination with catalytic combustion. After [60].

- Platinum catalyzed production of NO₂ at favorable temperatures.
- Platinum and cerium catalyzed synergetic oxidation of soot. The combination of platinum and cerium might lead to a reaction that is analogous to the one reported by Jellis et al. [104] (Figure 1.23).

The system has disadvantages. The trap should be cleaned periodically in connection with cerium deposits [60]. Many components are present: additives, additive storage, additive precision dosing pump, pre-oxidizer, pressure sensors, temperature sensors, common-rail fuel-injection system, and management system, make the system complex and expensive. To give a price indication: a traditional uncanned three-way catalyst, the construction of which is similar to the pre-oxidizer, may cost €40 to €150 [188]. An integrated catalytic trap for passenger cars will cost much more than that.
Figure 1.44: Schematic overview of the catalytic filter system which will be introduced in passenger cars in 2000. Courtesy of PSA Peugeot-Citroën.
1.8 Evaluation

Diesel particulate matter  In view of its complex formation process it is not surprising that many types of diesel particulate matter exist. What all types have in common is that they are suspected to cause respiratory diseases from bronchitis to lung cancer. In many countries legislation has been issued. In the coming years the emission standards for diesel powered vehicles will become so stringent that exhaust aftertreatment will become inevitable, especially for heavy-duty trucks and busses.

Whether the legislation of the last few years pushed emission reduction technology in the right direction is doubtful, because it only demanded, for the sake of simplicity, a decrease in total particulate mass. Recently, it became clear that decreasing the total particulate mass does not guarantee that toxicity will decrease, the opposite might in fact be true. For new legislation purposes the total particle number is currently often mentioned rather than the total particulate mass, but the particle number may also be erroneous. The best way to guarantee that diesel exhaust is safe will be to demand essentially zero particulate emission by using absolute filtration in combination with essentially complete catalytic oxidation of the hydrocarbons in the exhaust gas.

Diesel particulate matter abatement  For several reasons diesel particulate matter abatement poses a real challenge. There are numerous different engines for various applications (kW to MW applications, steady state to transient operations, 'clean' to 'dirty' fuels), which makes it impossible to develop one device that solves all problems. The device adopted should be able to operate under a wide range of conditions during the service life of the vehicle and it should not produce toxic by-products. In a sense removing the particulate matter from diesel exhaust is the easy part. Commercially available filters exist which are capable of filtering out more than 99% of the number of particles and 90% of the total particulate mass. Used in combination with a flow-through diesel oxidation catalyst and low-sulfur fuel the total particulate mass could even be further reduced. However, the necessary regeneration of the filter complicates filter technology. Especially light-duty diesel engines present a challenge, because their exhaust temperature is too low for even catalytic soot oxidation. Additional energy has to be put into the exhaust gas to enhance the oxidation rate. Two energy efficient strategies for regenerating the trap can be envisaged. First, the filter can be substantially loaded with particulate matter and then regeneration can be induced by temporarily raising the temperature to ignite an exothermic regeneration reaction that sustains itself. Engine controlled heating is the most promising method for igniting regeneration. By varying the timing of fuel injection the temperature can be raised without influencing drivability. When ignited the regeneration reaction might smother. To ascertain complete regeneration a catalyst can be applied. Catalytic fuel additives are the most suitable aids, because the rate of exothermic regeneration is high and intimate catalytic contact could be essential for the reaction to sustain itself. Second, additional energy can be introduced in a selective manner by using for instance a plasma or electrochemical reactor. Such reactors should be evaluated with great care, in view of the fact that some of the initial euphoria was based on the misinterpretation of experimental data. Plasmas have been reported to
produce all kinds of compounds besides H$_2$O, CO$_2$, and N$_2$. The possible production of toxic organic molecules should be checked. Significant increases in, for instance, nitro and oxy-PAHs would be most undesirable.

Clean diesel vehicles can become a reality. By integrating existing reduction, oxidation, and filtration techniques a total solution may be provided [189, 190]. Figure 1.45 shows a simplified design of an integrated system for heavy-duty vehicles based on NO$_x$ aided CRT and a DENOX catalyst [190]. Other options for NO$_x$ abatement might be reduction with hydrocarbons, or in the future direct dissociation of NO$_x$.

**Figure 1.45:** Illustration of a combined HC, CO, NO$_x$ and particulate matter abatement system. After [190].

One of the advantages of the diesel engine is its robustness. The application of advanced integrated catalyst technology will significantly increase the complexity of diesel powered vehicles, which might lead to decreased robustness. An alternative and more convenient way to total emission reduction might be the application of a simple aftertreatment device in combination with engine optimization. Optimizing the engine to produce less particulate matter will probably lead to more NO$_x$ because of trade-off effects. It might, however, not solve the particle number problem. Optimizing the engine to produce less NO$_x$ in combination with a catalytic filter might be more logical: the exhaust gas is oxygen rich which means that no additional chemical reactant is required; and filtration will not only solve the total particulate mass but it will also solve the particle number problem. Less NO$_x$ will, however, make filter regeneration more difficult, because NO$_x$ is an essential component for continuous, low-temperature regeneration. Also other trade-off effects might surface. The problem of the low NO$_x$ concentration might be solved by introducing advanced catalytic traps that use NO$_x$ more efficiently. Alternatively a low-temperature catalyst may be developed that does not require NO$_x$. Developing such an advanced catalytic trap will be one of the major challenges of catalytic filter engineering.
Bibliography


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Chapter 2

Experimental

2.1 Introduction

During the Ph.D. study various chemicals and equipment have been used to prepare, characterize, and test catalysts. The chemicals and equipment are described in this chapter. More details of the conduction of preparations and experiments will be given in the appropriate chapters.

2.2 Chemicals

2.2.1 Basic chemicals

Catalyst preparation Various chemicals were used for preparing catalysts. Table 2.1 lists the composition, purity, and suppliers.

Catalyst supports Different ceramic pellets and bricks varying in composition and texture were obtained to test as catalyst support. Table 2.2 lists them with physical characteristics and composition. The characteristics of the supports were measured with the methods as listed in Table 2.6.

2.2.2 Ceramic filters

Foam Three types of ceramic foam were obtained to test as catalyst support. Table 2.3 lists the ceramic foams with physical characteristics and composition. The foams were obtained in large plates. For testing in various equipment foam cylinders of diameter 7 mm, length 25 mm; and diameter 25 mm and length 30 mm were required. These cylinders were prepared by sawing with a cylindrical diamond saw that was cooled with tap water. The foam plates were too brittle for surviving the preparation of the 7 mm cylinders. In order to prepare such cylinders the foams were frozen overnight at -18°C in water, and the ice cube with foam was sawed; to slow down the melting of the ice the saw was not cooled with tap water.
### Table 2.1: List of chemicals used during research.

<table>
<thead>
<tr>
<th>name</th>
<th>composition</th>
<th>purity %</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>vanadium oxide</td>
<td>V₂O₅</td>
<td>&gt;99.6</td>
<td>Aldrich</td>
</tr>
<tr>
<td>molybdenum oxide</td>
<td>MoO₃</td>
<td>&gt;99.5</td>
<td>Merck</td>
</tr>
<tr>
<td>cesium sulfate</td>
<td>Cs₂SO₄</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>cesium carbonate</td>
<td>Cs₂CO₃</td>
<td>&gt;99.5</td>
<td>Merck</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>H₂C₂O₄·H₂O</td>
<td>&gt;99</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td>n-heptane</td>
<td>CH₃(CH₂)₆CH₃</td>
<td>&gt;95</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td>sodium sulfate</td>
<td>K₂SO₄·10H₂O</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>rubidium sulfate</td>
<td>Rb₂SO₄</td>
<td>&gt;99.8</td>
<td>Aldrich</td>
</tr>
<tr>
<td>lithium sulfate</td>
<td>Li₂SO₄·H₂O</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>potassium sulfate</td>
<td>K₂SO₄</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>phosphorus pentoxide</td>
<td>P₂O₅</td>
<td>&gt;98</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td>tungsten trioxide</td>
<td>WO₃</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>silver sulfate</td>
<td>Ag₂SO₄</td>
<td>&gt;99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>tetraammineplatinum chloride</td>
<td>Pt(NH₃)₄Cl₂·xH₂O</td>
<td>&gt;98</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

### Table 2.2: List of ceramic materials tested as catalyst support. The composition of the materials was determined with the methods of Table 2.6.

<table>
<thead>
<tr>
<th>material</th>
<th>supplier</th>
<th>type</th>
<th>geometry</th>
<th>composition wt %</th>
<th>SA m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>α alumina</td>
<td>Norton</td>
<td>XA25045</td>
<td>extrudates</td>
<td>99% Al₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>γ alumina</td>
<td>Alcoa</td>
<td>DD431</td>
<td>spheres</td>
<td>99% Al₂O₃</td>
<td>368</td>
</tr>
<tr>
<td>diatomaceous earth</td>
<td>Damolin</td>
<td>K</td>
<td>spheres</td>
<td>75% SiO₂</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10% Al₂O₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6% Fe₂O₃</td>
<td></td>
</tr>
<tr>
<td>silica</td>
<td>Norton</td>
<td>XS16080</td>
<td>extrudates</td>
<td>99% SiO₂</td>
<td>130</td>
</tr>
<tr>
<td>silicon carbide</td>
<td>Engelhard</td>
<td>37681</td>
<td>spheres</td>
<td>99% SiC</td>
<td>&lt;1</td>
</tr>
<tr>
<td>α alumina</td>
<td>Gimex</td>
<td>rough</td>
<td>tile</td>
<td>92% Al₂O₃</td>
<td>&lt;1</td>
</tr>
<tr>
<td>α alumina</td>
<td>Gimex</td>
<td>smooth</td>
<td>tile</td>
<td>99% Al₂O₃</td>
<td>&lt;1</td>
</tr>
<tr>
<td>cordierite</td>
<td>Gimex</td>
<td>Annacorit 50</td>
<td>tile</td>
<td>9% MgO</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>Gimex</td>
<td>SiSiC</td>
<td>tile</td>
<td>36% Al₂O₃</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>Gimex</td>
<td></td>
<td></td>
<td>48% SiO₂</td>
<td></td>
</tr>
<tr>
<td>silicon carbide</td>
<td>Gimex</td>
<td>SiSiC</td>
<td>tile</td>
<td>90% SiC</td>
<td>&lt;1</td>
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<tr>
<td></td>
<td>Gimex</td>
<td>RBSN</td>
<td>tile</td>
<td>99% Si₃N₄</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

*The tile is composed of sintered grains with a grain size of 10 to 300 μm. The external surface is very rough.*

*The tile is composed of sintered grains with a grain size of 5 μm. The external surface is very smooth.*
The ice in the foam pores provided additional strength during the sawing process. Small plates of $40 \times 40 \times 10$ mm were prepared by sawing with a high precision diamond-impregnated steel thread saw (diameter 0.22 mm, diamond particles 30 μm). This sawing technique was applied in order to prepare smooth samples with perfectly parallel surfaces.

**Wall-flow monolith** A Corning EX80 cordierite wall-flow monolith was obtained to test as catalyst support. Cylindrical samples, diameter 25 mm, length 40 mm, were prepared with a cylindrical diamond saw. The surface of the channel entrances were roughened for better adhesion during plugging by injecting a primer solution (Aremco Ceramabond 503 Primer) and drying at 90°C in air for 30 min and then they were alternately plugged by injecting ceramic paste (Aremco Ceramabond 503) ±5 mm deep into them. The monoliths were subsequently dried at 90°C for 90 min and calcined at 450°C in air for 4 h.

### 2.2.3 Model soot

In the laboratory of the Industrial Catalysis group diesel soot oxidation has been studied for several years (see Preface). In order to be able to conduct reproducible kinetic experiments and to compare the various results which have been produced by the various Ph.D. students a large amount diesel soot with constant properties was required. It is difficult to collect batches of diesel soot with constant properties over a period of years, because the composition of diesel particles depends on many motor characteristics, the way they are collected, and the way they are stored. Therefore, Neeft [1] chose to use Degussa Printex U soot, which is an industrial flame soot produced by high-temperature pyrolysis. He determined that in many respects its properties, particularly its reactivity, are similar to that of diesel soot. During the research Printex U soot has been used from the same batch that was used by Neeft [1], Mul [2], and Jelles [3]. Table 2.4 shows the main chemical and physical properties of Printex U.
### Table 2.4: List with properties of Printex U synthetic soot [1].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area</td>
<td>97 m²/g</td>
</tr>
<tr>
<td>Ø primary particles</td>
<td>20 nm</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>5.2 wt %</td>
</tr>
<tr>
<td>C-content</td>
<td>92 wt %</td>
</tr>
<tr>
<td>H-content</td>
<td>0.6 wt %</td>
</tr>
<tr>
<td>N-content</td>
<td>0.2 wt %</td>
</tr>
<tr>
<td>S-content</td>
<td>0.4 wt %</td>
</tr>
<tr>
<td>Metal ash content</td>
<td>Below detection limit</td>
</tr>
</tbody>
</table>

#### 2.3 Equipment

##### 2.3.1 Multi-flow reactor

Flow reactor experiments were performed with the so-called six-flow microreactor equipment [1], which is shown in Figure 2.1.

![Diagram of multi-flow reactor](image)

**Figure 2.1:** Simplified scheme of the equipment used for temperature programmed oxidation.

The equipment consists of a number of different sections:

**Oven and reactors** Basically the equipment consists of six parallel quartz reactor tubes with an internal diameter of 7 mm, in which the samples were placed between two
quartz wool plugs. The reactors were enclosed in an inconel block that was heated by an electrical oven. The inconel block acted as heat conductor and ensured an adequate temperature profile. The temperature was controlled with a programmable PID controller (model Eurotherm 818P4). A thermocouple (type N) was placed on top of each sample. The temperatures reported in the rest of the thesis for the flow reactor experiments were measured by these thermocouples. For a sample bed height of 0.5 cm the temperature of the sample was controlled with an accuracy of 0.5°C with no significant temperature difference between the different reactors. The pressure and pressure difference over the reactors was measured with electronic pressure transmitters (model Kulltic ITQ-1000-100-A).

**gas-mix section** A gas mixture with Ar as balance gas could be prepared in the gas-mix section. The section consists of 6 mass-flow controllers (model Brooks 5850), and a HPLC water pump (model Cynktok 480) with a water evaporator. Ar and O₂ were technical grade (Air products), the other gases were mixtures in Ar (Scott Specialty Gasses - certified grade).

**gas-feed section** The gas-feed section consists of six mass-flow controllers (model Brooks 5850) for feeding the prepared gas mixture in parallel to the six reactor tubes.

**gas analysis section** The product gas of each reactor is consecutively selected by a selection valve, and passed through a water permeable membrane (model Perma Pure MD-110-72S). A nondispersive infrared (NDIR) analyzer (model Hartmann and Braun Uras 10E) was used to measure CO, 0-2000 vppm; CO₂, 0-5000 vppm; SO₂, 0-1000 vppm; and NO, 0-2000 vppm. If required a chemiluminescence NOₓ analyzer (model ECO Physics CLD 700 EL th) could be placed in series with the NDIR analyzer. The effluent of each reactor was measured every 12 min for 10 sec and averaged.

**data acquisition and processing** All process and gas analysis data was recorded with a PC. One of the reactors was always used as a blank to be able to correct for background concentration of the gases. At the end of each experiment the temperature of the samples was raised to 625°C to oxidize the remaining soot in order to verify the soot mass balance. The soot oxidation rate \( r_{\text{soot}} \) (g/s) was calculated with equation 2.1.

\[
r_{\text{soot}} = q_v \cdot (c_{\text{CO}} - c_{\text{CO,blank}} + c_{\text{CO₂}} - c_{\text{CO₂,blank}}) \cdot 10^{-6} \cdot A_C \cdot V_m^{-1} \tag{2.1}
\]

\( q_v \), volumetric flow rate (l/s); \( c \), concentration (ppm = 10⁻⁶ 1/l); \( V_m \), molar volume gas, 24.5 l/mol (25°C, 1.01 bar); \( A_C \), atomic weight carbon, 12 g/mol.

**conditions** Isothermal experiments were conducted at 375 and 425°C; and TPO experiments with a heating rate of 0.2 and 1°C/min. The experiments were conducted at atmospheric pressure with 10 vol% O₂ in Ar; and the flow rate in each reactor was 200 ml/min, which resulted in realistic [4] space velocities of 20,000 to 100,000 1/l/hr. During an experiment at maximum an O₂ concentration of 200-300 ppm is converted, therefore, the effect of oxygen depletion on the reaction rate is negligible.
CHAPTER 2. EXPERIMENTAL

Two changes were made to the equipment originally described by Neeft [1]:

- One reactor with an internal diameter of 25 mm was incorporated in order to test larger samples. The conditions that were used for this reactor were identical to the smaller ones, except for the flow rate which was 800 ml/min.

- It was found that by stoichiometric gas-phase oxidation a significant amount NO (> 25%) was oxidized to NO₂ in the gas-mix and gas-feed sections. Therefore, it was impossible to perform experiments without NO₂ in the reactor feed gas. The equipment was adapted by fitting a gas tube from the oxygen mass-flow controller to the entrance of reactor 1 (as seen in Figure 2.1), in order to make the time O₂ and NO are mixed as short as possible. Experiments with this configuration were performed with a flow rate of 800 ml/min in order to make the residence time even shorter. For this configuration and conditions no NO₂ formation could be detected during blank experiments.

2.3.2 Thermal analysis

Thermal analysis was performed on two different thermobalances:

TGA-DTA Some powder samples were tested with a Stanton Redcroft STA 1500 simultaneous TGA-DTA analyzer, which is a microbalance with a hangdown that is placed in a very accurately controlled electrical oven. An aluminum oxide sample crucible (diameter 6 mm) together with an empty reference crucible can be placed on the hangdown, as shown in Figure 2.2. The advantage of the equipment is that it also measures heat effects, which make it more easy to identify some of the processes which can occur during catalytic soot oxidation. The temperature under each crucible is measured with thermocouples, from the temperature difference a heatflow (J/s) is calculated. During the investigation synthetic air was used with a flow rate of 50 ml/min.

![Figure 2.2: Illustration of DTA-TGA hangdown [5].](image)

TGA Some of the investigated supported catalysts did not fit in the sample crucible of the TGA-DTA equipment. These samples were tested with a Cahn TG 131 high-capacity
2.3. EQUIPMENT

thermal balance. The balance is similar to the DTA-TGA equipment, but lacks DTA analysis. During the investigation synthetic air was used with a flow rate of 50 ml/min. For a general description of thermal analysis techniques the reader is referred to Charsley and Warrington [6].

2.3.3 Engine bench

For testing catalytic foam filters in diesel exhaust gas under controlled conditions an engine test bench was built. Figure 2.3 shows a simplified scheme of the setup.

![Diagram of engine test-bench]

Figure 2.3: Simplified scheme of engine test-bench.

The engine (model Lister Petter LPW2) was fitted with a Stamford generator, which was loaded with a resistance bank (Perk Electrotechniek). The fuel used during all the experiments was a commercial summer quality diesel fuel containing 0.04 wt % sulfur. Table 2.5 shows the characteristics of the diesel generator set and its exhaust gas.

At the start of each experiment the engine was operated for 1 h at a load of 60%. After this warming-up period a part of the exhaust gas was pumped through a sideline with a membrane vacuum pump (KNF-Verder) that had a maximum capacity of 13 m³/h. The sideline contained a holder for test filters with downstream a wall-flow monolith (model Corning EX-80, ⌀ 60 mm) for protection of downstream equipment against soot deposits. The main exhaust-gas stream had thermal insulation from the exhaust manifold to the silencer, and the sideline had insulation and heat-tracing from the inlet to the wall-flow monolith. Thermocouples (type K) were placed 1 cm up and downstream of the test filters, and in the center and outer channels of the wall-flow monolith. The temperatures reported
Table 2.5: Specifications of diesel generator set.

<table>
<thead>
<tr>
<th>Engine Specification</th>
<th>Value</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>cooling</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>air intake (°C)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>fuel injection</td>
<td>DI</td>
<td></td>
</tr>
<tr>
<td>cylinders</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>cylinder cycle</td>
<td>4-stroke</td>
<td></td>
</tr>
<tr>
<td>bore (mm)</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>stroke (mm)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>displacement (l)</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>engine revolutions (rpm)</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>max. power (kW)</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Generator Set</th>
<th>Value</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>frequency (Hz)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>voltage (V)</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>max. load (kW)</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>applied load (kW)</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exhaust Composition at Applied Load</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ (vol %)</td>
<td>11</td>
</tr>
<tr>
<td>CO₂ (vol %)</td>
<td>6 (est.)</td>
</tr>
<tr>
<td>H₂O (vol %)</td>
<td>6 (est.)</td>
</tr>
<tr>
<td>NOₓ (ppm)</td>
<td>1200</td>
</tr>
<tr>
<td>SO₂ (ppm)</td>
<td>20 (est.)</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>300</td>
</tr>
<tr>
<td>HC (ppm)</td>
<td>110</td>
</tr>
<tr>
<td>dry soot</td>
<td>40 mg/m³</td>
</tr>
<tr>
<td>N₂</td>
<td>rest</td>
</tr>
</tbody>
</table>
in this thesis for the foam filters were recorded by the upstream thermocouple. The gas temperature was controlled with temperature controllers (models West 6100 and 4480) by heating the filter holders and gas tubes in front of the filter holders. The pressure drop over both filters was measured with pressure difference transmitters (model Validyne DP-15), and the pressure in the exhaust pipe with a pressure transmitter (model Druck PTX-1400). The flow rate was measured with an electronic rotameter (model Brooks MT-3809) and adjusted by a PID controller (model West 6100) that controlled a proportional valve (model Kämmer 20037-I/P-PN400). The test filters were placed in the equipment with the canning method that will be described in Section 2.3.4.

In a typical experiment a test filter was operated for a set amount of time in a controlled gas-flow rate at a controlled temperature. During the experiment the pressure drop over the wall-flow monolith and the test filter was constantly monitored. After finishing the engine experiment the amount of soot deposited on the wall-flow monolith and test filter could be determined by conducting temperature programmed oxidation in the setup, the procedure is similar to the one used for the multi-flow reactor equipment (Section 2.3.1).

The following TPO conditions were applied: gas, pressurized air; flow, 1.25 l/h/min; heating rate, 0.2°C/min. The test filter could also be removed from the engine equipment and regenerated in the multi-flow reactor equipment.

### 2.3.4 Aging

**Evaporation test** Equipment was built for testing the evaporation of catalysts. Figure 2.4 shows a schematic overview of the equipment. The setup consists of a quartz tube that

![Schematic overview of the equipment that was used for testing the volatility of catalysts.](image)

was placed in an electrical tube oven. Air could be fed through the glass tube with an rotameter (model Brooks 1350). The temperature of the oven was controlled with a PID controller (model Eurotherm 818P4). 1 g catalyst was placed in alumina dish in the center of the oven and a thermocouple (type K) was placed 5 mm above it. 1 cm downstream the dish a cooling coil was placed, which was cooled with water to 12°C. This cooling coil served to trap any material that was evaporated by the high temperature; a disadvantage of using the coil was that it was not possible to add steam to the gas while that would have condensed on the cooling coil. In a typical experiment 2 l/h/min synthetic air was fed to the tube, and the sample was kept at 750°C for 6 h.
Accelerated aging  For accelerated aging of catalytic filters a deactivation reactor was built. Figure 2.5 a shows a schematic overview of the accelerated aging equipment.

![Schematic diagram of accelerated aging equipment]

Figure 2.5: Equipment for aging catalytic filters: a, schematic overview of aging equipment; b, schematic overview of clamshells that are used for canning filters.

The setup contains three main parts. The first part, the evaporator, contains a bed of highly sintered 5 mm α alumina pellets to which water and air could be fed with a pump (model CFG Prominent A2001) and a rotameter with needle valve (model Brooks 1355), respectively. In the bed an electrical firerod was placed, the temperature was controlled at 160 °C with a PID controller (model West 6100). The second part contained an efficient gas heater that can heat gas up to 650°C. The temperature was controlled with a PID controller (model West 6100). Downstream the heater 2% SO₂ in N₂ (Scott Specialty Gasses) could be added, the flow was controlled with a rotameter with needle valve (model Brooks 1355). The third part is the actual reactor where the sample was placed, with a thermocouple (type K) upstream of the sample.

Figure 2.5 b shows how filters were mounted in the accelerated aging and engine setup. 3M Interam 100 intumescent ceramic fibre mat (see Section 1.5.4) with a thickness of 5 mm was wrapped around the filters (Ø 25 mm) with a notch to avoid gas bypassing, according to specifications of the supplier [7]. Stainless-steel shells were placed around the filter and mat in order to compress the mat to a thickness of 3 mm; and to be able to place the filter in the reactor with ease, viz. the outer diameter of the clamshells was identical to the inner diameter of the cylindrical reactor.

2.3.5 Catalyst characterization

ESEM  Most microscopy studies were performed with scanning electron microscopy (SEM). The technique has a few restrictions: the samples must be clean, dry and conductive; and the experiments must be performed at room temperature and high vacuum (typically 133 µPa). In some cases imaging at elevated temperatures in the presence of oxygen was required. Those cases were investigated with Environmental SEM (ESEM, model Electrosan E-3) at PennState University in the US. ESEM is also called Controlled Atmosphere Electron
2.3. **EQUIPMENT**

Microscopy (CAEM, see Section 1.5.1). Its advantage is that it does not require high vacuum and a conductive layer on the sample, because the gas in the sample chamber is ionized to eliminate charging of the sample. ESEM is well suited for in-situ experiments at pressures as high as 65 mbar depending on the gas used and at temperatures as high as 1500°C.

In a typical ESEM experiment the sample was placed on an α alumina crucible in the low-vacuum sample chamber. The temperature of the crucible was raised in incremental steps by heating an electrical filament that was placed under the crucible. During experiments the images were updated at frequencies of 0.05 to 1 Hz. Due to the constantly updated images microscopic processes that took place could be observed and recorded on video; these images are of low quality due to the high update frequency. If required, high-quality polaroid images could be taken by lowering the update frequency. ESEM experiments are labor-intensive, since the location of the sample, and the sharpness, brightness and contrast of the recorded image must be constantly monitored and adjusted, since these parameters are a function of the temperature. Especially controlling the location of the sample could give problems, because the complete sample crucible could shift due temperature effects or the analyzed particles could jump into the electron microscope's vacuum pump due to charging effects.

**TPR** Temperature programmed reduction (TPR) experiments were conducted with a flow reactor. Figure 2.6 shows a simplified scheme of the equipment.

![Scheme of TPR equipment](image)

The setup contained three sections:

**gas section** The gas section mixed Ar with H₂ by mass-flow controllers (model Sierra D-666). Traces water and oxygen were removed from the gasses (Chrompack Gas-Clean moisture filter 7971 and Chrompack Gas-Clean oxygen filter 7970).

**reactor section** The sample was located in the reactor section, which consisted of a tube oven in which a quartz reactor tube (internal diameter 4 mm) could be placed. The temperature was controlled with a PID controller (WEST Gardsman). Samples were placed in the reactor tube between quartz wool plugs with a thermocouple on top. The reactor effluent was dried with a water permeable membrane (model Perma Pure).
analysis section The analysis section determined the thermal conductivity of the reactor feed gas (baseline) and product gas with a thermal conductivity detector (model GOW-MAC 407-202). The equipment was calibrated with a high purity 10 wt % MoO₃/γ Al₂O₃ catalyst (Akzo Nobel).

In a typical experiment 20 mg sample was placed in the reactor, 30 ml/min Ar with 7 vol % H₂ is passed through the reactor, and the reactor is heated from room temperature to 1000°C with a heating rate of 10 °C/min.

Commercial analysis equipment Various standard, commercially available analysis techniques were used in order to characterize catalysts, catalyst supports, and filters. Their specifics have been listed in Table 2.6. For a description of the methods is referred to general literature [8–13].

Table 2.6: Standard laboratory equipment used during research, with references to general literature of the equipment.

<table>
<thead>
<tr>
<th>method</th>
<th>brand, type</th>
<th>remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>compression test</td>
<td>Instron, TTCMLM 1.4.6</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>flame-AES</td>
<td>Perkin-Elmer, 1100 B</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Perkin-Elmer, Plasma II ICP</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>Hg porosimetry</td>
<td>Carlo Erba, Porosimeter 2000</td>
<td>degasification</td>
<td>[10]</td>
</tr>
<tr>
<td>N₂ physisorption</td>
<td>Quantochrome, Autosorb 6 B</td>
<td>degasification</td>
<td>[10]</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>Jeol, 6400F/Pioneer</td>
<td>coated sample</td>
<td>[11]</td>
</tr>
<tr>
<td>XRD</td>
<td>Bruker AXS, D8 Advance</td>
<td>rad. Cu Kα₁</td>
<td>[12]</td>
</tr>
<tr>
<td>XRF</td>
<td>Philips, PW1480</td>
<td>data analysis: Uniquant</td>
<td>[13]</td>
</tr>
</tbody>
</table>

*Sampled were degassed before analysis: vacuum, 300°C, 15 h.
*SEM samples were coated with a thin gold layer to avoid electric charging. Samples that were analyzed with SEM/EDS were coated with a thin conductive carbon layer instead of gold to avoid interference with the EDS analysis.

Preparation of catalyst cross sections For analyzing the interior of porous ceramic samples with SEM-EDS a method for preparing cross sections was devised. Samples were loaded in a small gelatine container and then immersed in a capillary resin (Threebond 1361B). The sample was degassed at low vacuum and kept for 30 min at 70°C in nitrogen gas at atmospheric pressure in order to solidify the resin. The solidified resin was cut with a high precision diamond saw at the location that contained the sample. The cross section was polished before SEM analysis with Kemet diamond paste. In order to make a scratch free surface different diamond paste grades were successively used: 15, 6, 3, 1, and 0.25 μm diamond particle size.
2.3. EQUIPMENT

2.3.6 Basic laboratory equipment

Various standard laboratory equipment, like calcination furnaces, mills, sieves, etc. were used during the research. The most important ones have been listed in Table 2.7.

<table>
<thead>
<tr>
<th>equipment</th>
<th>type</th>
</tr>
</thead>
<tbody>
<tr>
<td>furnace</td>
<td>Vulcan 3-350; Carbolite PAF 16/3</td>
</tr>
<tr>
<td>ultrasonic transducer tank</td>
<td>Branson Ultrasonic (25 kHz, 1500 W)</td>
</tr>
<tr>
<td>sample bottle shaker</td>
<td>Janke+Kunkel KS 500</td>
</tr>
<tr>
<td>ball mill</td>
<td>Fritsch Pulverisette 8</td>
</tr>
</tbody>
</table>

Rotating oven  An oven with a 100 ml glass reactor with baffles (Figure 2.7 a) was used for the impregnation of support grains with liquid catalyst. In a typical experiment 1.6 g support grains (sieve fraction 400 to 825 μm) and 0.4 g catalyst powder (sieve fraction < 106 μm) were loaded in the reactor. The reactor was rotated at 200 RPM, while the temperature of the oven was raised with 5°C/min to 475°C in air, where it was kept at for 2 to 6 h. After the experiment the impregnated grains were sieved and the 400 to 825 μm sieve fraction was collected.

Powder filtration equipment  A foam holder with pump (Figure 2.7 b) was built for the deposition of catalyst powder on ceramic foams (Ø 25 mm) by filtration. The side of the foams was wrapped in a latex cover and layer of blotting paper, before they were placed in the glass tube (Ø 28 mm). The pump (Cole Palmer Masterflex) was connected to the tube with a rubber stopper. In a typical experiment a stirrer was placed 15 mm above the foam and rotated at 100 RPM. The tube was filled with 75 ml n-heptane, then 1 to 2 g catalyst powder (sieve fraction 100 to 212 μm) was added, and the pump was switched directly on in order to pump 1 to 10 ml/s suspension through the foam until all n-heptane had passed the foam. After the experiment the foam was dried at 80°C in air and calcined at 450°C in air.

Aerosol generator  A simple aerosol generator (Figure 2.7 c) was designed to deposit Printex U synthetic soot on foam filters in order to test them in the flow equipment. The aerosol was produced by fluidizing a mixture of silicon carbide particles (127 μm) and synthetic soot (mass ratio 65:1) in air, which was passed through the foam filters at room temperature. A realistic superficial gas velocity of 3 m/s was applied [14].
Figure 2.7: Illustrations of laboratory equipment: a, oven with rotating sample holder; b, setup for filtering particles from a suspension; c, equipment for generating a soot aerosol and depositing soot on filters.
Bibliography


Chapter 3
Screening of Liquid Catalysts\textsuperscript{1}

Different multi-component liquid catalysts were screened for soot oxidation. Their performance was tested under simulated conditions, and was at least as good as that of the commercially applied Ce catalytic fuel additive. Therefore, their activity seems promising for heavy-duty diesel applications, but for continuous operation in light-duty applications their operation temperature is too high. No direct proof was found to support the hypothesis that the liquid state is essential for catalytic soot oxidation at a high rate.

3.1 Introduction

Exhaust gas catalysts are solid materials that sometimes operate at demanding conditions. The solid state of the catalyst can cause a problem in the case of catalytic soot oxidation. Trapped soot will have poor contact with the catalyst (Section 1.5.2), which results in a too low oxidation rate for regeneration of a soot filter. Catalysts have been developed which can overcome the lack of contact by special means. Catalytic fuel additives are blended with the fuel and built into the soot, and NO\textsubscript{X}-aided CRT uses NO\textsubscript{2} as very reactive intermediate for the soot oxidation, see Sections 1.5.2 and 1.7.2. Practical systems based on these principles have been designed, but are not completely satisfactory. Fuel additives can be used for most engine types, but often at the cost of a complex system design. NO\textsubscript{2}-aided CRT is very simple and robust, but requires low-sulfur fuel and a minimum exhaust temperature which is approximately 100 to 150\textdegree{}C too high for application in passenger cars. There is not much experience with the in theory most elegant soot abatement device: a filter which is catalytically active itself and uses the abundantly present O\textsubscript{2} for oxidation. The poor-contact problem is thought to be the major reason for this.

It was early discovered that potential ‘solid’ catalysts that can oxidize graphite at a high rate often form mobile droplets to become active (Section 1.5.1). It is intriguing that a catalyst can be more useful when its physical state is changed. When the physical change

\textsuperscript{1}A part of the results presented in this Chapter are shared with Chapter 8 of the Ph.D. thesis of S.J. Jelles [1]; in this thesis Section 3.3.1, a part of Section 3.3.3, and Figure 3.7. Those results have been published in a joined publication: S.J. Jelles, B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Applied Catalysis B: Environmental, 21: 35-49, 1999.
occurs at temperatures which frequently occur in an exhaust pipe, it might even provide a solution for stable catalytic filter regeneration. Such catalyst should have two main properties: (1) at the atomic scale the catalyst should be capable of catalyzing an electron transfer or oxygen transfer reaction (Section 1.5.1) in order to create a carbon-oxygen complex, and (2) at the soot-particle scale the catalyst should be able to realize tight physical contact. For the purposes of catalyst selection this can be translated into two criteria: (1) a potential catalyst should contain at least one component that can provide active catalytic sites for oxidation, and (2) the catalyst should have a low melting point. Further selection criteria refer to the application in an exhaust pipe:

- The vapor pressure of the catalyst should be low. For instance, metal chlorides are suitable components for preparing catalysts with very low melting points, but they are known to evaporate in diesel exhaust gas, which makes them unsuitable (Section 1.5.4).

- The components of the catalysts should not catalyze the formation of toxic by-products. For instance, copper is unfit because it may catalyze the formation of dioxins and dibenzofurans (Section 1.5.3).

- The catalyst should not decompose in exhaust gas, since that would most probably change its melting point and other characteristics. For instance, sodium nitrate decomposes at 380°C.

- Toxic metals, like arsenic and cadmium are not preferred by car industry because of possible emissions during the lifetime cycle of the vehicle and recycling problems.

In this chapter the potential of low-melting liquid catalysts is investigated, and it will be determined if the liquid state of the catalyst plays an essential role in the oxidation mechanism.

3.2 Experimental

3.2.1 Catalyst selection and sample preparation

Eutectic \(^2\) mixtures of vanadium, molybdenum, and alkaline-metal oxides or sulfates meet the above mentioned criteria. Cs\(_2\)MoO\(_4\)-V\(_2\)O\(_5\), CsVO\(_3\)-MoO\(_3\), and Cs\(_2\)SO\(_4\)-V\(_2\)O\(_5\) were prepared according to recipes from literature [3,4]. For catalysts with alkali metals other than cesium no recipes were found, therefore, they were prepared with the same molar compositions as their cesium counterparts. KVO\(_3\)-KCl was also prepared for comparison, since it has been reported to be a promising catalyst [5]. The catalysts were prepared by fusion: the starting materials were mixed with a mortar, then heated in air above the melting point of the eutectic until all material became liquid. The liquid material was solidified by cooling to room

\(^2\)Eutectic is Greek for 'easily melted'. A liquid at eutectic composition freezes at a single temperature without first depositing components at higher temperatures [2].
temperature, crushed, and sieved in a sieve fraction smaller than 106 μm. Phosphate and tungsten trioxide catalyst promoters were incorporated in the catalysts by fusion. Attempts to fuse platinum oxide failed: phase separation was clearly visible, the solidified product contained a thin grey (platinum) layer. DTA analysis showed that the attempts to produce pure, eutectic catalysts were not always successful, often more than one phase was present. For example, Figure 3.1 a shows the DTA curve of CsVO₃·MoO₃ which had one phase that melted, and Figure 3.1 b shows an example of CsVO₃·NaVO₃·MoO₃ which had two phases that melted. The prepared catalysts and characteristics are listed in Table 3.1.

![Diagram](image)

Figure 3.1: Typical results of melting point determination by DTA: a, CsVO₃·MoO₃; b, CsVO₃·NaVO₃·MoO₃. Heating rate: 5°C/min in synthetic air.

### 3.2.2 Catalyst activity test

Samples with a loose physical contact between the catalyst and synthetic soot (Printex U) were prepared by mixing with a spatula. Samples with tight contact were prepared by mixing catalyst and soot in a ball mill for 1 h. All mixtures had a mass ratio of catalyst and soot of 2:1.

Experiments were performed with the flow-reactor equipment described in Section 2.3.1. 60 mg samples (40 mg catalyst, 20 mg soot) diluted with 400 mg SiC were used. During the experiments the temperature was raised to 500°C with 0.2°C/min in 10 vol % O₂ in Ar
<table>
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<th>Pd</th>
<th>KO ( \text{g})</th>
<th>KVO ( \text{g})</th>
<th>KYO ( \text{g})</th>
<th>C(\text{O}_3)(\text{MoO}_4)</th>
<th>C(\text{O}_3)(\text{MoO}_4)</th>
<th>C(\text{O}_3)(\text{MoO}_4)</th>
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</tbody>
</table>

Table 3.1: Composition, melting point and other data of the screened catalysts.
(200 ml/min, GHSV 20,000 l/l/h), subsequently the temperature was raised to 625°C with 1.5°C/min. A series of experiments was performed:

- The screening study was initiated with catalysts of which recipes were found in literature: CsVO₂⁻MoO₃, Cs₂MoO₄·V₂O₅, and Cs₂SO₄·V₂O₅. These catalyst will be referred to as the reference catalysts. Their performance was compared with MoO₃, V₂O₅, Cs₂SO₄, KVO₃·KCI, and uncatalyzed synthetic soot.

- Variations on Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃, where cesium was partly or fully replaced by other alkali metals, were screened to determine how replacement of cesium affects the catalyst performance.

- WO₃ and P₂O₅ were added to Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ as promoters to determine their influence on the catalyst performance.

After each experiment the reactors were visually inspected in order to verify if sublimation products from the catalyst were deposited.

3.2.3 High-temperature resistance test

Volutility is a critical parameter of an exhaust catalyst: it should be essentially zero in order to avoid catalyst loss by evaporation or sublimation. CsVO₃·MoO₃, Cs₂MoO₄·V₂O₅, Cs₂SO₄·V₂O₅, KVO₃·KCI, and Cs₂SO₄·V₂O₅ with 5 wt % P₂O₅ were subjected to the volatility test that was described in Section 2.3.4. The catalysts were kept at 750°C for 6 h in an air flow of 2 l/min. Cs₂SO₄·V₂O₅ with 5 wt % P₂O₅ was also kept at 450°C for 90 h in an air flow of 2 l/min. If deposits were formed on the cooling coil a sample was taken with an adhesive tape. The adhesive tape was then analyzed with EDS to determine the composition of the deposited material.

3.2.4 Study of the role of the liquid state

TGA-SEM

TGA-DTA experiments with MoO₃ and Cs₂MoO₄·V₂O₅ catalysts were performed at a constant temperature of 375°C in synthetic air. The catalysts were mixed with synthetic soot in a mass ratio of 2:1. The sample crucibles were filled with 6 mg sample. Silica sample crucibles were used in order to let the catalyst only interact with soot, e.g. the liquid catalysts have no affinity for silica (Chapter 4). The sample mass was constantly monitored and the experiments were stopped at 25 % soot conversion by quenching the sample to room temperature. The complete sample crucibles with contents were subsequently analyzed with SEM at room temperature.
Environmental SEM

During the TGA-SEM experiments the samples were analyzed ex-situ at room temperature. Supplementary in-situ SEM experiments at high temperatures were performed with the environmental SEM (ESEM) technique, as described in Section 2.3.5. The experiments were conducted in a similar manner to the TGA-SEM experiments, but there were some differences due to equipment limitations. The TGA experiments were performed at atmospheric pressure, while the ESEM experiments were performed at 5 mbar in pure oxygen. This was the maximum oxygen pressure allowed in ESEM which resulted in images of acceptable quality. During the TGA-SEM experiments 6 mg samples were used. Such amount fitted in the ESEM sample crucible but gave a lot of problems because large parts of the sample constantly disappeared into the electron microscope's vacuum system. This disappearance was avoided by placing a trace of sample on the crucible. The weight of the trace was too low to be measured with the available balances, it was roughly estimated to be in the order of 0.1 mg. Due to this low sample amount only two or three catalyst particles could be detected. The number was raised by crushing the < 106 μm catalyst particles into a 1 to 15 μm sieve fraction by means of a mortar before it was mixed with the soot.

TPR

The \( \text{Cs}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5 \) catalyst and different alkali \( \text{M}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5 \) (\( \text{M} \) is \( \text{Li} \), \( \text{Na} \), \( \text{K} \), \( \text{Rb} \), or \( \text{Cs} \)) catalysts were tested with \( \text{H}_2 \) TPR to study their reduction behavior. The equipment and procedures have been described in Section 2.3.5.

3.3 Results

3.3.1 Activity reference catalysts

Figure 3.2 shows the oxidation rate, calculated from the \( \text{CO} \) and \( \text{CO}_2 \) released (Equation 2.1)\(^3\) and normalized to the amount of soot initially present as a function of temperature for the reference eutectic catalysts, the single components from which the reference eutectic catalysts were composed, and non-catalytic soot oxidation. Soot without catalyst oxidized slowly from 300°C onwards. This causes that the onset temperature of most catalysts cannot be determined by pinpointing the temperature where the oxidation rate changes from zero to some significant value. Instead, the plot of non-catalytic soot oxidation can be used for determining the onset temperatures of the catalysts. In this chapter the onset temperature of the catalysts will be determined by pinpointing the temperature at which the rate of catalytic soot oxidation becomes higher than the rate of non-catalytic soot oxidation.

For the single metal components the oxidation rate gradually increased with temperature, like the non-catalytic oxidation of soot. At lower temperatures the oxidation rates

\(^3\)Information regarding the produced \( \text{CO} \) and \( \text{CO}_2 \) concentrations cannot be deducted from the reported oxidation rates. In general, \( \text{CO} \) had a 5 to 15% contribution to the calculated soot oxidation rates with average \( \text{CO} \) concentrations of 20 ppm and maximum recorded concentrations of 50 ppm.
Figure 3.2: Oxidation rate as function of temperature, heating rate 0.2°C/min, 10 vol % O₂: a, single components; b, multi-component reference catalysts.
are very similar and at higher temperatures they slowly shift from each other. The single metal oxide catalysts showed \( T_{\text{max, rate}} \) above 440°C: MoO₃, 442°C; Cs₂SO₄, 460°C; and V₂O₅, 480°C. CsVO₃·MoO₃, Cs₂MoO₄·V₂O₅, and Cs₂SO₄·V₂O₅ behaved differently. These catalysts became active in more well-defined temperature region of 330 to 360°C, and their oxidation rates were found to increase sharply above these temperatures. For CsVO₃·MoO₃ and Cs₂MoO₄·V₂O₅ \( T_{\text{max, rate}} \) could easily be determined, it was 375°C and 396°C respectively. For Cs₂SO₄·V₂O₅ an accurate determination of \( T_{\text{max, rate}} \) was not possible, because the oxidation rate showed a plateau in the range of 390 to 430°C. KVO₃·KCl had \( T_{\text{max, rate}} \) at 440°C which made it the least active of the investigated multi-component catalysts. It also showed two artifacts: it oxidized the silicon carbide diluent, and it sublimated: needles were found downstream of the catalytic in a cooler part of the reactor. EDS analysis showed that the needles contained KCl. Apparently, KCl sublimated during the experiment.

### 3.3.2 Activity adapted catalysts

**Alkali metal exchanged catalysts**

Various alternatives for the Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ catalysts were synthesized by exchanging the cesium partly or completely with other alkali metals. Figure 3.3 shows the oxidation rates as function of temperature of the different alternative catalysts. The complete or partial replacement of cesium by other alkali metals had no positive effect on the catalyst activity. In all cases, Figures 3.3 a, b, and c, \( T_{\text{max, rate}} \) shifted to significantly higher values compared to Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃. The following order in activity, based on \( T_{\text{max, rate}} \), was found: Cs > Rb > Li \( \approx \) K > Na. For catalysts where cesium was partly replaced by sodium, Figures 3.3 b and c, \( T_{\text{max, rate}} \) was found to be a function of the sodium content, viz. \( T_{\text{max, rate}} \) shifted to higher values with increasing sodium content. A small positive effect on the onset temperature was found for sodium and lithium, Figure 3.3 a, by replacing cesium with these metals the onset temperature was lowered by approximately 25°C. This positive effect was, however, largely offset by the overall lower activity of these catalysts compared to their cesium counterparts.

**Catalyst promoters**

P₂O₅ and WO₃ were screened as promoters for Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃, 1, 5, and 25 wt % concentrations were tested. Figure 3.4 shows the oxidation rate as a function of temperature. The addition of 1 and 5 wt % P₂O₅ enhanced the performance of Cs₂SO₄·V₂O₅ (Figure 3.4 a) and CsVO₃·MoO₃ (Figure 3.4 b) by lowering the onset temperature to approximately 260°C. The lower onset temperature was, however, not accompanied by a lowered \( T_{\text{max, rate}} \). It is interesting to note that the \( T_{\text{max, rate}} \) of both Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ responded differently to the addition of 1 and 5% P₂O₅: for Cs₂SO₄·V₂O₅ \( T_{\text{max, rate}} \) remained constant when 1 and 5% P₂O₅ were added, while for CsVO₃·MoO₃ \( T_{\text{max, rate}} \) shifted to higher temperatures when the same amounts of P₂O₅ were added. This in contrast to the onset temperatures, on which P₂O₅ had the same effect for both catalysts. The addition of various amounts of WO₃, Figures 3.4 c and d, did not affect the catalyst performance significantly.
3.3. RESULTS

![Graphs showing oxidation rate versus temperature for different catalysts and conditions.](image)

**Figure 3.3:** Oxidation rate as function of temperature, heating rate 0.2°C/min, 10 vol % O_2:
- a, M_2SO_4·V_2O_5, M = Li, Na, K, Rb, or Cs;
- b, Na_2SO_4·V_2O_5, Cs_2SO_4·V_2O_5, Cs_2SO_4·Na_2SO_4·V_2O_5;
- c, NaVO_3·MoO_3, CsVO_3·MoO_3, CsVO_3·NaVO_3·MoO_3.
Figure 3.4: Oxidation rate as function of temperature, heating rate 0.2°C/min, 10 vol % O₂: a, Cs₂SO₄·V₂O₅ with P₂O₅; b, CsVO₃·MoO₃ with P₂O₅; c, Cs₂SO₄·V₂O₅ with WO₃; d, CsVO₃·MoO₃ with WO₃.
3.3.3 High-temperature resistance

Cs$_2$SO$_4$·V$_2$O$_5$, CsVO$_3$·MoO$_3$, Cs$_2$MoO$_4$·V$_2$O$_5$, KVO$_3$·KCl, and Cs$_2$SO$_4$·V$_2$O$_5$ with 5 wt % P$_2$O$_5$ were exposed to a temperature of 750°C for 6 h. Table 3.2 shows the elemental composition of the tested catalysts and the composition of the sublimated deposits.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>components</th>
<th>composition catalyst</th>
<th>composition deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$MoO$_4$·V$_2$O$_5$</td>
<td>Cs:Mo:V</td>
<td>2:1:2</td>
<td>8:2:0</td>
</tr>
<tr>
<td>CsVO$_3$·MoO$_3$</td>
<td>Cs:Mo:V</td>
<td>3:1:3</td>
<td>8:1:0</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$·V$_2$O$_5$</td>
<td>Cs:V:S</td>
<td>2:2:1</td>
<td>no deposit</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$·V$_2$O$_5$</td>
<td>Cs:V:S</td>
<td>2:2:1</td>
<td>no deposit</td>
</tr>
<tr>
<td>(5 wt % P$_2$O$_5$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KVO$_3$·KCl</td>
<td>K:V:Cl</td>
<td>2:1:1</td>
<td>1:0:1</td>
</tr>
</tbody>
</table>

Cs$_2$SO$_4$·V$_2$O$_5$ and Cs$_2$SO$_4$·V$_2$O$_5$ with 5 wt % P$_2$O$_5$ did not evaporate. For Cs$_2$MoO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$ some sublimation product was found on the cooling coil. The evaporated amount was so low that no difference could be measured with TPO [1]. KVO$_3$·KCl showed significant evaporation during the first 10 minutes of the evaporation test: the cooling coil was completely covered with white material.

For both Cs$_2$MoO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$, the concentration of the cesium in the sublimated deposits is higher than in the original catalyst. Apparently, the catalysts lost components in a selective manner. The deposits of the KVO$_3$·KCl catalyst consisted of KCl, apparently, the catalyst lost all KCl due to evaporation.

The Cs$_2$SO$_4$·V$_2$O$_5$ catalyst with 5 wt % P$_2$O$_5$ did not loose any material during the short test at 750°C and the longer test at 500°C for 90 h, which was a very promising result. These catalysts were tested with TPO analysis in the flow equipment in order to verify if their performance was changed due to the high-temperature treatments. Figure 3.5 shows the results. The performance of the Cs$_2$SO$_4$·V$_2$O$_5$ catalyst with 5 wt % P$_2$O$_5$ did not change due to the treatment at 500°C for 90 h. This was not the case for the catalyst that was kept at 750°C for 6 h. Its interesting low onset-temperature increased with approximately 75°C, because of which it performed like the reference Cs$_2$SO$_4$·V$_2$O$_5$ catalyst that contained no P$_2$O$_5$, which activity was unchanged after the high-temperature treatment [1].

3.3.4 Study of the role of the liquid phase

Effect of the degree of physical contact

Figure 3.6 shows the results of the TPO analysis of the oxidation of synthetic soot that was mixed in a loose and tight manner with Cs$_2$SO$_4$·V$_2$O$_5$. The oxidation of the tight contact sample differed substantially from the loose contact sample. Oxidation started at 200°C, which is approximately 150°C lower than for loose contact. $T_{\text{max. rate}}$ was found at 295°C, which is approximately 100°C lower than for loose contact.
Figure 3.5: Oxidation rate as function of temperature for Cs$_2$SO$_4$·V$_2$O$_5$ catalysts with 5 wt% P$_2$O$_5$ that were given different high-temperature treatments, heating rate 0.2°C/min, 10 vol % O$_2$.

Figure 3.6: Oxidation rate as function of temperature for Cs$_2$SO$_4$·V$_2$O$_5$ mixed with synthetic soot in loose and tight contact, heating rate 0.2°C/min, 10 vol % O$_2$. 
3.3. RESULTS

TGA-SEM

Various catalysts have been tested with TPO analysis. Each TPO experiment started at room temperature, where the catalyst is mixed as a powder with the soot: a situation for which can be imagined that it might be quite different from the situation during soot oxidation when the catalyst is liquid. In order to determine how the liquid catalyst distributes itself, a number of TGA-DTA experiments were performed that were stopped at 25% soot conversion. The complete thermobalance sample crucibles with contents were analyzed with SEM analysis at room temperature. Figure 3.7 shows results of the TGA-SEM study.

The sample with MoO\textsubscript{3}, Figure 3.7 a, looked identical to the starting situation (not shown). The area of the white circle is magnified in Figure 3.7 b. Figure 3.7 c shows a typical Cs\textsubscript{2}MoO\textsubscript{4}·V\textsubscript{2}O\textsubscript{5} particle at 25% soot conversion. The physical appearance is totally different compared to the MoO\textsubscript{3} catalyst. All catalyst is present as spheres, with sizes typically in the range of 1500 \( \mu m \), whereas the initial catalyst particles consisted of a sieve fraction smaller than 106 \( \mu m \). The existence of large spheres at room temperature indicates that the catalyst agglomerated to large droplets due to the low affinity for silica (Section 3.2.4). The 1500 \( \mu m \) particles were cut with a razor blade and analyzed with SEM, Figures 3.7 d and c. Large cavities and large soot agglomerates were clearly visible, Figure 3.7 d. In the cavities small soot agglomerates were visible, as shown in Figure 3.7 e, which is an enlargement of the area indicated with a white circle in Figure 3.7 d.

Environmental SEM

Figure 3.8 shows the melting process of a Cs\textsubscript{2}SO\textsubscript{4}·V\textsubscript{2}O\textsubscript{5} particle. From room temperature up to 360°C the solid particle remained unchanged. At 360°C the particle melted and formed a droplet that collapsed within seconds and started to wet the surface of the alumina sample crucible. A small amount of solid material did not melt up to 500°C, which indicates that the catalyst contained at least two phases.

Several soot oxidation experiments were performed. Figure 3.9 summarizes the main observations. From room temperature up to 365°C the catalyst did not change. At 365°C it melted and formed an immobile smooth droplet. The droplet remained stable and did not spread over the soot. The image remained static for several hours, apparently, the oxidation reaction was very slow, obviously due to the low oxygen-pressure of 5 mbar. It was estimated that at least four days would be required to complete the experiment. This was not practical for two reasons: ESEM analysis needs constant personal monitoring since the image quality varied in time, and such long experiments would run a high risk, because the complete monitored sample-location sometimes disappeared into the electron microscope's vacuum system, which would have ruined the experiment. In order to speed-up the oxidation process the temperature was slowly raised. The particle surface slowly transformed from smooth to a solid, structured sphere with a crystalline appearance: it looked a little bit like a cauliflower. The 'cauliflower' melted at 520°C and formed a smooth sphere, that again slowly transformed into a sphere with some structure in its surface.
Figure 3.7: SEM images at 25% soot conversion, samples were placed in silica sample crucibles:
a, MoO₃ with soot; b, detail of MoO₃ with soot; c, sphere of Cs₂MoO₄·V₂O₅ and soot; d, cleaved Cs₂MoO₄·V₂O₅ sphere with soot; e, detail of a cleaved Cs₂MoO₄·V₂O₅ sphere with soot. The locations of the details are indicated with white circles.
3.3. RESULTS

25°C

\[ \text{Start} \]
Catalyst particle (light) on ceramic sample holder (dark).
Notice: the sintered grain structure of the ceramic sample holder is clearly visible.

360°C

\[ \text{Collapsing droplet} \]
The catalyst melted and formed a droplet that collapsed within seconds.
Notice: the sintered grain structure of the sample holder is still visible.

370°C

\[ \text{Wetting catalyst} \]
The molten catalyst started wetting the surface of the sample holder.
Notice: the sintered grain structure of the ceramic sample holder is not visible.

380°C

\[ \text{Remaining solid material} \]
A fraction of the catalyst did not melt and remained*. The fraction that was molten continued with wetting. See left picture: white spot, particle; dark area, wetted sample holder; light area, nonwetted sample holder.

500°C

\[ \text{Melting remaining solid material} \]
The solid fraction melted at a higher temperature and spread over the sample holder.

* The images are in 2D which may result in a misleading perception. The particle at 380°C looks only a bit smaller compared to the particle at 25°C. Its volume was actually appreciably reduced due to a significant decrease in height.

Figure 3.8: A series of chronological images of the melting process of a Cs₂SO₄·V₂O₅ particle.
Start
Left: soot and catalyst.
Right: enlargement of catalyst particle.

Melting catalyst
At 365°C the catalyst melted instantly, and formed a smooth droplet. The catalyst did not spread or move over the soot. This also did not happen at various other locations in the sample. (The situation did not change for hours.)

Droplet metamorphosis
At 450°C the droplet started to change in appearance. It slowly transformed into a droplet with a crystalline arrangement.

Melting for the second time
At the 520°C the crystalline droplet melted again to a smooth droplet.

Particle metamorphosis
The smooth droplet slowly changed again in appearance.

Figure 3.9: A series of chronological images of a Cs$_2$SO$_4$·V$_2$O$_5$ particle during the oxidation of soot.
3.3. RESULTS

TPR

In Figure 3.3 a an interesting relationship in activity was established for the series of alkali M₂SO₄·V₂O₅ catalysts. This relationship approximated the order in electronegativity of the alkali elements, but Li and K were interchanged (Table 3.3).

<table>
<thead>
<tr>
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<th>Electronegativity</th>
<th>T_{max. rate}</th>
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<tr>
<td>Cs</td>
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</tr>
<tr>
<td>Rb</td>
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</tr>
<tr>
<td>Li</td>
<td>0.97</td>
<td>447</td>
</tr>
<tr>
<td>K</td>
<td>0.91</td>
<td>453</td>
</tr>
<tr>
<td>Na</td>
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<td>475</td>
</tr>
</tbody>
</table>

Table 3.3: Electronegativity of alkali metals and T_{max. rate} of different M₂SO₄·V₂O₅ catalysts, where M represents the different alkali metals. The electronegativities are according to the Allred-Rochow scale [6].

H₂ TPR experiments were performed to determine if the order in activity also shows a relationship with the reducibility of the catalysts. Figure 3.10 a shows repeated TPR experiments of a commercial MoO₃ hydrotreating catalyst. It is clear from the figure that the equipment operates in a reproducible manner. The experiments with the liquid catalysts were, however, not reproducible. Figure 3.10 b shows three independent TPR experiments that were performed on Cs₂SO₄·V₂O₅. The reproducibility of the experiments was low: the location of the peaks shifted, the sum of the peak surface-areas varied, and the peak surface-areas relative to each other varied from experiment to experiment. A likely reason for the poor reproducibility is that the catalyst morphology changed dramatically during the TPR experiments: the catalyst was loaded in the TPR reactor as a powder and melted during the experiments, some molten catalyst even trickled out of the hot zone of the reactor. The changing morphology in combination with vanadium oxide, which is a difficult compound to study with TPR due to its multiple oxidation states, caused most probably the poor experimental results. Due to this it was not possible to measure, for instance, reduction activation energies or quantify the different phases present in the catalysts, which were the original goals of the TPR study. At best the location of the reduction peaks in the plots might be used to discover some general trends in reduction behavior. Figure 3.11 a shows a possible trend in reduction behavior which fits the order in activity of the M₂SO₄·V₂O₅ catalysts to some degree. The TPR peaks of the more active Cs₂SO₄·V₂O₅ and Rb₂SO₄·V₂O₅ catalysts are shifted to lower temperatures compared to the less active Li₂SO₄·V₂O₅ and Na₂SO₄·V₂O₅ catalysts. On the other hand K₂SO₄·V₂O₅ did not fit the trend, which is something for which no explanation can be given, except that the TPR experiments were problematic. Figure 3.11 b shows a trend that matches the order in activity of the Cs₂SO₄·Na₂SO₄·V₂O₅, Cs₂SO₄·V₂O₅, and Na₂SO₄·V₂O₅ catalysts that was found in Figure 3.3 b. With increasing sodium content the reduction peaks shift to higher temperatures, and in Figure 3.3 b it was found that with increasing sodium content T_{max. rate} increases.
Figure 3.10: Hydrogen consumption as function of temperature, heating rate 10°C/min: a, MoO₃/γ alumina, duple experiment; b, Cs₂SO₄·V₂O₅, triple experiment.

Figure 3.11: Hydrogen consumption as function of temperature, heating rate 10°C/min: a, V₂O₅, Cs₂SO₄·V₂O₅, K₂SO₄·V₂O₅, Li₂SO₄·V₂O₅, Na₂SO₄·V₂O₅, Rb₂SO₄·V₂O₅; b, Cs₂SO₄·V₂O₅, Cs₂SO₄·Na₂SO₄·V₂O₅, Na₂SO₄·V₂O₅.
3.4 Discussion

3.4.1 Catalyst performance

Activity

Several aspects of a catalyst are important to judge its potential. Two important ones are the onset temperature and the activity at common exhaust temperatures. It is, however, difficult to translate results of powdered catalysts tested under laboratory conditions to their performance in an exhaust pipe when deposited on a filter. Therefore, the data was compared with data from the commercially applied Ce catalytic fuel additive (Rhodia DPX 9) in Figure 3.12. Data from Jelles [1] was used as reference because he measured catalyzed diesel soot (7 mg Ce/g soot) that was collected with a dedicated engine bench, and the TPO curve he reported was measured with the same flow equipment and conditions that were used for screening the current liquid catalysts.

![Graph showing oxidation rates](image)

Figure 3.12: Oxidation rate as function of temperature of Ce catalytic fuel additive [1] and the Cs₂SO₄·V₂O₅ liquid catalysts. The catalysts were tested with identical equipment and conditions.

It can be concluded on basis of comparison with the Ce catalyzed diesel soot that the activity of the liquid catalysts is very promising. The results of the different catalysts were benchmarked as follows: (1) the activity of a liquid catalyst is promising when $T_{\text{max,rate}}$ is found below 400°C, because then the activity is considerably higher than the activity of the Ce fuel additive; and (2) the onset temperature is considered very promising when oxidation is initiated below 300°C. The results of the bench-marked catalysts are shown in Table 3.4.
Table 3.4: List of bench-marked catalysts. Criteria: low onset temperature, < 300°C; high activity, \( T_{\text{max rate}} < 400^\circ C \).

<table>
<thead>
<tr>
<th>( T_{\text{max rate}} &lt; 400^\circ C )</th>
<th>( T_{\text{max rate}} &gt; 400^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>onset temp. &lt; 300°C</td>
<td>Cs2SO4·V2O5 with 1 and 5 % P2O5</td>
</tr>
<tr>
<td></td>
<td>CsVO3·MoO3 with 1 % P2O5</td>
</tr>
<tr>
<td></td>
<td>CsVO3·MoO3 with 5 and 25 % P2O5</td>
</tr>
<tr>
<td>onset temp. &gt; 300°C</td>
<td>MoO3, V2O5, Cs2SO4</td>
</tr>
<tr>
<td></td>
<td>K2SO4·V2O5, Na2SO4·V2O5</td>
</tr>
<tr>
<td></td>
<td>Cs2SO4·Na2SO4·V2O5</td>
</tr>
<tr>
<td></td>
<td>Rb2SO4·V2O5, Li2SO4·V2O5</td>
</tr>
<tr>
<td></td>
<td>CsVO3·NaVO3·MoO3</td>
</tr>
<tr>
<td></td>
<td>NaVO3·MoO3</td>
</tr>
<tr>
<td></td>
<td>KVO3·KCl</td>
</tr>
</tbody>
</table>

The different catalysts will be separately discussed:

**Reference catalysts** CsVO3·MoO3, Cs2MoO4·V2O5 and Cs2SO4·V2O5 are very promising catalysts. Their activity in the TPO reactor is similar to that of the Ce fuel additive catalyst. Their activity might be sufficient for heavy-duty diesel applications, and compared to the catalytic fuel additives they have the advantage that no dosing strategy is required, and no filter plugging will occur by catalyst-ash deposits. The onset temperature is still approximately 150°C too high for the continuous regeneration of a passenger car soot filter. The performance of the KVO3·KCl catalyst, which was mentioned as potential catalyst in literature [5], does not exceed that of MoO3, Cs2SO4 and V2O5. It will not be further investigated.

**Adapted catalysts** The reference catalysts were modified by partly or fully replacing cesium by other alkali metals. This was done in order to investigate the effect on the melting point and with that the catalyst onset temperature. It was found that the activity had no relationship with the melting point, but that the activity might have a relationship with the ease of reducibility of the catalysts and the electronegativity of alkali metals. The reducibility is an important variable in the oxygen-transfer (or redox) soot oxidation mechanism, which is the favored mechanism in literature for the catalytic oxidation of carbonaceous materials (Section 1.5.1). Reduction of alkali metals at the reaction temperatures is not possible, but reduction of V2O5 is. For instance, Silva et al. [7] showed in a study with in-situ high-temperature XRD that V2O5 particles in contact with soot and air are reduced to V6O13 at temperatures between 300 and 400°C, which is the same temperature range that was used in the present study. The presence of the alkali metals might influence the reduction behavior of the V2O5 by means of their very low electronegativity. Maybe Cs2SO4·V2O5, CsVO3·MoO3, and Cs2MoO4·V2O5 were the most active catalysts because they contain the least electronegative element, cesium, which is in fact the least electronegative element that exists! It is in agreement with this reasoning that Na2SO4·V2O5 was the least active catalyst: sodium is the most electronegative alkali metal; and the catalysts that contained both cesium and sodium had intermediate activities.
3.4. DISCUSSION

promoters It was mentioned above that V₂O₅ might provide the catalytic sites for soot oxidation. If so, then it might be worthwhile to investigate if the performance of V₂O₅ can be promoted. Well-known V₂O₅ promoters are P₂O₅ and WO₃. P₂O₅ is used in the V₂O₅-P₂O₅ catalyst as promoter for the oxidation of butane to maleic anhydride, viz. its addition increases the concentration of V=O surface species without acting as reduct site itself [8]; WO₃ is used as V₂O₅ promoter for various oxidation reactions and acts as promoter for vanadium based SCR catalysts. WO₃ increases the concentration of V=O surface sites and also acts as reduct site itself [9]. Based on this literature data it was decided to test P₂O₅ and WO₃ as promoters for soot oxidation catalysts.

P₂O₅ had a dramatic effect on the catalyst onset temperature, which was lowered to just above 250°C. This onset temperature may be considered as a breakthrough, because such a low temperature was never found before for catalytic loose-contact soot-oxidation. It is, however, not sure if the 'breakthrough' delivers new chances for filter regeneration strategies, because the lowered onset temperature was not accompanied by a lowered $T_{\text{max-rate}}$. It is not known why P₂O₅ lowered on one hand the onset temperature, while on the other hand not $T_{\text{max-rate}}$. In fact, for CsVO₃-MoO₃ $T_{\text{max-rate}}$ increased with increasing P₂O₅ content. More should be known about the chemistry and mechanism of the liquid catalysts to answers such questions. Helpful tools to answer such questions might be, for instance, in-situ high-temperature XRD and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. With high-temperature XRD it is possible to identify the different phases that are contained in a catalyst at different temperatures, and with DRIFT spectroscopy it is possible to determine the with the reaction rate related amount of carbon-oxygen complexes (Section 1.4.1) present on the soot surface at different temperatures. The liquid state of the catalyst might, unfortunately, restrict the potential outcome of such experiments. For instance, it is doubted if the catalyst, when it is molten, contains phases that have the required long-range ordering for XRD analysis.

The addition of various amounts of WO₃ to the liquid catalysts did not affect the catalyst performance significantly. This is surprising because it is intuitively expected that the presence of WO₃ should at least lower the catalyst activity by a dilution effect when it is inert. (WO₃ is inert as single metal-oxide catalyst [10].) It is, actually, difficult to argue what should be the effect of the dilution of Cs₂SO₄-V₂O₅, because on one hand the amount of catalytic active phase decreases when WO₃ is added, while on the other hand the total amount of the catalyst material, and, therefore, the catalyst-soot contact area, should remain constant when a constant amount of catalyst material is used. When it is not known which parameter was rate-limiting in the oxidation reaction it is difficult to argue what was the effect of the dilution. Actually, WO₃ could be of help with determining the rate-limiting step of the reaction, while it, apparently, can act as inert diluent. The used experimental setup was, however, not well suited for such investigation. During the experiments the catalyst melted, because of which it was not possible to determine how large the catalyst-soot contact area was during the reaction. Supported liquid catalysts are better suited for such investigation.
Stability

In previous studies (Sections 1.5.2 and 1.5.4) the CuKMo(Cl) and CuKV(Cl) soot oxidation catalysts were considered very promising. It turned out that they are highly volatile, which would make catalyst emissions and deactivation unavoidable. Therefore, in the early phase of the current investigation the volatility in air at 750°C of the most promising catalysts was tested. Four types of results were found:

1. No evaporation, and no deactivation: $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$.

2. No evaporation, but catalyst deactivation: $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$ with $\text{P}_2\text{O}_5$. The fresh catalyst had a low onset temperature, but after being exposed to temperatures of 750°C for 6 h the onset temperature was increased with approximately 75°C, which made the catalyst performance essentially the same as that of $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$. It will be difficult to avoid such temperatures under realistic conditions, for instance, they can be easily reached during a small thermal runaway in the filter.

3. Evaporation, but no catalyst deactivation observed: $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$ and $\text{CsVO}_3\cdot\text{MoO}_3$. These catalysts lost a very low amount of material when exposed to temperatures of 750°C. The amount that was lost was too low to have any effect on the activity.

4. Excessive evaporation: $\text{KVO}_3\cdot\text{KCl}$. This catalyst lost all its KCl, which is unacceptable.

$\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$, $\text{CsVO}_3\cdot\text{MoO}_3$, and $\text{Cs}_2\text{MoO}_4\cdot\text{V}_2\text{O}_5$ are promising catalysts for further development, where $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$ is the most promising one, while it showed no tendency to evaporation at high temperatures. However, because of the restrictions of the test method (see Section 2.3.4) the experiments were conducted without steam. Steam is known to accelerate the evaporation of many materials. In Chapter 6 the stability will be investigated under more realistic conditions with steam. There a more final judgement about the catalyst stability can be made.

The addition of $\text{P}_2\text{O}_5$ seems futile, because it could not resist high temperatures. Nevertheless, because the catalysts that contained $\text{P}_2\text{O}_5$ had such low onset temperatures, it might be worthwhile to investigate the deactivation mechanism in order to verify if the catalyst can be re-activated. A likely explanation for the deactivation at high temperatures is the formation of less reactive cesium or vanadium phosphate compounds; a process which can be studied with XRD. It is doubted if the formation of such compounds can be reversed by some kind of re-activation strategy.

3.4.2 Study of the role of the liquid phase

The formulations of the currently investigated catalysts were selected because of their low melting points. The hypothesis was that if the catalyst is liquid, it can establish a tight physical contact by some kind of wetting process, and by that enforce a high activity at relatively low temperatures. Different experiments were performed to determine if the hypothesis is correct:
effect of physical contact If the catalyst is capable of creating a tight contact distribution out of a loose one, then tight and loose mixtures of catalyst and soot should give similar TPO profiles. This was, however, not the case. The oxidation of tight contact samples occurred at 100 to 150°C lower temperatures than the oxidation of loose contact samples. Such differences were also found for solid catalysts (Figure 1.24).

TGA-SEM Mixtures of catalyst and partially oxidized soot were analyzed with SEM in order to get an impression of the distribution between catalyst and soot during catalytic oxidation. Spheres of 1500 μm were observed that contained all the soot. The spheres also contained gas bubbles, which could be formed by CO and CO₂ formed during soot oxidation or by enclosed air. It is in particular interesting that the soot agglomerates were visible even though the catalyst was given all the opportunity for wetting the soot by placing it on a silica surface for which the catalyst has no affinity. It is clear that the catalyst enclosed the soot, but did not wet the soot because the soot was still visible.

ESEM A complementary in-situ study was conducted with ESEM. Three important observations were done during the study:

1. The catalyst did not wet the soot. Instead it minimized the contact area by forming droplets on top of the soot. Apparently, it had no high affinity for soot.

2. The catalyst was immobile at reaction conditions (temperatures in the range of 300 to 600°C). No channeling-type processes were observed, like was illustrated in Figures 1.18 and 1.19. Apparently, the catalyst can oxidize the soot by some other process.

3. The catalyst melted at a temperature that was predicted by DTA, and formed a smooth sphere. After that, it transformed to a cauliflower-like structure, which melted again at higher temperatures. The reason of this transformation is unknown. It could be caused by a change in the catalyst composition. For instance, Silva et al. [7] showed that V₂O₅ can be reduced by soot. When such reduction in the liquid catalyst leads to the formation of a new eutectic phase with higher melting point, then crystallization could occur. The cauliflower might, therefore, well be a crystallized structure. High-temperature XRD analysis could be of help to determine if such crystallization indeed takes place. It is, however, expected that such measurements are troublesome since the catalyst is molten, because of which it probably does not have a high degree of long-range ordering, which is required for XRD analysis.

Although very active catalysts were prepared, there exists no evidence that the liquid catalyst can overcome the contact problem, or that the liquid state is essential for catalytic oxidation. Furthermore, catalysts that contained P₂O₅ as additive had onset temperatures that were 50 to 100°C below their melting point, which also suggests that the liquid state is not essential.
3.5 Conclusions

- The Cs$_2$SO$_4$·V$_2$O$_5$ liquid catalyst is a promising catalyst for heavy-duty diesel applications. It did not evaporate and performed under simulated conditions at least as good as the commercially applied cerium catalytic fuel-additive.

- The onset temperature of 250°C of the mixed oxide Cs$_2$SO$_4$·V$_2$O$_5$·P$_2$O$_5$ catalysts is a breakthrough in loose-contact soot oxidation at low temperatures. The stability of the current formulations is, however, not high enough to consider them for application.

- The Cs$_2$SO$_4$·V$_2$O$_5$ catalyst is not suitable for continuous catalytic regeneration of a particle filter for passenger cars. Its operation temperature is too high for that.

- The liquid state of the tested soot oxidation catalysts has no decisive influence on their performance. On the contrary all evidence indicates that the catalysts do not wet the soot. The liquid state does not solve the loose contact problem.
BIBLIOGRAPHY

Bibliography


Chapter 4

Screening of Catalyst Supports

An exploratory study has been carried out to find a support for liquid soot-oxidation catalysts. High-temperature, high-strength, low-porous ceramics and conventional catalyst supports were screened, i.e. α alumina, γ alumina, cordierite, diatomaceous earth, silica, silicon carbide, and silicon nitride. When molten, the catalysts can be directly deposited at the external surface of the different supports. Synthetic soot was deposited on the catalyst surface in loose contact, oxidation rates similar to the unsupported catalysts were observed. Important requirements for the interaction between the support and the liquid catalyst are: (1) the catalyst should wet the support, (2) the catalyst should 'anchor' to the support, and (3) the support should keep the catalyst accessible for the soot. Ceramic soot filters themselves might be promising supports for the liquid soot-oxidation catalyst.

4.1 Introduction

In Chapter 3 unsupported liquid soot-oxidation catalysts were screened. It was anticipated that a support for the liquid catalyst will play an important role in further development, because, when an improperly supported liquid catalyst is installed in a canister it might trickle out.

Ceramic materials are selected as support, because molten salts are very corrosive. Simple geometries will be used, because they can be obtained in a wide variety of different compositions. In contrast ceramic particle filters can mainly be obtained as cordierite or silicon carbide. A liquid catalyst will be preferably deposited on the surface of the filter wall, because that is the location where soot deposits. Catalysts with such distribution are known as 'eggshell' catalysts. Soled et al. [1] showed that impregnating a catalyst in its molten state is a good way for preparing such catalysts. Their method will be adapted here for the preparation of supported liquid soot-oxidation catalysts.

In this chapter the following aspects are investigated: potential supports, preparation of eggshell catalysts, the distribution of the catalyst, and the activity of the supported catalysts.

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CHAPTER 4. SCREENING OF CATALYST SUPPORTS

4.2 Experimental

4.2.1 Catalyst preparation

Impregnation of the ceramic grains was carried out in a rotating reactor, as described in Section 2.3.6. By varying the impregnation time the catalyst loading of the support particles was controlled. For a catalyst loading of approximately 10 wt % an impregnation time of 2 h was required. A series of Cs₂MoO₄-V₂O₅/γ alumina particles with varying catalyst loading was prepared. After impregnation the series was treated at 475°C in static air for different periods of time in order to investigate the stability of the catalyst distribution.

The ceramic tiles were sawed into small bricks of 15 x 15 x 5 mm. 10 mg catalyst powder (< 106 μm sieve fraction) was rubbed on the topside of a brick, after which the brick with catalyst was kept at 475°C for 24 h in static air.

4.2.2 Catalyst characterization

The catalyst composition was either determined with flame-AES for the cesium content or ICP-OES for the molybdenum and vanadium content.

The external surface of the particles before and after impregnation was analyzed with SEM analysis. Cross sections of the catalyst particles were made with the method described in Section 2.3.5 in order to determine the interior composition of the catalysts with SEM-EDS analysis.

4.2.3 TPO procedures

Soot deposition

Printex U synthetic soot was deposited on the supported-catalyst particles by adding 800 mg of the particles (impregnated with approximately 80 mg of catalyst) with 40 mg soot to a cylindrical bottle (height 50 mm, diameter 25 mm) that was mixed under ambient conditions with an electrical shaking device at a rotational speed of 400 rpm. In order to verify if a realistic loose contact between the catalyst and soot existed, the oxidation of soot by CsVO₃-MoO₃/α alumina particles was investigated as a function of mixing time, viz. 1, 3, 5, 15, 30, 60, 300, 480, 1440, and 2880 min.

Synthetic soot was deposited on the supported-catalyst bricks by rubbing 5 mg soot on the area where the catalyst had been deposited. The catalyst surface of one brick was partially covered with soot and the brick was analyzed with SEM with a rotated position of the sample holder (angle 55°). The thickness of the deposited soot layer was estimated to be 35 μm.

Oxidation activity experiments

The soot oxidation rate of the supported-catalyst particles was determined using the flow-reactor system described in Section 2.3.1. The reactor tubes were packed with 210 mg of the
4.3. RESULTS

mixture of catalyst particles and soot (200 mg supported-catalyst particles and 10 mg soot). The temperature was raised in argon to the desired reaction temperature of 375 or 425°C. At these temperatures 10 vol % oxygen was introduced. The CsVO_3·MoO_3/α alumina particles that were mixed with soot for different periods of time were also examined with DTA-TGA analysis in synthetic air. A heating rate of 10 °C/min was used. The DTA-TGA sample crucibles were filled with 35 mg of the catalyst-soot mixture.

The supported-catalyst bricks were tested with the high-capacity thermal balance in an isothermal mode, because the bricks did not fit in the reactor tubes of the flow equipment. The bricks were heated to 425°C in nitrogen and at this temperature oxygen was introduced. The weight loss rate was used as a measure for the soot oxidation rate. To verify whether the results, that were produced with TGA, are consistent with the results that were produced with the flow equipment, one of the catalyst samples was tested both with the flow equipment and the high-capacity thermal balance: the results were consistent.

4.3 Results

4.3.1 Catalyst preparation

The catalyst was well anchored to the supports, except for the silica oxide, nitride and carbide particles: the silica particles were not wetted during impregnation, and the catalyst detached from the silicon carbide particle during soot oxidation experiments and contaminated the flow reactor equipment. The catalyst had a high affinity for the α alumina brick with a smooth surface. The catalyst did, however, not anchor to the area where it was originally deposited: it crept all over the brick and it detached partially from the brick by the formation of drops of liquid catalyst at the underside of the brick. It was estimated that only 15 % of the catalyst was still on the topside.

The impregnation of the other supports was more successful. By visual inspection of cut supported-catalyst particles it was found that the (yellow) catalyst was mainly located near the external surface. Figure 4.1 shows the results of a SEM-EDS analysis of the region near the external surface of a 2.5 wt % Cs_2MoO_4·V_2O_5/γ alumina particle. In this figure the Al and V signals are given. The Mo and Cs signals (not presented) were similar to the V signal. The catalyst was located at the external surface of the support in a layer of approximately 3 μm thick, where it remained even after heating for a week at 475°C in air. Figure 4.2 shows SEM images of the external surface of γ alumina particles: a, not impregnated with catalyst; b, impregnated; and c, impregnated with additional treatment at 475°C for 48 h. The surface of the impregnated particles is smoother than the surface of the particles that were not impregnated: it seems that the liquid catalyst filled the irregularities in the surface. The external surface of the impregnated γ alumina particles that were additionally treated at 475°C for 48 h is very similar to the surface of the particles that were not impregnated: it looks like the liquid catalyst penetrated the support during this additional heat treatment.
Figure 4.1: SEM-EDS analysis of the location of CsVO$_3$-MoO$_3$ (2.5 wt %) supported by a γ alumina particle: a, image of a cross section of supported catalyst in which the position of the line scans in Figure b has been given; b, EDS signal for aluminum and vanadium as function of the position on the line scan. The vanadium signal is also representative for cesium and molybdenum.
Figure 4.2: Images of the surface of γ alumina:
a, without catalyst;
b, impregnated with CsVO₃-MoO₃;
c, impregnated and additional treatment of 48 h at 475°C in air.
4.3.2 Type of contact between catalyst and soot

After mixing of the catalyst and soot up to 15 min, supported-catalyst particles covered with soot and separate unattached soot could easily be distinguished visually. Figure 4.3 shows SEM images of supported-catalyst particles covered with soot that had been mixed for 1 and 60 min. The large lumps of 500 to 800 \( \mu \text{m} \) are supported-catalyst particles, on which soot has been deposited. The soot layer on the particles that were mixed for 1 min looks more fluffy (Figure 4.3 a) than the soot layer on the particles that had been mixed for 60 min which looked smooth and very compact (Figure 4.3 b).

Figure 4.4 shows DTA and isothermal flow reactor activity measurements of samples with different mixing times. The profile of the heat flow was similar for all samples up to 560°C (Figure 4.4 a). At 360°C an endothermal process was observed which was ascribed to melting of the catalytic phase (indicated with an open circle in the figure). The heat production from approximately 360 to 560°C is ascribed to the catalytic oxidation of soot. The samples that had been mixed for less than 15 min also showed oxidation in the range of 560 to 620°C, which is ascribed to non-catalytic oxidation of soot, while it is known that \( T_{\text{max, rate}} \) of the non-catalytic oxidation of Printex U at a heating rate of 10°C/min in synthetic air occurs in that temperature region [2]. The soot of the samples that were mixed for 1 and 5 min was partially converted during the flow-reactor experiments at 425°C (Figure 4.4 b). The catalytic oxidation reaction essentially stopped at 70% conversion. The reaction was completed when the reactor was heated to 625°C. The rates of the samples that were mixed for 1 and 5 min are lower than the rates of the samples that were mixed for a longer time (Figure 4.4 b). This not caused by actual differences in activity, but by the normalization to the amount of soot initially present in the reactor. The plots can be coincided when the rates and conversion in Figure 4.4 b are normalized to the amount of soot that was combusted catalytically (not shown).
4.3. RESULTS

Figure 4.4: Characterization of the type of contact of a series of CsVO$_3$·MoO$_3$ (15 wt %)/α alumina particles/soot mixtures that were mixed for different periods of time: a, heat flow as function of temperature as measured with DTA, heating rate 10°C/min, synthetic air, the open circles indicate the endothermic melting process of the catalyst; b, oxidation rate at 425°C in 10 vol % O$_2$ as function of conversion as measured in a flow reactor.
4.3.3 Catalyst activity

The soot oxidation rates of the supported-catalyst particles and catalytic ceramic bricks are given as function of conversion in Figure 4.5.

Figure 4.5: Soot oxidation rate at 425°C in 10 vol % O₂ as function of catalyst support: a, CsVO₃·MoO₃ and Cs₂MoO₄·V₂O₅ supported by different ceramic particles; b, Cs₂MoO₄·V₂O₅ supported by different ceramic bricks.

Oxidation rates in the range of 50 to 150 μg/g_initial/s were observed, which are in the same order of magnitude as were found for the unsupported catalysts.

Figure 4.6a shows the soot oxidation rate at 425°C as function of conversion of a series of 2.5 wt % CsVO₃·MoO₃/γ alumina particles that had been heat treated for different periods of time. During the heat treatments no mass loss was observed. The oxidation rate of the sample that had not been heat treated was the highest. It declined with increasing treatment time, but stabilized between 4 and 8 h of heat treatment. This effect of heat treatment on the oxidation rate was also found for the other types of support particles. Figure 4.6b shows the soot oxidation rates at 425°C as function of conversion of a series of CsVO₃·MoO₃/γ alumina particles that had been prepared with varying catalyst loading, and were kept at 475°C in air for 48 h in order to stabilize the catalyst distribution. The oxidation rate depended positively on the catalyst loading, but decreased by the thermal treatment. However, supported-catalyst particles with a higher loading were relatively less affected by the thermal treatment.
4.3. RESULTS

Figure 4.6: Oxidation rate at 425°C in 10 vol% O₂ as function of catalyst loading and high-temperature treatment time: a, soot oxidation rate of Cs₂MoO₄·V₂O₅ (2.5 wt %)/γ alumina particles, that have been heated in air at 475°C for different periods of time; b, oxidation rate of a series of Cs₂MoO₄·V₂O₅/γ alumina particles with varying catalyst loading and treated at 475°C in air for 48 h.
4.4 Discussion

4.4.1 Supports for the liquid catalyst

The catalysts have been deposited on the external surface of the supports: the location where soot would deposit on under practical conditions. The catalysts showed no or a low affinity for silicon carbide, nitride and oxide particles. Figure 4.7 a shows an illustration of the situation that occurs: droplets are formed that roll off due to for instance gravity.

Figure 4.7: Illustrations of different possible distributions of a supported liquid catalyst: a, no affinity \(\rightarrow\) catalyst forms droplets ; b, affinity, smooth surface \(\rightarrow\) catalyst spreads completely and may even detach; c, affinity, rough external surface \(\rightarrow\) catalyst finds stable distribution in the irregularities of the surface; d, affinity, porous support \(\rightarrow\) a fraction of the catalyst may find a stable distribution inside pores, that fraction may be difficult to access for soot.

Affinity for the support is an important requirement for a stable catalyst distribution. In the case that the liquid catalyst shows affinity for the support, it wets the support and creeps all over, showing no adhesion to the location where it was originally deposited (see Figure 4.7 b for an illustration). Such wetting process was in fact already shown in Figure 3.8. In that figure the catalyst was placed on an \(\alpha\) alumina crucible, which surface was identical to the surface of the smooth \(\alpha\) alumina brick used here. In Figure 3.8 a the large dark area is wetted by catalyst and the light area on the right side of the image is alumina that is not wetted yet. During the experiment the complete crucible was wetted by the catalyst, including the underside. This tendency of liquid metal oxides to creep over nonporous alumina was also observed by Hayden et al. [3]. They observed that MoO\(_3\) spreads over nonporous alumina and attributed it to a strong oxide-oxide interaction. Silva et al. [4] did not find such interaction between MoO\(_3\) and silica, which agrees with the observation of the low interaction of molten salt catalysts with silica made here. A high affinity for a support is an important requirement for a liquid catalyst, but the high affinity should not result in a catalyst that spreads over the surface of the support completely. In a practical application a spreading catalyst would migrate out of the filter and corrode the exhaust pipe or it would be emitted. Fortunately, the liquid catalyst 'anchors' on supports with a rough external
4.4. DISCUSSION

surface (see Figure 4.7 c for an illustration). The rough surface probably eliminates creeping by providing a situation with a favorable total free surface energy \( (G_s) \). Of course more distributions probably exist with a favorable total free surface energy, but it is known that supported liquid-phase catalysts have an infinite number of distributions satisfying \( dG_s > 0 \), because of which the ultimate distribution depends on where the liquid has been introduced to the support [5], which is in this case on the external surface.

4.4.2 Type of contact between catalyst and soot

Oxidation rates measured with synthetic soot are only representative when the synthetic soot is distributed on the catalyst in a realistic manner. Nceft defined this manner as loose contact for laboratory preparations (Section 1.5.2). For unsupported catalysts, mixing soot and catalyst powder with a spatula will create loose contact. For supported catalysts simply mixing with a spatula is not sufficient since here the soot should not only be mixed with the catalyst, but also deposited on the catalyst surface. Therefore, new ways of loose contact soot deposition had to be developed.

Soot has been deposited on the supported-catalyst particles by mixing in a shaking device. With DTA-TGA and flow reactor analysis it was observed that the catalytic oxidation of soot is not influenced by the mixing time. Therefore, the physical contact between soot and catalyst was loose. For the samples that were mixed less than 15 min it was observed that not all soot was deposited on the catalyst surface, which is an unwanted situation, because it resulted in incomplete catalytic oxidation of soot. To ensure that all soot is deposited on the supported-catalyst particles the mixing time in the shaking device should exceed 15 min.

The soot was deposited on the supported-catalyst bricks by gently rubbing. The resulting soot layer was approximately 35 \( \mu \)m thick, which is a large distance in terms of catalytic soot oxidation. This indicates a loose physical contact, because the distances in tight-contact catalytic soot oxidation are in the sub-micron range [2].

4.4.3 Catalyst performance

The difference in soot oxidation rates between the supported and unsupported catalysts is probably not caused by changes in the intrinsic activity of the catalyst. A more likely cause is the different soot distribution over the supported catalysts compared to the unsupported catalysts. The differences in activity between the supported catalysts themselves are most probably not caused by the different chemical nature of the supports. Interactions between catalyst and support are normally found for catalytic sites with distances between catalytic phase and support in the range of atomic dimensions [6]. In the present catalysts the catalyst layer is at least several micrometers thick, which is a large distance in terms of such interactions. The differences in activity are, besides the small differences in catalyst loading, probably caused by the differences in texture and morphology of the supports. It is possible that some supports insulate the catalyst more from the soot than others, which might have its influence on the measured soot oxidation rate. For instance the catalytic \( \alpha \) alumina brick with a smooth surface had a higher activity than the rough catalytic \( \alpha \) alumina brick. Also
catalysts that were heated again after impregnation became less active and did not show a maximum in the oxidation curve: maybe the liquid catalyst penetrated the support a bit deeper during re-heating, because of which it becomes less accessible for the deposited soot (see Figure 4.7 d for an illustration). This support penetration process should be well controlled. A possible way to suppress it might be the use of a support with a very low pore volume, and a rough surface, in combination with a high catalyst loading.

The discrimination between the different porous particles and the ceramic bricks only on basis of the determined soot oxidation rates is cumbersome. The current differences in activity are not large enough to justify the exclusion of some of the supports from further investigation. Due to the small differences in activity other aspects can be taken into account. Internal surface area is thought to be unimportant for the catalyst, which means that a high surface area washcoat is not required. This also means that a filter which is prepared of the appropriate ceramic material can act as support itself.

4.5 Conclusions

- Supported liquid soot-oxidation catalysts with a stable distribution and activity can be prepared by directly impregnating the support with molten catalyst. The catalytic phase is concentrated at the external surface of the support, the location where under practical, realistic conditions diesel soot would deposit on.

- At least three requirements should be fulfilled to prepare a supported liquid-catalyst with a stable configuration: (1) the catalyst should have affinity for the support by means of strong oxide-oxide interaction in order to wet it; (2) the wetted support should enforce a stable liquid distribution, for which an irregular external surface seems to be a good choice; and (3) the support should stabilize the catalyst in such a way that the catalyst remains accessible for the deposited soot, for which low-porous ceramic materials seems a good choice.

- Low-porous, high-temperature, high-strength ceramics are very promising supports for the liquid soot-oxidation catalyst. This makes the surface of ceramic filters itself suitable.

- Alumina, cordierite, and diatomaceous earth showed good support properties, while silicon carbide, silicon oxide and silicon nitride are inadequate.

- The activity of fresh supported catalysts decreases to a constant value when treated at high temperatures.

- The activity of supported catalysts is a function of the loading of the catalyst phase.
Bibliography


Chapter 5

Catalytic Filters\textsuperscript{1}

Ceramic filters were tested as support for liquid soot-oxidation catalysts. Ceramic foam seems most suitable to act as support. The catalytic foam filters have a first-order oxidation-rate dependency in the soot, catalyst, and molecular oxygen concentration; and CO, NO, and hydrocarbons are not oxidized. Based on these considerations a model equation was formulated to convert TPO data to an estimated 'real world' performance. The estimated performance seems not yet adequate for continuous regeneration strategies for most current diesel engine technologies. An engine bench study should be performed to determine if the estimated performance is correct.

The liquid catalysts are thought to operate according to a spillover oxidation mechanism. An important implication of this mechanism might be that it could limit further optimization.

5.1 Introduction

In Chapter 4 it was predicted that liquid soot-oxidation catalysts can be supported by a bare ceramic filter without a washcoat. In this chapter this hypothesis will be verified. It was decided to test two different filter types: the wall-flow monolith, which is a surface filter; and ceramic foam, which is a deep-bed filter. From many perspectives the wall-flow monolith is the preferred filter, especially because of its high filtration efficiency over the complete range of diesel particle sizes, including the highly undesired nanoparticles. However, in order to have surface filtration the gas has to pass through the porous filter surface, and this process might be difficult when a catalyst is deposited on top of the filter surface (Section 1.6.1). In the case of a liquid catalyst it can be anticipated that the catalyst might block the pores or that the exhaust gas pushes the catalyst to the other side of the filter wall. In that respect ceramic foam seems to be more promising, because its open-pore structure should be less susceptible for blockage by a deposited catalyst.

In this chapter ceramic foam and wall-flow monolith filters will be evaluated as support for the liquid soot-oxidation catalyst. Different impregnation methods will be tested.

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The performance of the catalytic filters will be evaluated by measuring the oxidation rate of deposited synthetic soot with micro-flow reactor equipment. The basic kinetics will be evaluated to formulate a simple kinetic model that will be used to convert the activity derived from the flow reactor equipment to an estimated 'real world' performance. Further, the oxidation mechanism and its implications will be discussed.

5.2 Experimental

5.2.1 Filter selection

Different major ceramic foam producers were contacted for supplying samples: Foseco (Germany), Porvair Advanced Materials/Selee (USA), and Ceraplast (France). Alumina, cordierite, and mullite open-pore foams with pore sizes in the range of 15 to 40 pores/cm were requested: pore sizes in this range should give a compromise between filtration efficiency and pressure drop [1–3]. Only silicon carbide foam was commercially available in a wide range of characteristics. Unfortunately, it is not compatible with the liquid catalysts (Chapter 4). Initially only Porvair Advanced Materials could prepare special samples by request, and the choice was limited to 20 pores/cm alumina and zirconia-toughened mullite (ZTM). Later during the study 18 pores/cm zirconia-toughened alumina (ZTA) was made available by Ceraplast.

Corning (USA) and NOTOX (Denmark) were contacted for supplying wall-flow monolith filters. NOTOX supplied silicon carbide filters, and Corning supplied cordierite EX-80 filters. The silicon carbide filters were not investigated due to the incompatibility with the liquid catalysts.

Filters of the appropriate size were prepared by sawing with high-precision diamond saws. The channels of the prepared wall-flow monoliths were plugged. The details of procedures can be found in Section 2.2.2.

5.2.2 Preparation of catalytic filters

Catalytic foam In Chapter 4 grains and flat bricks were impregnated with relative ease, because their external surface could be easily reached. The surface of a filter is more complex, because it is contained within the filter body. Alternative methods were evaluated to deposit the liquid catalysts on 20 pores/cm alumina ceramic foam (diameter 7 mm, length 25 mm) and 20 pores/cm mullite foam (diameter 25 mm, length 30 mm) for testing with the flow-reactor equipment.

Two impregnation methods were tried for the preparation of catalytic foams. In the first method catalytic foams were prepared by dipping foam cylinders directly into the liquid catalyst at 450°C. The excess catalyst was removed from the saturated foam by blowing pressurized air through the pore structure at 450°C for 5 h. The removal of the excess catalyst by means of gravity was also included. The saturated foam was kept at 450°C in air on top of a bed of γ alumina absorbent particles for 4 to 48 h until the liquid catalyst stopped trickling out of the foam cylinder. In the second method catalyst powder was distributed
5.2. EXPERIMENTAL

evenly over the filter surface before impregnation. Impregnation was carried out by keeping the foam and catalyst powder at 450°C in air for 100 h. Two methods were tried to distribute the catalyst powder evenly over the filter surface:

- Oxalic acid powder (< 250 μm sieve fraction) was mixed with catalyst powder (< 106 μm sieve fraction). 25 ml of the powder mixture and a foam cylinder were placed into a 30 ml sample bottle. The closed sample bottle was treated in an ultrasonic transducer tank for 1 h to allow penetration of the foam pores. Oxalic acid powder was only used as diluent; it was selected because it is solid at room temperature and it can be removed by combustion.

- Catalyst particles were deposited on foam by filtration from a suspension. The procedure is slightly similar to a method that was used by Hartwig and Chatham [4]. The details of the procedure can be found in Section 2.3.6.

Catalytic wall-flow monolith The small wall-flow monoliths (diameter 25 mm, length 40 mm) were impregnated with liquid catalyst. Before impregnation the catalyst was distributed through the monolith channels as a powder. The loading was controlled by diluting the catalyst powder with oxalic acid powder. An oxalic acid:catalyst ratio of 7:1 was used to obtain a catalyst loading of 40 g\textsubscript{catalyst}/l\textsubscript{monolith}. The powder was forced into the channels by placing the monolith vertically in a plastic pipe, with the powder mixture on the top. The channel entrances on the down side were plugged with aluminum foil to avoid that catalyst powder entered on that side. The pipe was placed into an ultrasonic transducer tank for 10 min to fill the monolith channels with the powder mixture. After filling the monolith channels with the powder the monolith was placed horizontally in an oven and calcined in air; the temperature was raised from room temperature to 450°C at a rate of 5°C/min. After impregnation the aluminum foil plugs were removed. Two alternative methods were tried to avoid that the catalyst would only impregnate one side of the square channels. In the first method the monolith was slowly rotated in the rotating reactor described in Section 2.3.6, but it proved to be difficult to align the sample perfectly horizontal, which caused that the catalyst was mainly located near the channel entrances. The second method gave the best results, in this method the powder mixture was diluted to an oxalic acid - catalyst ratio of 28:1, and the impregnation procedure was four times repeated, during each time another side of the channels was placed under.

Pt/γ alumina 1 wt % platinum supported by γ alumina grains was prepared by pore volume impregnation. Akzo Nobel 003-1.5e γ alumina (grain size 63 to 100 μm) was impregnated with dissolved tetraammmineplatinum chloride. The impregnated catalyst was dried at 80°C for 2 h and then heated with 0.5°C/min to 450°C in air where it was kept at for 2 h.

5.2.3 Soot deposition on catalytic filters

For evaluation of the catalytic foams a realistic laboratory soot deposition method was required. Both a realistic method, and a more convenient method were evaluated. These
were modifications of the methods used by Inui et al. [5]. The realistic method was based on filtration from a soot aerosol. The procedure was described in Section 2.3.6. The convenient method was based on impregnation: 1.5 mg soot was mixed with 50 ml heptane for 24 h, then ceramic foam was immersed in the dispersion for 1 min, and dried for 1 h at 70°C.

5.2.4 Testing of catalytic filters under simulated realistic conditions

The catalytic foams were tested with the flow-reactor equipment that was described in Section 2.3.1. For isothermal experiments the temperature was raised to 375°C in a 200 ml/min argon (GHSV 12,500 1/l/h) flow, and at 375°C 10 vol % oxygen was introduced. For temperature programmed experiments the temperature was raised at a rate of 0.2 or 1°C/min in 200 ml/min 10% O₂ in argon. Different experiments were conducted:

- The influence of the two different soot deposition methods of Section 5.2.3 was studied.

- The influence of the oxygen concentration on the soot oxidation rate was studied in the range of 5 to 15 vol % oxygen. These are typical diesel exhaust gas oxygen concentrations (Table 1.3).

- The influence of the catalyst’s impregnation time on the soot oxidation rate was studied. Impregnation times of 3, 4, 24, 100, 336, and 720 h were used.

- The influence of catalyst loading on the soot oxidation rate was studied. A series of catalytic foams with loadings in the range of 0 to 80 gcat/loam was tested.

- The influence of NO on the soot oxidation rate was studied. The performance of Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ was compared with 50 mg 1 wt % Pt/γ alumina (the platinum catalyst was placed upstream of the soot). A representative NO concentration of 500 ppm was used (Table 1.3). During these experiments O₂ was introduced at the reactor entrance, instead of in the gas mixing chamber in order to minimize NO₂ formation before the reactor as was explained in Section 2.3.1. The NO and NO₂ concentrations were monitored with a chemiluminescence NOₓ analyzer.

- The oxidation of CO and propene (representative for hydrocarbons in exhaust gas) by Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ catalytic foams was measured. 50 mg 1 wt % Pt/γ alumina catalyst was tested for comparison. The catalysts were studied with TPO at a heating rate of 1°C/min in the presence of 500 ppm CO, 800 ppm propene, and 10 vol % oxygen.

- The performance of 90 gcat/loam Cs₂SO₄·V₂O₅ on zirconia-toughened mullite foam was determined with synthetic soot in order to make a comparison with the combustion of real diesel soot in Chapter 7. The TPO procedure was identical as for the above experiments. The only differences were that a reactor with a diameter of 25 mm and a flow rate of 800 ml/min were applied.
5.3 Results

5.3.1 Catalyst preparation

Impregnation by means of dipping foams into liquid catalyst led to completely saturated samples. It took days at high temperatures to remove a part of the excess amount of catalyst from the saturated foam. Attempts to blow the excess amount of liquid catalyst out of the foam were neither successful: during TPO catalyst droplets trickled out of the foam and contaminated the equipment. The dipping method was abandoned in further research. Suitable samples were prepared with the other method, where before impregnation catalyst powder mixed with oxalic acid powder was distributed through the foam. Homogeneous catalytic foams with a wide range of catalyst loadings were prepared. Attempts to impregnate cylindrical foams with diameters larger than 10 mm with this method were less successful. The powder mixture penetrated only 5 mm into the outer layer of the foams, which led to an inhomogeneous catalyst distribution. The method where catalyst powder was distributed throughout the foam by filtration was more successful in this respect.

The preparation of catalytic wall-flow monoliths based on cordierite was not successful. It was aimed for to deposit the catalyst on one side of the porous filter walls. However, the walls turned out to be transparent for the catalyst. The catalyst distributed throughout the complete filter structure. Most catalyst was present inside the monolith walls. (Some engine experiments were performed during which the catalyst distribution even worsened.)

5.3.2 Type of contact between catalytic filters and soot

Synthetic soot was deposited on the catalytic foams by both impregnation of dispersed soot and filtration from an aerosol. The soot loading could be controlled by varying the soot concentration of the dispersion or by varying the amount of aerosol that was passed through the foams. It was chosen to use a loading of 10 gsoot/gfoam, because loadings in this order of magnitude have been reported for wall-flow monolith filters (Figure 1.31). Figure 5.1 a shows the activity at 375°C as function of the conversion of soot that had been deposited on catalytic foams by both deposition techniques. Both methods resulted in identical oxidation rates. Apparently, the degree of physical contact was the same. In the range of 10 to 80% conversion a linearly decreasing oxidation rate was measured, which indicated a reaction order in soot of 1. Only oxidation rates in the range of 10 to 80% conversion were plotted, because in that region the conditions were constant. At low conversions typically very high oxidation rates were observed which occurred at the moment when oxygen was introduced. This is in agreement with observations of Neeft et al. [6] who found high oxidation rates in the first 10% conversion of Printex-U which they attributed to the more reactive parts of the soot (e.g. hydrocarbons). They omitted the first 10% from the calculation of reaction parameters. Rates above 80% conversion were not plotted, because they were not measured at isothermal conditions: the experiments were fully automated: after a pre-programmed time at 375°C the temperature was automatically raised to 625°C to oxidize the remaining soot in order to verify the carbon mass balance, which happened in this case at 80 % conversion.
Figure 5.1: Soot oxidation rates measured for 50 g\textsubscript{catalyst}/l\textsubscript{foam} Cs\textsubscript{2}SO\textsubscript{4}•V\textsubscript{2}O\textsubscript{5}/\alpha aluminia at 375°C in 10 vol % O\textsubscript{2}: a, oxidation rate in the presence of 10 vol % oxygen as function of conversion for catalytic foams on which synthetic soot was deposited by filtration or impregnation; b, oxidation rate at 30% soot conversion as function of oxygen concentration.
5.3.3 Influence of the oxygen concentration

Figure 5.1 b shows the oxidation rate at 30% conversion as function of the oxygen concentration. The oxidation rate increased linearly with the oxygen concentration, which indicates a reaction order in oxygen of 1.

5.3.4 Influence of catalyst impregnation time

Cs$_2$SO$_4$·V$_2$O$_5$ catalytic foams were heated at 450°C for different time periods during impregnation. Figure 5.2 a shows the oxidation rates of these foams at 30% conversion as a function of the impregnation time.

![Figure 5.2: Soot oxidation rates of catalytic foams at 375°C in the presence of 10 vol % oxygen: a, activity at 30% conversion as function of impregnation time at 450°C, 50 g$_{\text{catalyst}}$/l$_{\text{foam}}$ Cs$_2$SO$_4$·V$_2$O$_5$/α alumina; b, activity at 30% soot conversion as function of catalyst loading, Cs$_2$SO$_4$·V$_2$O$_5$/α alumina.](image)

For the Cs$_2$SO$_4$·V$_2$O$_5$ foam that was kept at 450°C for 3 h a rate of 13 μg/g$_{\text{initial}}$/s was observed. The rate decreased to a stable value of approximately 9 μg/g$_{\text{initial}}$/s by increasing the impregnation time to 100 h at 450°C.
5.3.5 Influence of catalyst loading

Figure 5.2 b shows the soot oxidation rate at 30% soot conversion as a function of the catalyst loading of Cs$_2$SO$_4$·V$_2$O$_5$ catalytic foams that were impregnated for a period longer than 100 h. A soot oxidation rate of 5 μg/g$_{\text{initial}}$/s was observed at a loading of 10 g$_{\text{catalyst}}$/l$_{\text{foam}}$. The rate increased linearly when the catalyst loading was increased. The rate was 14 μg/g$_{\text{initial}}$/s at a loading of 80 g$_{\text{catalyst}}$/l$_{\text{foam}}$. Some parallel experiments were conducted with CsVO$_3$·MoO$_3$ to verify if this catalyst shows a similar trend. The reference experiments with CsVO$_3$·MoO$_3$ catalytic foams showed the same effect of pre-treatment time on the activity of the catalytic foam as for the Cs$_2$SO$_4$·V$_2$O$_5$ foams. The CsVO$_3$·MoO$_3$ loading had like the Cs$_2$SO$_4$·V$_2$O$_5$ loading a positive effect on the oxidation rate, but not enough points were measured to determine if the dependency is linear.

5.3.6 Influence of NO

NO oxidation is essential in NO$_x$-aided CRT for maintaining a high soot oxidation rate (Section 1.7.2). The catalytic foams were designed to oxidize soot directly with O$_2$, but they might benefit substantially from the presence of NO. In order to verify if there is a benefit the catalysts were tested in the presence of NO. Figure 5.3 a shows the amount of NO$_2$ formed by Cs$_2$SO$_4$·V$_2$O$_5$/α alumina foam, CsVO$_3$·MoO$_3$/α alumina foam and Pt/γ alumina; and the NO$_2$ equilibrium concentration, calculated in Appendix A, page 187. The platinum catalyst started to oxidize NO at approximately 225°C, and from that temperature the concentration increased until a maximum was reached at 480°C. At higher temperatures the NO$_2$ concentration decreased due to the unfavorable chemical equilibrium. This NO$_2$ dependency is typical for NO oxidation over platinum; Cooper and Thoss [7] reported similar behavior. In contrast to platinum, the liquid catalysts did not oxidize NO below 400°C.

Figure 5.3 b shows the rate of the oxidation reaction catalyzed by Pt/γ alumina and Cs$_2$SO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$ supported by alumina foam with and without the presence of 500 ppm NO. The platinum catalyst clearly benefited from NO, because in the presence of it soot oxidation took place at 100°C lower temperatures. This performance is not the maximum capability of platinum, for instance it may be improved by increasing the amount of NO oxidation. That was, however, not the goal of the research; platinum was only used for comparison reasons. For further reading about this type of catalysis is referred to Cooper and Thoss [7] and to Jelles [8].

The catalytic foams did not benefit from the presence of NO, which is in agreement with the observations made in Figure 5.3 a.

5.3.7 Oxidation of CO and hydrocarbons

Figure 5.4 shows the CO and propene conversion by Pt/γ alumina and Cs$_2$SO$_4$·V$_2$O$_5$ catalytic foam as function of temperature. The platinum catalyst oxidized all CO and hydrocarbons from 225°C, which is in the expected temperature range (Section 1.7.1). The liquid catalysts did not show any significant activity.
Figure 5.3: Performance of Cs$_2$SO$_4$·V$_2$O$_5$/$\alpha$ alumina (60 $g_{\text{catalyst}}/l_{\text{foam}}$), CsVO$_3$·MoO$_3$/$\alpha$ alumina (60 $g_{\text{catalyst}}/l_{\text{foam}}$) and 50 mg $1$ wt.$\%$ Pt/$\gamma$ alumina in the presence of 500 ppm NO and $10$ vol.$\%$ O$_2$ measured with a heating rate of $1$°C/min: $a$, NO$_2$ concentration as function of temperature, no soot was present; $b$, soot oxidation rate as function of temperature.
5.4 Discussion

5.4.1 Preparation of catalytic filters

In Chapter 4 grains and bricks were impregnated directly with the liquid catalyst. This impregnation method has been adapted for the impregnation of ceramic foam and wall-flow monolith filters. Impregnation by dipping foam in liquid catalyst failed. The channels in the foam were completely filled with catalyst, and the excess catalyst was hard to remove. These catalytic foams emitted much liquid catalyst during experimentation in the flow-reactor equipment. The dipping method was abandoned from further investigations. Impregnation of foam by forcing a powdered mixture of catalyst and oxalic acid particles into the foam channels and subsequently calcination in air is a method that is well suited for the preparation of catalytic foams for lab-scale kinetic experiments. The method is easy to perform and produces homogeneous catalytic foams with adjustable, reproducible catalyst loading. The disadvantage of the method is that it can only be applied on small foam pieces. Also ultrasonic sound waves were tried for transporting the powder deep into the foam channels, but they were muffled by the foam structure. More mechanical energy will be required if the powdered mixture has to be transported over a longer distance. It is expected that the mechanical energy needed for forcing the powder mixture into a foam filter of, for instance, 2 l is too high for the foam to absorb without damage. Therefore, no attempts were made for optimization and scaling up. Filtration of suspended catalyst powder and subsequently calcination is more promising for scaling up. Parameters that can be further optimized are: the type of liquid, particle size distribution, flow rate, design of stirrer and vessel. For the
present research the current procedure will be sufficient.

The preparation of a catalytic monolith was not successful. The catalyst distributed throughout the monolith, instead of on the filter surface. This catalyst distribution will probably lead to an very inefficient catalyst use.

5.4.2 Type of contact between catalytic filters and soot

Soot oxidation rates determined under laboratory conditions with synthetic soot can only be representative when the soot is distributed on the catalyst in a realistic manner. Neef et al. determined that realistic contact is loose (Section 1.5.2). A closer, less realistic contact, defined as 'tight contact' is often encountered in literature and can be created by exerting physical force by means of a mortar or ball mill during the preparation of the mixture of catalyst and soot.

For unsupported catalysts, mixing soot and catalyst powder with a spatula will create loose contact. In Chapter 4 soot was deposited in loose contact on grain supports by mixing for a period of time, and on flat ceramic surfaces by rubbing. These methods are not applicable on ceramic foams supports. Ceramic foams have a complex structure, which means that the available area for depositing soot is difficult to access. Soot was deposited on catalytic foams by filtering synthetic soot from an aerosol at a realistic superficial gas velocity. The contact that is created with this method will be approximately similar to the contact that would be encountered in diesel exhaust gas. This deposition method proved to be useful, but it is laborious. A more simple soot deposition method was aimed for. Therefore, the deposition by impregnation of soot dispersed in heptane was examined. This method proved to be fast, easy to perform and reproducible. The oxidation rates found for this method are similar to that of synthetic soot filtered on catalytic foam. Therefore, the oxidation rates of impregnated soot can be considered realistic.

5.4.3 Basic properties of catalytic filters

The catalysts supported by ceramic foam have initially a high activity, which stabilizes during heat treatment to a lower, but constant level which depends positively on the catalyst loading. A constant soot oxidation rate has been observed for catalytic foams that were impregnated for longer than 100 h. The oxidation rate was even stable after 720 h of heat treatment. This effect was also observed in Figure 4.6 a; there it was tentatively concluded that after heating less catalyst was present on the external surface of the pore walls, which caused the observed lower oxidation rates.

5.4.4 Catalyst performance in different gas atmospheres

The performance of the catalyst in different gas atmospheres was studied. The results were quite clear: the liquid catalysts do not oxidize CO, hydrocarbons, and NO, at the relatively low space velocity of 12,500 1/h. The space velocity in a reasonable sized filter will probably be higher (for comparison diesel oxidation catalysts have space velocities of
50,000 to 300,000 l/l/h, Section 1.7.1), which will make the conversions even lower. For the application of the catalytic foam it means that additional (platinum) catalyst functionality will be required when also the CO and hydrocarbon concentrations need to be lowered for legislation requirements.

5.4.5 'Real world' performance

In this and the previous chapters the activity of catalysts was determined with synthetic soot as reactant, and the results were reported as TPO plots. In Chapter 7 Cs₂SO₄·V₂O₅ supported by 20 pores/cm zirconia-toughened mullite will be tested in diesel exhaust gas. The current TPO plots have to be translated to 'real world' data if they are to be compared with the results from the engine bench.

**Kinetic data** The Cs₂SO₄·V₂O₅ catalytic foam that will be used in Chapter 7 was tested with TPO. Figure 5.5 shows the TPO plots of non-catalytic and catalytic oxidation.

![Graphs showing oxidation rate and conversion](image)

Figure 5.5: Measured and modeled oxidation rate of Printex U synthetic soot as function of temperature, 0.2°C/min, 10 vol % O₂: a, non-catalytic soot oxidation; b, catalytic soot oxidation, 90 g\textsubscript{catalyst}/l\textsubscript{foam} Cs₂SO₄·V₂O₅/mullite foam, initial soot loading 14 g\textsubscript{soot}/l\textsubscript{foam}.

The figure also shows the modeled oxidation rates which were calculated using a general kinetic model (Equation 1.2), with the Arrhenius equation (Equation 1.3) to account for...
the temperature dependent reaction constant $k(T)$, and a $n^{th}$ order model (Equation 1.7) to account for the amount of soot present. $n_x$ was set to 1, since it was observed in Figure 5.1 a that the oxidation rate had a first order dependency for the soot conversion. The following model equation was used:

$$ r = k' e^{-\frac{E_a}{RT}} \cdot (1 - x) $$  

(5.1)

where $k'$ is a generic pre-exponential factor. The parameters $k'$ and $E_a$ were fitted with a least squares fit using the parameter fitting software package *Scientist* [9]. Data of the conversion range of 0.1 to 1 was used, the data of the range of 0 to 0.1 was omitted because in this part adsorbed hydrocarbons are oxidized. (Neeft et al. [6] omitted this part for the same reason in the modelling of the oxidation of Printex U soot.) The calculated curve fitted the measured data accurately. Table 5.1 shows the calculated kinetic parameters for the non-catalytic and catalytic oxidation of synthetic soot.

**Table 5.1:** Kinetic parameters of non-catalytic and catalytic (C$_2$SO$_4$-V$_2$O$_5$/mullite foam) synthetic soot oxidation. Data from Figure 5.5; model equation, Equation 5.1.

<table>
<thead>
<tr>
<th>Oxidation type</th>
<th>$E_a$ (kJ/mol)</th>
<th>s</th>
<th>95% CI</th>
<th>$k'$ (s$^{-1}$)</th>
<th>s$^{-1}$</th>
<th>95% CI</th>
</tr>
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<tbody>
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<td>Non-catalytic</td>
<td>168</td>
<td>1.9</td>
<td>164-172</td>
<td>2.3 $\cdot$ 10$^7$</td>
<td>0.69 $\cdot$ 10$^7$</td>
<td>1.0 - 3.7 $\cdot$ 10$^7$</td>
</tr>
<tr>
<td>Catalytic</td>
<td>166</td>
<td>2.5</td>
<td>161-171</td>
<td>2.6 $\cdot$ 10$^8$</td>
<td>1.10 $\cdot$ 10$^8$</td>
<td>0.4 - 4.8 $\cdot$ 10$^8$</td>
</tr>
</tbody>
</table>

$s$, standard deviation; CI, confidence interval.

**Case study**  
Equation 5.1 and the determined values for $E_a$ and $k'$ (Table 5.1) will be used for estimating the steady-state performance of non-catalytic and catalytic (90 g$_{catalyst}$/lfoam C$_2$SO$_4$-V$_2$O$_5$) foams at semi ‘real world’ conditions. A number of assumptions was made:

- The catalyst requirements were estimated for the engines in Table 1.3. Table 5.2 shows the estimated soot concentration in the exhaust gas of different diesel applications.

- Diesel particulate matter contains different fractions (Section 1.2.2) of which the soluble organic fraction (e.g. adsorbed hydrocarbons) can be a large one. In order to make a comparison with Printex U possible it was assumed that the particulate matter from Table 1.2.2 only contained ‘dry’ soot.

- Optimal space velocities are not known, since their is not much practical experience with foam filters. Space velocities are used that are typical for flow-through diesel oxidation catalysts, these are in the range of 50,000 to 300,000 l/h (Section 1.7.1).

- For the equilibrium filter loadings a range of 1 to 16 gsoot/lfoam is used (Figure 1.31).

- It is assumed that the conditions are isothermal and no thermal runaways occur.

- It is assumed that the exhaust gas contains 10 vol % O$_2$, and that no pre-oxidation catalyst and, therefore, no NO$_2$ is present.
Table 5.2: Exhaust mass flow \( q_m \), soot production \( q_{soot} \) and estimated particle concentration \( c_{soot} \) of different diesel applications. Data from Table 1.3 and [10].

<table>
<thead>
<tr>
<th>engine</th>
<th>( q_m )</th>
<th>( q_{soot} )</th>
<th>( c_{soot} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>car</td>
<td>0.26</td>
<td>1.7*</td>
<td>2</td>
</tr>
<tr>
<td>truck</td>
<td>0.39</td>
<td>16.8</td>
<td>13.3</td>
</tr>
<tr>
<td>MW-generator</td>
<td>8.3</td>
<td>1975</td>
<td>76.6(^b)</td>
</tr>
</tbody>
</table>

\(^a\) The amount of 1.7 g/h is typical for an Euro III engine which should not produce more than 0.05 g/km particulate matter during the European drive cycle (Table 1.5). During the European drive cycle the average speed is 33.5 km/h (Figure 1.7), at which speed 0.05 g/km of particles amounts to 1.7 g/h.

\(^b\) At full load the engine produces 112.5 mg/m\(^3\) dry particulate matter when it runs on a typical fuel with a sulfur content of 1% and an ash content of 0.05%. When it is assumed that all sulfur is combusted to SO\(_2\) of which 2% reacts to H\(_2\)SO\(_4\) (Section 1.2.2) then the following composition for the particulate matter can be calculated: soot 76.5 mg/m\(^3\), ash 16.2 mg/m\(^3\) and H\(_2\)SO\(_4\) 19.8 mg/m\(^3\).

Figure 5.6 shows Arrhenius plots of the performance of non-catalytic and catalytic foam at different soot loadings and the soot deposition rates at different space velocities for the three diesel engine applications. The intersections in the plots indicate balance temperatures: the temperatures where the soot combustion rate equals the soot deposition rate. Tables 5.3 and 5.4 list the balance temperatures for the different cases. For passenger cars with a catalytic foam filter the balance temperatures are in the range of 330 to 440°C. For trucks and generators which produce more soot, balance temperatures of respectively 40 and 80°C higher were calculated. It should be noted that the balance temperatures in the tables are estimations, and they should be verified with engine experiments.

The potential for continuous regeneration applications estimated from TPO data indicates that the Cs\(_2\)SO\(_4\)-V\(_2\)O\(_5\) catalyst has a competitive activity compared to alternatives tested by the car industry: the lowest reported operation temperature of a catalytic filter is 375°C and for catalytic fuel additives 350°C [11]. Such operation temperatures are, however, still too high to make the catalyst applicable for continuous regeneration strategies for passenger cars, which have average exhaust temperatures at the exhaust manifold lower than 200 to 250°C (Figure 1.5). The operation range of the catalyst comes closer to the exhaust temperatures of trucks and busses, but compared to the alternative NO\(_x\)-aided CRT system (Section 1.7.2) a catalytic filter with a liquid catalyst will be less flexible because its operation window will be approximately 50°C higher. For large electricity generators the balance temperatures are also on the high side, besides the effects of the high sulfur and ash fraction were not even considered yet. The advantage of these engines is, however, that they do not have very severe size limitations. For instance for a 3 m\(^3\) filter the operation temperature is estimated to be in the range of 370 to 430°C. In terms of size restrictions such a large filter may be not such a problem because this type of engines can have a silencer as large as 20 m\(^3\) with a weight of 5,000 kg [12].
Figure 5.6: Arrhenius plot of modeled oxidation rates in 10 vol. % oxygen, and soot deposition rate in catalytic filter vehicles as function of engine type and gas hourly space velocity: a, non-catalytic filter; b, catalytic filter, 90 g_{catalyst}/l_{foam} Cs_{2}SO_{4}:V_{2}O_{5}/mullite foam.
Table 5.3: Balance temperatures \((T_{eq})\) for non-catalytic foam filter as function of the soot loading of the filter and the gas hourly space velocity (GHSV). 10 vol % oxygen, 100% filtration efficiency.

<table>
<thead>
<tr>
<th>GHSV 1/1/h</th>
<th>loading (g_{soot}/l_{foam})</th>
<th>(T_{eq,car}) °C</th>
<th>(T_{eq,truck}) °C</th>
<th>(T_{eq,generator}) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25,000</td>
<td>1</td>
<td>444</td>
<td>496</td>
<td>551</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>411</td>
<td>457</td>
<td>507</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>380</td>
<td>422</td>
<td>467</td>
</tr>
<tr>
<td>50,000</td>
<td>1</td>
<td>462</td>
<td>517</td>
<td>575</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>427</td>
<td>476</td>
<td>528</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>395</td>
<td>439</td>
<td>486</td>
</tr>
<tr>
<td>100,000</td>
<td>1</td>
<td>481</td>
<td>539</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>444</td>
<td>496</td>
<td>551</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>411</td>
<td>457</td>
<td>507</td>
</tr>
<tr>
<td>150,000</td>
<td>1</td>
<td>493</td>
<td>552</td>
<td>616</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>455</td>
<td>508</td>
<td>564</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>420</td>
<td>468</td>
<td>519</td>
</tr>
<tr>
<td>300,000</td>
<td>1</td>
<td>514</td>
<td>576</td>
<td>644</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>473</td>
<td>529</td>
<td>589</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>437</td>
<td>487</td>
<td>541</td>
</tr>
</tbody>
</table>

Table 5.4: Balance temperatures \((T_{eq})\) for catalytic foam filter as function of the soot loading of the filter and gas hourly space velocity. Catalyst, 90 \(g_{catalyst}/l_{foam}\) Cs\(_2\)SO\(_4\)·V\(_2\)O\(_5\); 10 vol % oxygen; 100% filtration efficiency.

<table>
<thead>
<tr>
<th>GHSV 1/1/h</th>
<th>loading (g_{soot}/l_{foam})</th>
<th>(T_{eq,car}) °C</th>
<th>(T_{eq,truck}) °C</th>
<th>(T_{eq,generator}) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25,000</td>
<td>1</td>
<td>379</td>
<td>422</td>
<td>467</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>351</td>
<td>390</td>
<td>431</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>325</td>
<td>361</td>
<td>398</td>
</tr>
<tr>
<td>50,000</td>
<td>1</td>
<td>394</td>
<td>439</td>
<td>487</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>365</td>
<td>406</td>
<td>449</td>
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<tr>
<td></td>
<td>16</td>
<td>338</td>
<td>375</td>
<td>414</td>
</tr>
<tr>
<td>100,000</td>
<td>1</td>
<td>410</td>
<td>457</td>
<td>508</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>379</td>
<td>422</td>
<td>467</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>351</td>
<td>390</td>
<td>431</td>
</tr>
<tr>
<td>150,000</td>
<td>1</td>
<td>420</td>
<td>469</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>388</td>
<td>432</td>
<td>479</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>359</td>
<td>399</td>
<td>441</td>
</tr>
<tr>
<td>300,000</td>
<td>1</td>
<td>437</td>
<td>488</td>
<td>543</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>404</td>
<td>450</td>
<td>499</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>373</td>
<td>415</td>
<td>460</td>
</tr>
</tbody>
</table>
5.4. DISCUSSION

As discussed the estimated values depend on a number of assumptions. A very important parameter that should be investigated for this filter type is soot reentrainment. Unlike in the wall-flow monolith filter, in the foam filter diesel soot can reentrain into the exhaust gas; the conditions at which it occurs will depend on the soot loading and the interstitial\(^2\) gas velocity. Within a range of acceptable pressure drops the lowest balance temperature can be reached at the highest loading at which no reentrainment occurs. The degree of reentrainment will be the lowest at low interstitial gas velocities. The interstitial gas velocity at set space velocities can be controlled by filter design. Ideally the most optimal filter structure would be a wall-flow monolith that fully operates according to a deep-bed filtration mechanism instead of surface filtration. Intermediate filter types do also exist, a good example is the z-filter reported by Gabathuler et al. [2], which is an ordinary foam filter in which a cross-flow pattern is established by taking out channels in a checkerboard manner resulting in a structure somewhat similar to the wall-flow monolith.

It should be noted that not all effects of the exhaust gas components have been studied yet, these are studied in a parallel Ph.D. study, see Preface. The effect of these compounds will influence how much the estimated performances agree with the real performance in diesel exhaust gas. In Chapter 7 it will be determined how much the estimated performance agrees with the real performance.

5.4.6 Mechanistic aspects

In order to judge the quality of a design of a soot oxidation catalyst, it should be known how it operates at different size-scales (see also Section 1.5.1), because at the different size-scales limitations may be encountered that limit the overall performance. If the oxidation mechanism is known it can be evaluated if and where improvements are needed.

Critical processes

**Mass transport limitations** Like in all catalytic processes mass-transport limitations can severely limit the performance of a soot oxidation catalyst. In the case of gas or liquid-phase substrates this type of limitation can be overcome by removing diffusion barriers by for instance designing a certain pore topology in the catalyst support. For soot oxidation such measures have hardly any effect because there is no mass transport of deposited soot at all! This problem is also known as the contact problem. Neeft et al. (Section 1.5.2) defined two types of contact that can exist. (1) Loose contact exists when the soot has limited physical interaction with the catalyst. This is illustrated in Figure 5.7 a by one catalyst particle that is surrounded by many soot particles that have no or limited contact. Neeft et al. established that under realistic conditions this type of contact prevails. (2) Tight contact is a more advantageous situation because the catalyst has a very intimate physical contact with the soot, which results in relatively high oxidation rates. This situation occurs when soot is intimately mixed with a catalyst in a ball mill or mortar. It has been illustrated in Figure 5.7 b. The figure shows many soot particles which are intimately mixed with catalyst

\(^2\)Interstitial, situated between the cells of a structure [13].
CHAPTER 5. CATALYTIC FILTERS

Figure 5.7: Impressions of possible distributions between catalyst and soot: a, loose contact; b, tight contact.

particles. It remains debatable what changes the oxidation rate. One of the obvious explanations for the changed oxidation rate is the increased amount of contact points. Besides the catalyst and soot particles are reduced in size, and they have been exposed together too high mechanical forces which could have generated some kind of chemical interaction before the actual TPO experiment. The tight contact reactivity of some catalysts seems to be adequate for application, but unfortunately, it cannot be realized at practice. It would be a breakthrough when a catalyst could somehow facilitate the transition of loose to tight contact without compromising on the stability.

Carbon-oxygen reaction In general, catalysts lower activation energies of reactions by providing alternative reaction pathways that avoid the slow, rate-determining steps of uncatalyzed reactions. The redox soot oxidation mechanism (Section 1.5.1) works according to this principle. The pathway provided is reduction of the catalyst by the carbon present in the soot and subsequently re-oxidation of the catalyst by gas-phase oxygen, etc. This is a typical reaction pathway where tight contact between the catalyst and soot is essential for a fast reaction. Figure 5.8 a shows a schematic impression of where soot will be oxidized in a catalytic filter that operates according to this mechanism. The figure implicates that only soot that touches the catalyst is catalytically oxidized and the rest has to wait for their turn, this means that ideally a 0th reaction order in soot could be expected [14].

The spillover soot oxidation mechanism (Section 1.5.1) follows a different principle. It has been reported [14,15] to resemble closely the non-catalytic soot oxidation mechanism (Section 1.4.1). This means that the activation energies are not changed and rate increases should come from an increased pre-exponential factor. In a catalytic filter that operates according to this mechanism the reaction area would then resemble Figure 5.8 b. Spillover oxygen is produced at the catalyst surface and transferred to the soot, where it reacts like it was a non-catalytic oxidation reaction. This means that most soot will not touch the catalyst surface, but it experiences the presence of the catalyst by the increased amount of
5.4. DISCUSSION

Figure 5.8: Schematic impressions of the reaction area in catalytic filters: a, redox mechanism; b, spillover mechanism.

reactive oxygen. As a result a 1st reaction order in soot should be found ideally, i.e. for a homogeneous soot with constant reactivity. It is in line with this reasoning that the type of physical contact is thought to be less important for spillover oxidation [14].

Evaluation

In Chapters 3 and 4 various observations were made which might fit the characteristics of certain oxidation mechanisms. They will be discussed here to verify if they are consistent.

In Chapter 3 it was concluded that the liquid state of the catalysts has no decisive influence on the catalyst performance. On the contrary all evidence indicated that the catalysts avoid any contact with the soot. It was also found that catalysts that were mixed loosely with soot could not make the transition from a loose to a tight physical interaction. In addition in Chapter 4 it was found that supported catalysts that were mixed with soot for different time intervals oxidized the soot at similar rates, while SEM analysis revealed that the density of the soot increased and thus the average distance between catalyst and soot decreased with increasing mixing time. These observations raise a few interesting questions. First, why is the catalyst capable of oxidizing soot at a high rate while having a (inferior) loose contact? Second, why does the soot oxidation reaction appears to be insensitive for the distance to the catalyst? Third, why does a liquid catalysts that is designed to overcome the contact problem still benefit from tight-contact sample preparation? (The benefit was as large as was the case for solid catalysts!)

The observations made in this chapter can help answer the questions. It was found that the catalyst can oxidize soot at a fast rate with a 1st reaction order in soot, and that the catalyst is capable of accelerating oxidation without changing the activation energy. These observations, together with the observation that contact is not important, fit the spillover oxidation mechanism very well. There remains one question that should be answered. Why does the catalyst benefit from tight contact? The study of Mul et al. [16] with labeled oxygen atoms answers this question. They found that some catalysts in tight contact, amongst others V₂O₅, can oxidize soot according to two mechanisms at temperatures of 375-400°C: evidence was found that a redox and spillover mechanism took place simultaneously. Unfortunately,
they did not report results of the combustion of loose contact samples, but they discussed that only catalysts that can create spillover oxygen are active in loose contact soot oxidation. Based on their results and hypothesis, and the current results of the liquid catalysts it seems that the degree of physical contact controls the contribution of two independent oxidation mechanisms to the overall oxidation rate. (1) In loose contact only spillover oxidation occurs with the aid of spillover oxygen. (2) In tight contact the intimacy between the catalyst and soot is high enough for the redox mechanism to occur. During filtration soot deposits in a loose manner, which means that spillover oxidation will be the predominant reaction mechanism in a catalytic filter that uses solely O₂ for oxidation.

**Implications of the mechanism**

The role of a spillover oxidation catalyst is the production of adsorbed oxygen atoms by dissociation. Different parameters can be envisaged that might influence the overall reaction rate. For the catalyst these are: (1) the molecular oxygen dissociation rate; (2) the mobility of adsorbed oxygen atoms on the catalyst surface; (3) the amount of adsorbed oxygen that the catalyst surface can contain; and (4) the ease of transfer of adsorbed oxygen from the catalyst surface to the soot surface. For the soot substrate the only parameter that influences the reaction rate is the concentration of carbon-oxygen complexes (Section 1.4.1). The only way to raise the reaction rate is to raise \( k' \) by raising the concentration of carbon-oxygen complexes present on the soot surface. Whether this is possible or not will depend on the fraction of the active surface area that is occupied by carbon-oxygen complexes and to which amount the surface might be oversaturated. When it has been established that the maximum saturation level has not been reached yet, then it should be determined which of the catalyst parameters is rate limiting. This parameter can then be improved in order to 'pump' more dissociated oxygen to the soot surface in order to increase the concentration of carbon-oxygen complexes, and thereby the soot oxidation rate.

The required \( k' \) for lowering the operation range of the catalyst by 150°C was calculated in order to give an impression of what kind of improvement is needed in order to make the catalyst attractive for light-duty applications: whereas the current catalyst formulation increased \( k' \) by one order in magnitude, an additional increase of four orders in magnitude will be required in order to lower the operation range by another 150°C. Establishing such an increase will be a great challenge.
5.5 Conclusions

- Two attractive methods for the deposition of a liquid catalyst on ceramic foams have been developed. Reproducible catalytic foams for lab-scale kinetic experiments can be produced if a powdered mixture of catalyst and a solid diluent is impregnated and subsequently calcined in air. For the preparation of catalytic foams of larger dimensions, the deposition by filtration of a suspension of catalyst particles forced through foam is more suitable.

- The oxidation of soot by catalytic foam filters follows simple kinetic considerations: a first reaction order in oxygen, soot, and catalyst concentration; no significant oxidation of CO, NO, and hydrocarbons occurs.

- The current catalytic foam filters are unfit for continuous regeneration applications for passenger cars. It is estimated that their activity is on the low side for busses, trucks, and large electricity generators. A study under realistic conditions should be conducted to verify if this estimation is valid or not.

- It is tentatively concluded that liquid catalyst based catalytic filters operate according to a spillover oxidation mechanism.
Bibliography


Chapter 6

Stability of Catalytic Foam Filters

The durability of catalytic alumina and zirconia-toughened mullite ceramic foam filters was tested by exposing them to severe conditions. The catalytic performance, composition, and mechanical strength were constantly monitored. It was concluded that the mechanical strength of the catalytic filters may be reduced by the presence of the catalyst in combination with certain compounds of the ceramic filter. This effect can be minimized by carefully controlling the composition of the ceramic filter. The stability of the current catalyst phases themselves is too low for application in diesel exhaust gas. Due to partial evaporation, emission of catalyst compounds into the environment is likely and when that happens significant deactivation of the catalytic phase is unavoidable. The catalyst was also found to be soluble in water, which might be disastrous in the case of condensation.

6.1 Introduction

Legislation demands a minimum distance in which a vehicle should fulfill the emission standards. Catalysts are key in fulfilling legislation, and controlling their stability controls the long-term environmental performance of vehicles. Stability is especially important for a catalytic filter, because catalyst deactivation may cause additional pressure drop in the exhaust pipe; and increases the chance on extreme thermal runaways, which might compromise the safety.

It is not surprising that because of potential hazards many car manufacturers are not enthusiastic about applying filtration technology, and might only consider application when 100% robustness is guaranteed.

The stability of catalytic filters is a complex topic because various failure schemes may exist, see Figure 1.33. Investigating all possible failures in parallel will be time-consuming. A division has to be made between primary failures, to be taken into account in the first stage of filter development, and secondary failures to be studied at a later stage.

primary failures Primary failures are due to the intrinsic properties of the original components of the catalytic filter. These failures are relatively easy to anticipate. Well-known
primary failures are catalyst deactivation due to common exhaust conditions, and to destructive interactions between the catalytic phase and the filter material.

1. Catalysts are in general metastable materials. This means that in time their properties will change, which is often accompanied by deactivation. The combination of high temperatures and steam, also known as hydrothermal conditions accelerates this type of deactivation [1].

2. During a cold start in winter the exhaust gas passes through the cool catalytic filter and cools down because of which some condensation of water might occur. The condensed water might be blown out the filter, or it might stay in the filter and evaporate again when the filter has become hot. Another case where condensation might occur is during a long traffic-jam in winter (at temperatures of for instance -20°C) where the engine runs idle for a long time, in which case condensed water is likely to trickle out. A water-soluble catalyst in combination with condensed water might prove to be a disastrous combination. The effects are hard to predict because knowledge about the cold start temperatures, insulation, thermal mass etc. should be known in detail.

3. One of the best known failures in the history of catalytic soot filters is due to inferior mechanical properties. In 1985 a catalytic filter was introduced on the Californian passenger car market (Section 1.5.4). During operation ceramic pieces broke off that destroyed the turbo charger’s radial turbine. It was probably a chemical reaction between the cordierite filter and the mixed metal-oxide catalyst that caused the reduction in mechanical strength.

**secondary failures** The best examples of secondary failures are found amongst the possible detrimental effects of inorganic ashes, see for instance Section 1.5.4. Their presence and effect will differ from case to case, and will sometimes be extremely difficult to anticipate. For instance there exists a large market (not as a part of the official car dealer distribution network) of additives for 'improving' the vehicle's performance. Such additives are blended by the car owner into the fuel or lubricating oil and might end up in the catalytic trap, where they might compromise its performance.

In this chapter possible primary failures are investigated. Cs$_2$SO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$ supported by alumina or zirconia-toughened mullite foams will be exposed to different simulated aging conditions. Their hydrothermal stability and resistance to liquid water will be investigated. The key parameters of the catalytic foams that will be monitored are the catalytic performance, the composition, and the mechanical strength.
6.2 Experimental

6.2.1 Interaction between catalyst and filter

For this study 60 mullite and 60 alumina ceramic foam plates of 40×40×10 mm were used. From each foam type 20 samples were used as reference, i.e. without catalyst; 20 samples were loaded with 75 g_{catalyst}/l_{foam} CsVO_{3·}MoO_{3} each; and 20 samples with 75 g_{catalyst}/l_{foam} Cs_{2}SO_{4·}V_{2}O_{5} each. As catalyst deposition method the procedure with oxalic acid diluent described in Section 5.2.2, was used. Each sample was kept for 6 h at 450°C, 50 h at 720°C, 2 h at 800°C, and 2 h at 850°C in air to simulate the high temperatures that can be encountered downstream of the turbocharger of a diesel engine and during thermal runaways, see for instance Tables 1.3 and 1.15. These temperatures are more realistic for diesel passenger cars than for large stationary diesel engines. For these large engines the used temperatures are a worst-case scenario.

Mechanical strength determination

The mechanical strength of the different ceramic foam samples was investigated with a compression bench. The samples were placed between two layers of thick kitchen cleaning cloth to get an even distribution of the compression force. Figure 6.1 shows failed and

![Figure 6.1: Example of displacement-force diagrams.](image)

successful experiments. Successful experiments showed breakage of the sample at a well defined point, i.e. the bulk of the sample broke at a well defined displacement and load,
CHAPTER 6. STABILITY OF CATALYTIC FOAM FILTERS

i.e. the uniaxial compressive strength \(^1\). Failed experiments had local breakage instead of breakage of the bulk, which translated itself in a disordered diagram with no well-defined point of failure present. Only successful experiments were used for calculation of the mean uniaxial compressive strengths. The population distributions of the determined compressive strengths were analyzed and the 95% confidence intervals were calculated. The details of the statistical methods and the results of the analysis of the population distribution have been given in Appendix B, page 189.

Formation of new phases

The different foam samples and unsupported catalysts were analyzed with XRD (after the compression tests) to investigate the formation of new phases. The samples were crushed to a \(< 200 \mu m\) sieve fraction. They were analyzed from 5 to 100\(^\circ\) with steps of 0.020\(^\circ\) at a step time of 1 s. The measured diffractograms were compared with the Powder Diffraction Files (PDF) of the International Center for Diffractional Data (1998 version).

6.2.2 Hydrothermal stability

Hydrothermal treatments were given with the equipment described in Section 2.3.4. Alumina and zirconia-toughened mullite cylinders with a diameter of 25 mm and a length of 30 mm were used, they were impregnated with 75 \(g_{\text{catalyst/foam}}\) Cs\(_2\)SO\(_4\)-V\(_2\)O\(_5\) and 50 \(g_{\text{catalyst/foam}}\) CsVO\(_3\)-MoO\(_3\). Conditions typical for diesel passenger cars were used: 600\(^\circ\)C (Table 1.3), space velocity 180,000 1/l/h pressurized air (Section 1.7.1), 10 vol% steam (Table 1.3), 20 ppm SO\(_2\) [3] and 180 h in cycles of 45 h. For the combination of 600\(^\circ\)C and 180 h was chosen in order to conduct accelerated aging: 600\(^\circ\)C is the most demanding temperature of the exhaust gas temperature range; however, temperatures of 600\(^\circ\)C occur seldom (Figure 1.5), because of which a duration of 'only' 180 h was used.

The experiments with Cs\(_2\)SO\(_4\)-V\(_2\)O\(_5\) and CsVO\(_3\)-MoO\(_3\)/alumina foams failed right away. The catalytic foams did not survive the canning procedure with the intumescent fiber mat. The mat compressed the foam to a course powder. Such problems were not encountered for alumina foam without catalyst.

The hydrothermal treatment procedure used for catalytic mullite foams consisted of different steps: (1) the foams were canned and kept for 6 h at 600\(^\circ\)C in order to verify whether they would survive the canning procedure at all, (2) the soot oxidation performance was determined with TPO, the equipment and procedures of Sections 2.3.1 and 5.2.3 were used, and (3) the samples were treated four times for 45 h, and after each 45 h cycle the soot oxidation performance was determined with TPO. The mechanical strength of catalytic mullite foams showed no problems whatsoever. It was also observed that the liquid catalyst did not creep into the intumescent mat. The mat did stick to the catalytic foam, which caused a minor problem with the TPO experiments because during deposition of the soot a small soot fraction attached to the intumescent mat remains, which was combusted non-catalytically.

\(^1\)Compressive strength: the ratio of the maximum load to the original cross-section area [2], unit N/m\(^2\) or Pa.
After completion of the hydrothermal treatments the samples were crushed into a very fine powder (< 10 µm sieve fraction) to analyze the composition with XRF and XRD.

### 6.2.3 Catalyst solubility

The effect of catalyst solubility was investigated by simple, but drastic, means. On two plates (30 \times 30 \times 10 \text{ mm}) mullite foam Cs$_2$SO$_4$·V$_2$O$_5$ (75 \text{ g}_{\text{catalyst}}/\text{l}_{\text{foam}}) and CsVO$_3$·MoO$_3$ catalysts (50 \text{ g}_{\text{catalyst}}/\text{l}_{\text{foam}}) were deposited. Two small pieces were broken off the 'fresh' plate in order to determine the composition with XRF and to test it with TPO. The plates were put in 20 ml water each for 5 min at 20°C, then placed on paper kitchen cleaning cloth to remove the excess water and then dried at 110°C in air. The mass difference was measured, and two pieces were broken off again for XRF and TPO analysis. The complete procedure was repeated for a couple of times.

### 6.3 Results

#### 6.3.1 Interaction between catalyst and filter

**Mechanical strength**

Tables 6.1 and 6.2 show the summarized statistical data of the compressive strength tests. Procedures according to Appendix B. The results in Table 6.2 show that Cs$_2$SO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$ did not alter the compressive strength of the zirconia-toughened mullite foam. On the other hand CsVO$_3$·MoO$_3$ and Cs$_2$SO$_4$·V$_2$O$_5$ reduced the mechanical strength of the alumina foam by approximately 50%. The difference between the Cs$_2$SO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$ alumina foams themselves was not significant.

**Formation of new phases**

Catalytic and non-catalytic foams were analyzed with XRD to determine if new phases were formed when catalysts and foam were combined. The most important results will be shown here, the complete set of results are given in Appendix C, page 193. Figure 6.2 shows the XRD diffractogram of CsVO$_3$·MoO$_3$/alumina foam. For Cs$_2$SO$_4$·V$_2$O$_5$/alumina foam analogous observations were made. In the diffractogram three phases were positively identified; their location and intensity matched those of the reference compounds from the powder diffraction files. Of course alumina was detected. Also aluminum phosphate (AlPO$_4$) and pollucite (CsAlSi$_2$O$_6$) were detected. The formation of these compounds is clearly related to the presence of the catalyst, because they were not detected in the non-catalytic foam. The phosphate and silicon originated from the alumina foam, which contained 13 wt % P$_2$O$_5$ and 2 wt % SiO$_2$ (Table 2.3). In the catalytic zirconia-toughened mullite foams no new phases were detected, see Figures C.3 and C.4 in Appendix C.
<table>
<thead>
<tr>
<th>MPA</th>
<th>H0</th>
<th>H1</th>
<th>α</th>
<th>1 - α</th>
<th>t</th>
<th>Critical Value</th>
<th>a</th>
<th>Critical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>H0</td>
<td>H1</td>
<td>0.1</td>
<td>0.9</td>
<td>2.146</td>
<td>14</td>
<td>1.770</td>
<td>0.956</td>
</tr>
<tr>
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<td>H1</td>
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<td>1.8</td>
<td>0.990</td>
</tr>
<tr>
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<td>0.975</td>
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<td>2.179</td>
<td>0.997</td>
</tr>
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<td>H1</td>
<td>0.01</td>
<td>0.99</td>
<td>2.846</td>
<td>17</td>
<td>2.375</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 6.2: Statistical data of two sample t-test used to determine the equality of the different compressive strengths.

Table 6.1: Statistical data of single sample t-test used for calculating the confidence intervals of the compressive strengths.
Figure 6.2: XRD diffractogram and identification of CsVO₃·MoO₃/ alumina foam. The open markers indicate the location and relative intensity of the reference compounds from the powder diffraction files.
CHAPTER 6. STABILITY OF CATALYTIC FOAM FILTERS

6.3.2 Hydrothermal stability

Figure 6.3 shows the results of the hydrothermal stability study. The hydrothermal conditions lowered the activity of both catalysts substantially, as shown in Figures 6.3 a and b. The composition analysis of the hydrothermally aged catalytic foams, Figure 6.3 c, provided information regarding the cause of deactivation. Due to the hydrothermal conditions 10 to 20% V₂O₅, 40 to 50% Cs₂O and essentially all MoO₃ and SO₃ were gone. With XRD no new phases were detected, which explains why mechanical strength problems were not encountered.

6.3.3 Catalyst solubility

Figure 6.4 shows the results of the solubility study. Figure 6.4 a shows that Cs₂SO₄·V₂O₅ and CsVO₃·MoO₃ are not resistant to water. 40 to 50% of the catalyst masses dissolved. The catalysts dissolved in a selective manner, mainly the Cs₂O, MoO₃ and SO₃ components dissolved, see Figure 6.4 b. The effect on the catalyst performance was high, see Figure 6.4 c, especially for Cs₂SO₄·V₂O₅ which lost almost all its activity.

6.4 Discussion

For the successful application of catalytic soot filters various criteria should be met. Durability is a very important one. There exists, however, a wide variety of failure schemes for catalytic soot filters. In this chapter important possible failures have been investigated that are directly related to the intrinsic properties of the catalytic phase and ceramic filter, and aging effects by general exhaust conditions.

6.4.1 Failure schemes

Mechanical failure. Possible interactions between the different catalysts and ceramic foams have been accelerated by giving a thermal treatment. The effect of the catalysts on the ceramics differed dramatically.

The combination of zirconia-toughened mullite with the catalysts did not lead to the formation of new phases. This resulted in constant mechanical properties. Therefore, catalytic mullite foams could be canned with success by a commercial canning procedure, and withstood hydrothermal aging undamaged.

The combination of alumina with the catalysts led to deterioration, and as a result cannng was not possible. This failure was due to the additives present in the alumina and not to the alumina itself. The alumina foam contained 13 wt % P₂O₅ and 2 wt % SiO₂, out of which in the presence of the cesium containing catalysts AlPO₄ and CsAlSi₅O₁₆ (pallucite) phases were formed. The formation reaction of AlPO₄ was probably catalyzed by the liquid soot-oxidation catalyst, because AlPO₄ was not formed when no catalyst was present. Clearly, the alumina applied should not contain these additives.
Figure 6.3: Results of hydrothermal stability study on catalytic mullite foams: a, TPO results of CsVO$_3$·MoO$_3$ mullite foam as function of aging time; b, TPO results of Cs$_2$SO$_4$·V$_2$O$_5$ mullite foam as function of aging time; and c, results of XRF composition analysis.
**Figure 6.4:** Results of solubility study for catalytic mullite foams: a, relative amount of catalyst present after each contact with water; b, results of XRF composition analysis; and c, TPO results.
6.4. DISCUSSION

Deterioration mechanism  Ceramic foam is produced by coating a polymeric sponge with a slurry of ceramic grains that are subsequently sintered [4]. The resulting polycrystalline body has a complicated microstructure which consists of the grains and the locations where different grains have merged, the grain boundaries (Figure 6.5 a).

![Diagram showing the formation of voids and cracks in ceramic foam](image)

Figure 6.5: Simplified mechanism of the formation of voids and cracks in the microstructure of ceramic foam.

The properties of the grain boundaries differ from the bulk. It is in this context an important fact that impurities tend to segregate along the grain boundaries [5], as illustrated in Figure 6.5 b. Therefore, it is reasonable to assume that the AlPO₄ and CsAlSi₂O₆ contaminations that were formed in the catalytic foam were located alongside the alumina grain boundaries. AlPO₄ and CsAlSi₂O₆ have thermal expansion coefficients of 53 [6] and 0 [7] µm/m°C, respectively, while α alumina has a thermal expansion coefficient of 8 µm/m°C [8]. During heating AlPO₄ expands more than α alumina which causes stress in the sintered grain structure, resulting in microcracks in the grain boundaries, as shown in Figure 6.5. This mechanism is also known as thermal expansion mismatch (Section 1.5.4).

Catalyst degradation  Exhaust catalysts can operate at high temperatures and, in time, thermal degradation might occur by processes like sintering, reactions between catalyst and support, or evaporation. Degradation is in general accelerated by high temperatures in combination with steam [1]. Sintering will most probably not play an important role for the investigated soot oxidation catalysts, because the catalyst are liquid and have already a low dispersion. On the other hand, evaporation may not be excluded. For instance Bielański et al. showed that MoO₃ from MoO₃·V₂O₅ mixed metal oxide catalysts evaporates significantly during oxidation reactions at temperatures below 500°C [9].

Like the catalyst of Bielański the current catalysts did not have a high tolerance for hydrothermal conditions. Postmortem analysis revealed that the cesium, molybdenum and sulfate content was significantly reduced (by 60 to 90 wt %). This had a clear effect on the
catalyst performance: its operation temperature shifted to 30 to 40°C higher temperatures. Postmortem XRD analysis showed that no new phases were found during the hydrothermal treatment, which agrees well with the results found for mullite in Section 6.3.1.

Condensation of water is also a failure source that was investigated. A solubility test showed that water condensation might well lead to deactivation.

6.4.2 Applicability of catalytic filters

Different stability aspects of the liquid catalyst based catalytic foam filters were investigated in order to determine their applicability.

The catalytic alumina foam filter used in this study is clearly not applicable as exhaust purification device. The filter would break completely during the canning procedure. The mullite foam showed a good compatibility with the catalysts, because of which mechanical problems due to catalyst-support interactions are not anticipated. It should be reminded that ash contaminants originating from lube oil, fuel, or a ‘performance improver’ may be introduced during operation. Their effect will be hard to predict. It cannot be excluded that also the mullite foam will be damaged in due time. The best way to exclude problems with ashes is by investigating their effects under realistic conditions.

The operation range of the catalyst was estimated to be similar to catalytic fuel additives in Chapters 3. Unfortunately, hydrothermal aging and catalyst solvation during water condensation may shift the operation range of the catalyst to 30 to 40°C higher temperatures. This is accompanied by highly unwanted secondary emissions of catalyst compounds. For these two reasons the application of the current liquid catalyst formulations is not advised.

6.5 Conclusions

- Liquid soot-oxidation catalysts, containing Cs₂O, MoO₃, and Cs₂SO₄, degrade under hydrothermal aging conditions. Such soot oxidation catalysts will not be applicable in diesel exhaust gas. Catalyst deactivation and secondary emissions of toxic catalyst compounds is likely.

- Liquid soot-oxidation catalysts, containing Cs₂O, MoO₃, and Cs₂SO₄, are partly soluble in water. This is undesired in the case of condensation in an exhaust pipe.

- The presence of liquid soot-oxidation catalysts may lower the mechanical strength of ceramic foam by at least 50%. This effect relates to the combination of the catalyst, the ceramic material, and the additives mixed with the ceramic material during the production of the ceramic foam. The combination of these materials may result in the formation of new phases with a higher thermal expansion coefficients than the ceramic foam, which will give rise to the formation of microcracks during heating of the filter. The effect can be minimized by carefully controlling the composition of the catalytic filter.
Bibliography


Chapter 7

Engine Bench Tests\(^1\)

A liquid-catalyst based catalytic foam filter was tested in diesel exhaust gas. Its performance can be characterized by four processes: soot deposition, penetration, reentrainment, and oxidation. This makes the interpretation of results complex: for instance the pressure drop over the filter cannot be used as a tool for monitoring the catalyst performance, because different equilibrium situations, corresponding with the same pressure drop, may exist. The filtration performance of the tested foam filter cannot compete with the wall-flow monolith filter. The design of the foam filter was, however, simple. It is expected that its performance can be improved by designing a better geometry.

In diesel exhaust gas the catalyst is more active than was predicted with TPO. The difference may be caused by the absence of steam during the TPO experiments. Due to this higher reactivity the activity of the catalyst might be adequate for some heavy-duty diesel applications, like for instance large electricity generators. Synthetic soot applied in loose contact proved to be a good substitute model compound for diesel soot in laboratory studies.

7.1 Introduction

In the previous chapters the performance of liquid soot-oxidation catalysts has been analyzed with synthetic soot. The physical contact between the catalyst and soot has been kept loose in those chapters, because it was assumed that such contact would occur in a catalytic filter that supports a liquid catalyst. Based on these loose contact results it has been predicted (Chapter 5) that the activity of the catalytic filters, although similar to some alternatives, is not sufficient.

There has been, however, quite some controversy about the type of contact that occurs in a filter and various results were published with different types of contact (Table 1.10). This does not only make it very difficult to compare different results, but also, it should be verified if the type of contact that occurs in the current catalytic filter is indeed loose.

\[^1\]A part of this chapter has been accepted for publication: B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, On the type of contact between an oxidation catalyst and diesel soot deposited by filtration from an exhaust stream, Appl. Catal., B, in press.
It is common practice to determine the performance of a soot oxidation catalyst for continuous regeneration by monitoring the pressure drop buildup over the filter as a function of time (Section 1.5.2). This method has been mainly applied on wall-flow monolith filters, but has not been validated yet for foam filters. A priori, the method might not be applicable on foam filters because they have an open structure. This open structure could cause reentrainment of soot, which could be misinterpreted as evidence for catalytic activity.

In this chapter the performance of a liquid-catalyst based catalytic foam filter will be tested for passenger car conditions at elevated temperatures. The performance of the catalyst will be analyzed by monitoring the pressure drop over the filter, and the soot conversion will be determined ex-situ in order to verify if it corresponds with the pressure drop results. It will also be verified if a model soot deposited with simple laboratory methods gives satisfactory results compared to diesel soot that is deposited in a realistic manner. For the investigation a dedicated engine test-bench has been built.

7.2 Experimental

7.2.1 Catalyst preparation

20 ppc (pores per cm) zirconia-toughened mullite foam was used as filter. The foam was sawed into cylinders with a diameter of 25 mm and a length of 30 mm. Catalytic foam filters with a loading of $90 \text{ g}_{\text{catalyst}} / \text{L}_{\text{foam}}$ were prepared by filtering $\text{Cs}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5$ particles from a suspension that was forced through the foam, and subsequently drying and calcination in air (Section 5.2.2).

7.2.2 Catalyst activity

The activity of the catalytic foam filter was determined with diesel soot using the same TPO procedures that were used in Chapter 5 with synthetic soot. The following TPO samples were prepared:

- The engine (Section 2.3.3) was operated at a load of 60%. The major part of the exhaust gas was vented through a silencer. 5.5 $\text{m}^3 / \text{h}$ exhaust gas was pumped through the catalytic filter for 2 h. The temperature of the catalytic foam filter was controlled at 200°C to avoid soot oxidation. After the soot deposition the sample was quenched to room temperature in synthetic air to avoid condensation of the exhaust fumes.

- Diesel soot was collected at 200°C for non-catalytic oxidation.

- 175 mg diesel soot was mixed with 350 mg $\text{Cs}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5$ powder for 1 h in a Fritsch Micro-Mill Pulverisette 8 ball mill.
7.2. EXPERIMENTAL

7.2.3 Performance of a catalytic filter in diesel exhaust gas

Catalytic (90 g catalyst/l foam Cs₂SO₄·V₂O₅) and non-catalytic mullite foam filters with a diameter of 2.5 cm and a length of 6 cm² were tested with the engine equipment (Section 2.3.3) at different temperatures. During the experiments the engine was operated at a load of 60% and 4 m₃/h exhaust gas was pumped through the filter. This created a realistic gas hourly space velocity for passenger cars of 135,000 l/h (Section 1.7.1). Two types of experiments were conducted:

- A well-known method for determining the performance of a catalytically regenerated filter is by recording the pressure drop over the filter as function of time and temperature in order to determine balance temperatures. This method has been applied with success on wall-flow monolith filters, see Section 1.5.2, but has also been reported recently for determining the performance of catalytic foam filters [1]. The experiments were performed at temperatures of 250, 300, 350 and 410°C with and without catalyst deposited on the filter.

- The performance of the catalytic filters was measured by determining the actual soot conversion. The conversion was measured ex-situ by regenerating the foam filter and the downstream wall-flow monolith at periodic time intervals and by quantifying the amounts of soot that were deposited on the filters by analyzing the amounts of CO and CO₂ that were released during regeneration. When it is known how much soot is produced by the engine and how much is collected on the filters, then the difference tells us how much is converted by the catalyst.

Two series of experiments were performed. In the first it was verified if a reproducible amount of soot can be collected on a filter. During this series of experiments no test filter was placed in the test filter holder, which means that practically all soot was collected on the downstream wall-flow monolith. The engine was operated at a load of 60% and during 5 h 4 m₃/h exhaust gas pumped through the monolith which temperature was controlled at 200°C. The filter was subsequently regenerated in air at a flow rate of 1.25 l/min and a heating rate of 0.2°C/min. The CO and CO₂ production was monitored as a function of time, and the soot amount was calculated by integrating the concentrations. The experiment was repeated 4 times.

In the second series the 90 g catalyst/l foam Cs₂SO₄·V₂O₅/zirconia-toughened mullite foam was operated at 375°C for different time periods: 15, 30, 60, 120, 300, and 480 min. After each time period the filters were alternately regenerated in air at a flow rate of 1.25 l/min and a heating rate of 0.2°C/min. The CO and CO₂ concentrations were monitored in order to determine the amounts of deposited soot.

²A length of 6 cm was created by placing 2 samples of 3 cm in series.
7.3 Results

7.3.1 Catalyst activity

Figure 7.1 shows the catalytic and non-catalytic oxidation rates of synthetic and diesel soot in 10% O₂ as a function of temperature and of how it was deposited. Table 7.1 summarizes the characteristic temperatures.

7.3.2 Performance of a catalytic filter in diesel exhaust gas

Balance temperature determination Catalytic and non-catalytic foams were tested in exhaust gas at temperatures of 250 to 410°C. It was not possible to gather any information from the pressure drop development over the filters or to determine balance temperatures. In all cases nearly constant pressure drops were observed. Each time the integrity of the filter, pressure-difference transducers and canning mat was verified but no irregularities were found. Figure 7.2 shows a typical result of the pressure drop over a foam filter as a function of time.

Soot concentration exhaust gas 4 m³/h exhaust gas was passed for 5 h through the wall-flow monolith of the engine bench, which subsequently was regenerated carefully while measuring the CO and CO₂ concentrations as function of time. By integration of the concentrations the amount of soot was calculated. The following soot concentrations in the exhaust gas were determined: 38.0, 38.5, 39.0 and, 40.0 mgsoot/m³, which values appear to be distributed normally. The average value was 38.9 mgsoot/m³ with a standard deviation of 0.85 mgsoot/m³ and a 95% confidence interval of 37.5 to 40.2 mgsoot/m³.

Soot conversion by a catalytic foam filter A series of experiments was conducted to determine the amount of soot trapped and converted by a catalytic foam filter at 375°C. The catalytic foam was operated at identical conditions for different time periods. After each experiment the wall-flow monolith and catalytic foam were regenerated in order to verify the filtration efficiency and soot conversion. Figure 7.3 summarizes the results. Figure 7.3 a shows the amount of soot accumulated on the catalytic foam as a function of time. The amount sharply increased, and slowly leveled off. Figure 7.3 b shows the amount of soot accumulated on the wall-flow monolith as a function of time. This amount increased linearly with time. Figure 7.3 c shows the amount of soot accumulated on the foam and monolith as a function of time. The amount increases essentially linearly with time. Figure 7.3 d shows the filtration efficiency of the catalytic foam as function of time. During the first hour it was approximately 35%, after which it dropped fast to 10 to 15%.

The data of Figure 7.3 c was analyzed with linear regression. The regression line was estimated with a least square estimation [2]. The coefficient of determination (or correlation coefficient) was 0.996 meaning that 99.6% of variation in the amount of soot collected on both filters can be explained with the linear regression model. For the intercept of the slope of the line a value of 11 mg with standard deviation of 14.0 mg and a 95% confidence
7.3. RESULTS

Figure 7.1: Oxidation rate as function of temperature and of how the soot was deposited on the catalyst: a, diesel soot; b, Printex U synthetic soot (data of Printex U oxidation from Chapters 3 and 5.)

Table 7.1: List of temperatures at which oxidation and maximum oxidation rates occurred during TPO of mixtures of Cs₂SO₄-V₂O₅ catalyst and soot.

<table>
<thead>
<tr>
<th></th>
<th>oxidation range (°C)</th>
<th>no catalyst</th>
<th>ball mill</th>
<th>foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>diesel soot</td>
<td>T_max. rate (°C)</td>
<td>250-575</td>
<td>200-425</td>
<td>300-525</td>
</tr>
<tr>
<td>Printex U</td>
<td>T_max. rate (°C)</td>
<td>275-550</td>
<td>200-425</td>
<td>300-500</td>
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<tr>
<td></td>
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<td>315</td>
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<tr>
<td></td>
<td></td>
<td>505</td>
<td>295</td>
<td>440</td>
</tr>
</tbody>
</table>
interval of -25 mg to 47 mg was calculated. For the slope of the line 33.3 mgsoot/m₃ was calculated with a standard deviation of 0.95 mgsoot/m₃ and a 95% confidence interval of 30.9 to 35.8 mgsoot/m₃.

For the soot concentration in the exhaust gas with no catalytic foam filter present an average value of 38.9 mgsoot/m₃ was calculated in the beginning of this section. With a catalytic foam present it was calculated that the concentration reduced to 33.3 mgsoot/m₃. It was calculated with a confidence level of 95% that during the experiments with the catalytic filter the soot concentration was reduced by 4.2 to 6.9 mgsoot/m₃.

### 7.4 Discussion

#### 7.4.1 Catalyst activity

It is clear from Figure 7.1 that diesel soot is catalytically and non-catalytically oxidized in the same temperature regions as Printex U synthetic soot, which is why Printex U may be used as substitute for diesel soot in laboratory studies, like Neeft et al. [3] concluded. The catalytic oxidation of diesel soot with a liquid catalyst occurred in the temperature region of loose contact oxidation (compare for instance with Figure 3.6). Therefore, it can be concluded that loose contact occurs in exhaust gas, and that the results of samples prepared with a tight type of contact are not realistic.
7.4. DISCUSSION

Figure 7.3: Results of engine-bench study with 90 g\textsubscript{catalyst}/l\textsubscript{foam} Cs\textsubscript{2}SO\textsubscript{4}.V\textsubscript{2}O\textsubscript{5}/zirconia-toughened mullite foam at 375°C: a, soot accumulation on catalytic foam as function of time; b, soot accumulation on down-stream wall-flow monolith as function of time; c, sum of soot accumulation on foam and monolith as function of time and amount of gas passed through filters; d, filtration efficiency of catalytic foam as function of time.
Although the diesel soot was oxidized in the same temperature region as Printex U, the kinetics seems to differ. Figure 7.4 a shows the non-catalytic oxidation rate as function of time modeled according to Equation 5.1 which assumes a first order reaction dependency in soot. Table 7.2 shows the determined model parameters. The model equation does not describe the combustion curve very well like it did for the non-catalytic oxidation of Printex U synthetic soot (Figure 5.5 a). Despite this result it is not thought that the diesel soot was oxidized according to a mechanism different from Printex U. It could well be that the diesel soot contained two phases, because the TPO curve (Figure 7.1 a) appears to consist of two separate merged curves. The supposed merged curves were split with a Chi-

Figure 7.4: Measured and modeled non-catalytic oxidation rates of diesel soot: a, complete curve modeled; b, curve modeled after deconvolution.

Table 7.2: Kinetic parameters of the non-catalytic oxidation of diesel soot. Data from Figure 7.4, model Equation 5.1.

<table>
<thead>
<tr>
<th>curve</th>
<th>SA(^b)</th>
<th>(E_a)</th>
<th>(s)</th>
<th>95% CI</th>
<th>(k')</th>
<th>(s)</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>s(^{-1})</td>
<td>s(^{-1})</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>original curve</td>
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<td>422</td>
<td>220.5</td>
<td>-13 - 885</td>
</tr>
<tr>
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<td>65.4</td>
<td>0.23</td>
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<td>1.1</td>
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<td>1.0 - 1.3</td>
</tr>
<tr>
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<td>0.35</td>
<td>252.1 - 253.4</td>
<td>100 (\cdot 10^{10})</td>
<td>5.0 (\cdot 10^{10})</td>
<td>90.0 - 112.4 (\cdot 10^{10})</td>
</tr>
</tbody>
</table>

\(^{b}\)SA, relative peak surface area.
squared minimization using a peak fitting software package Galactic Peaksolve [4]. The best results were obtained by assuming a log-normal distribution. Figure 7.4 b shows the results of the deconvolution and the modeled curves according to Equation 5.1. Table 7.2 shows the kinetic parameters. The modeled curves approximate the split curves very good, which indicates that the oxidation rates of the two phases have first order kinetics, like was found for Printex U in Chapter 5. Because the oxidation of the two phases was very similar to Printex U, it is possible that they consisted of two different soot types with reactivities different from Printex U soot. These soot phases might be the phases observed by Ishiguro et al. (Section 1.2), who observed a stable concentric platelet structure with perpendicular orientation to the particle center and a less stable turbostratic structure contained within the concentric structure. The hypothesis of two phases is an alternative to the explanation of Neeft et al. [3] for an apparently changing reactivity during oxidation of diesel soot, which they attributed to changes in the reactive surface area. Unfortunately, they did only report isothermal experiments and did not report TPO curves of the non-catalytic oxidation of their diesel soot which could have given a more definite explanation of their results.

If the diesel soot indeed consists of two separate phases, then it could make the determination of true kinetic parameters difficult. Figure 7.5 shows the modeled oxidation rate of the catalytic oxidation of diesel soot.

![Graph showing oxidation rate and conversion against temperature.](image)

**Figure 7.5:** Measured and modeled (Equation 5.1) oxidation rate of the catalytic oxidation of diesel soot.

The kinetic parameters of the curve are: $E_a \ 103.4 \pm 0.95 \text{ kJ/mol}$ with a 95% confidence interval of $101.5 - 105.3 \text{ kJ/mol}$, and $k' \ 2.7 \pm 0.43 \cdot 10^3 \text{ s}^{-1}$ with a 95% confidence interval of $1.8 - 3.5 \cdot 10^3 \text{ s}^{-1}$. Based on the results of the non-catalytic oxidation of diesel soot it could well be that the curve in Figure 7.5 is the sum of two merged curves of Figure 7.4 b. But
compared to non-catalytic oxidation (Figure 7.4) curve 2 was affected more by the presence
of the catalyst as it lies completely in its operation window, which resulted in one totally
merged curve in Figure 7.5. If this is the case, then the kinetic parameters may be best
described as apparent parameters.

It should be noted that the activation energies calculated for catalytic oxidation in Fig-
ure 7.5 and for the non-catalytic oxidation of diesel soot without spectral deconvolution in
Figure 7.4 a are the same. It is not known if this is a coincidence. It could be that the model
describes the curve in Figure 7.4 a well in an average sense, despite the poor fit. Such an
unchanged activation energy is not unexpected since it was also found for the catalytic and
non-catalytic oxidation of Printex U synthetic soot in Section 5.4.5. However, for Printex U
the model gave a better fit of the non-catalytic oxidation curve.

7.4.2 Performance of a catalytic filter in diesel exhaust gas

Catalyst performance On-line monitoring of the performance of a diesel soot oxidation
catalyst in diesel exhaust gas is a great analytical challenge. A popular way is by monitoring
it indirectly by recording the pressure drop of the filter as function of time, where the lowest
temperature at which a constant pressure drop is observed is called the balance temperature
(Section 1.5.2). For absolute filters like the wall-flow monolith this is a proven method, but
when reentrainment of diesel soot is possible, then it may be very inaccurate.

The constant pressure drops over the foam filters measured during the engine bench
tests are very suspicious. They indicated constant performance at every temperature, even
at 250°C for which TPO predicted that the catalysts would not be active at all. Such
constant pressure drops have already been interpreted for catalytic foam filters as evidence for
continuously catalytic regeneration in literature [1], but it is thought that such interpretation
could be incorrect. It is thought that soot reentrainment can also cause constant pressure
drops, because it was observed that the filtration efficiency declined as a function of time
(Figure 7.3 d) while the pressure drop remained constant. An initial filtration efficiency of
35% was found that rapidly declined to 10 to 15%. It was also determined that the catalyst
converted roughly 10 to 15% of the soot, which is too low for causing a constant pressure
drop. It is proposed that the catalytic filter traps soot until it reaches such a soot loading
that it starts to reentrain soot, at that moment a steady-state situation is reached where the
soot deposition and reentrainment are in equilibrium, because of which a filtration efficiency
of 0% should be observed. When a soot oxidation catalyst is applied, then a part of the
filtered soot is oxidized and cannot be reentrained anymore, which should result in a higher
net filtration efficiency. Figure 7.6 shows an illustration of the proposed operation of a
catalytic foam filter.

It has been shown that reentrainment of soot may have a considerable impact on the
performance of a catalytic foam filter, but it should be noted that the soot concentration in
the exhaust gas of the engine-bench is at least 20 times as high as for an Euro III passenger
car engine. Therefore, it could well be that if a such engine had been used the catalyst
activity had been sufficient for oxidation of all deposited soot, and that then a steady-state
filtration efficiency of 35% would have been observed.
Matching TPO with real world performance The role of TPO during the development of soot oxidation catalysts is a quick prediction of the performance of a catalyst. It will be very difficult to get a perfect match between engine bench results and TPO results due to differences between the techniques:

**temperature control** The used sample volume of TPO experiments is very low, because of which a very accurate temperature control could be realized. During the engine experiments the temperature control was less ideal: during the first hour of the experiments the temperature down and upstream of the filter slowly fluctuated due to the large thermal mass of the equipment and the changed thermal equilibrium due to the introduced gas flow; the temperature could deviate 5°C from the desired reaction temperature. Thereby, the filter temperature itself was not measured, which can also be a cause of deviations.

**data collection** During TPO the oxidation rate is monitored on-line, while the oxidation data from the engine experiments resulted from analysis after the experiments and only give an idea of the catalyst performance in an average sense.

**gas composition** The most important difference is the gas composition. During TPO only O₂ was present as gas-phase reactant, whereas in the exhaust gas a wealth of components was available.

Although a perfect match between TPO and engine experiments seems unlikely it is interesting to determine how good it is. The equilibrium temperature for the conditions during the engine experiments was calculated like was done in Section 5.4.5. The following parameters were used: the 'apparent' $E_a$ of 103.4 kJ/mol and $k'$ of $2.7 \cdot 10^3$ s⁻¹ (Section 7.4.1); a gas hourly space velocity of 135,000 1/l/h (Section 7.2.3); soot concentration of 38.9 mgsoot/m³ (Section 7.3.2); a soot conversion of 12.5% (Section 7.3.2); and an average soot filter loading of 2.5 gsoot/lfoam which was calculated from integration of the curve in Figure 7.3 c. From these values an average balance temperature of 440°C can be calculated, which is 65°C higher than the measured temperature. This is a large difference. $k'$ should be raised by a factor of 5 in order to match the TPO results with the performance in diesel exhaust gas.
The variation in exhaust composition between the engine and TPO experiments are probably the reason for the difference in the actual and estimated operation temperature. This difference is probably not caused by NO\textsubscript{x}, CO, or hydrocarbons, because it was found in Chapter 5 that the catalyst shows no reactivity with these compounds. It is more likely that steam, of which 9 vol % was present during the engine experiments (Table 2.5), is the cause of the difference, because preliminary results [5] indicate that the presence of 5 % steam raises the activity of the catalytic foam filter already by a factor of 3 to 4.

**Outlook** The Cs\textsubscript{2}SO\textsubscript{4}·V\textsubscript{2}O\textsubscript{5} liquid catalyst is more active in diesel exhaust gas than was predicted by TPO. Despite the higher activity it will not be adequate for continuous regeneration strategies for passenger cars. On the other hand the higher activity broadens the possibilities for heavy-duty diesel applications. For the diesel electricity generator of Table 1.3 the activity of the catalyst will probably not be the bottleneck of the application anymore. However, there remain some other topics that need to be solved in order to make the catalytic filter applicable: the effects of the high ash concentration, the low hydrothermal stability of the catalyst, and the filter performance. It is expected that a filter of several cubic meters will be required for dealing with the high amount of particulates that is emitted by this engine type. The production and canning of such a filter deserves some serious attention.

The filtration performance of the current foam filter is promising but not yet sufficient. A higher initial filtration efficiency and a lower tendency towards soot reentrainment are required. A lower tendency towards reentrainment will be advantageous for the environmental performance of the filter, and for the continuous regeneration reaction. A possible route towards a lower tendency for reentrainment will be by lowering the interstitial gas velocity by applying a different filter configuration [6].

A complicating factor in the overall design of the catalytic foam filter is the spillover mechanism: the spillover mechanism requires a high soot loading for a high oxidation rate, while a foam filter requires a low soot loading in order to avoid reentrainment.

It should be noted that further optimization of the foam filter is only worthwhile when there is an adequate regeneration catalyst available. If no satisfactory catalyst formulation is available then the wall-flow monolith is to be preferred, because currently the wall-flow monolith has a superior filtration efficiency and shows no tendency for reentrainment. These properties are especially advantageous for automotive applications, because due to their lower average exhaust temperatures periodical regeneration seems currently the best option. In order to give periodical regeneration a high energy efficiency the regeneration interval should be made large, which will mean that on average higher soot loadings will be present. In the case of a foam filter it is likely that reentrainment will occur, while in the wall-flow monolith the pressure drop will rise due to the increased flow resistance, which also has the advantage that it can be used for monitoring the soot loading.
7.5 Conclusions

- A liquid-catalyst based catalytic filter is capable of oxidizing soot in diesel exhaust gas. The prototype demonstration showed 10 to 15% conversion at 375°C.

- There is a large difference between the catalyst performance estimated by TPO and the actual performance in diesel exhaust gas. Indications are that this difference is caused by the absence of steam in the TPO gas mixture.

- The activity of the catalytic foam filter is too low for continuous regeneration strategies for light-duty diesel applications. The activity shows more potential for some heavy-duty applications. Unfortunately, a catalyst formulation with an adequate hydrothermal stability is not available yet (Chapter 6).

- The type of physical contact that occurs in a catalytic foam filter is loose. Tight contact measurements lead to overestimation of the catalyst performance.

- The performance of a catalytic foam filter is characterized by deposition, penetration, reentrainment, and oxidation. In contrast, the performance of a wall-flow monolith is mainly characterized by deposition and oxidation.

- The spillover mechanism complicates the overall design of a catalytic foam filter: the spillover mechanism requires a high soot loading for a high oxidation rate, while a foam filter requires a low soot loading in order to avoid reentrainment.

- Reentrainment is in view of the environmental performance of a vehicle highly undesired. However, it may be controlled by optimization of the filter geometry.

- The filtration performance of the tested foam filter cannot compete with the wall-flow monolith filter. Its design was, however, simple, it is expected that its performance can be improved by designing a better geometry.

- The pressure drop over a foam filter cannot be used as diagnostic tool for monitoring the catalyst performance, because different undistinguishable equilibrium situations may exist, i.e. an equilibrium between deposition and oxidation, or deposition and reentrainment.

- Synthetic soot is a useful model compound for the investigation of diesel soot oxidation catalysts.

- Diesel soot may exist of different soot phases.
Bibliography


Chapter 8

Summary and Evaluation

8.1 General context

Background

In the beginning of the new millennium the development of a total solution for diesel emissions abatement might seem old-fashioned: (1) there is much speculation on how new alternative power sources will drive the vehicles of the future, and (2) research to what is sometimes called "the holy grail"\(^1\) of diesel purification, a device that can clean diesel NO\(_x\) and soot, started already in the early 1980s. One is tempted to conclude that diesel engines belong to the past. Nevertheless the diesel engine with its high durability and efficiency is at the moment in view of a sustainable society the most viable power source for transport over the road and water, and will play a major role for at least 25 years.

Governments are not very enthusiastic about the pollution of diesel engines in densely populated areas. They strongly advocate cleaner vehicles by demanding severe emissions reductions within 5 years from now. Car manufacturers could always postpone the introduction of advanced diesel exhaust aftertreatment devices by engine optimization in combination with 'partial' aftertreatment techniques (i.e. the flow-through oxidation catalyst). However, it is in general believed that the environmental performance of current state-of-the-art diesel engines has reached its limit, and that to fulfill future legislation engine manufacturers are forced to apply advanced aftertreatment technologies. As the "holy grail" of diesel exhaust purification has not been invented yet, diesel emission abatement research is far from being 'old news', and will be in the coming decade one of the most challenging topics of applied catalysis.

General trends in diesel pollution abatement The "holy grail" of diesel emission abatement would be a cost-effective device that can remove CO, hydrocarbons, and particulate matter by oxidation, and NO\(_x\) by reduction, without producing any toxic by-products.

\(^1\)See: G.E. Walters et al., Combined NO\(_x\) and particulate removal from diesel exhaust using a non-thermal plasma, Proceedings of the 22nd CIMAC conference (Copenhagen) 1998, 1157-1166.
In theory it should be possible to develop such a device because all pollutants are thermodynamically unstable. The purification reactions of the pollutants have, however, unique reaction pathways that are extremely difficult to conduct in one box. Some attempts tried to develop such a 'box' by applying electro or plasma chemistry. However, these alternative approaches have their limitations and are currently not considered for application. As an one-box device seems to be no option, it is likely that combinations of different technologies will be applied. There exist two possible pathways: (1) application of both oxidation and reduction aftertreatment devices and; (2) the use of the NOx-soot trade-off effect for lowering the emission of one pollutant while raising the other, which is then converted by aftertreatment. It is likely that different combinations will be used depending on vehicle type and engine design.

**Trends in diesel oxidation catalysis** Flow-through diesel oxidation catalysis cannot convert the solid diesel soot fraction. Therefore, it is in general assumed that the application of filters is unavoidable. Filtration technology is very mature and many issues have already been solved. The wall-flow monolith is the preferred filter because of its superior filtration efficiency and low production costs. The bottleneck of filtration technology is the regeneration of the filter, which should be efficient and reliable. Oxidation catalysis will be the key to a solution: by lowering the onset temperature and activation energy a complete regeneration can be guaranteed at a minimum energy expense. Three catalytic regeneration options are currently considered:

**continuous** Continuous regeneration is the cheapest and most reliable method, and is currently the only option that can be classified as fit-and-forget. It is not suited for all engine types, because it needs relatively high temperatures which makes it only suitable for some heavy-duty applications. There exist two types. One uses molecular oxygen for oxidation and has currently 350 to 375°C as minimum operation temperature, the other uses the more reactive NO₂ molecule and has currently 275 to 325°C as minimum operation temperature for low sulfur fuels.

**periodical** Periodical regeneration is very versatile, because it has essentially no minimum operation temperature. It uses the energy released during the exothermic regeneration for completion of the reaction. The regeneration must, however, be initiated which is the bottleneck of the method. An ignition and control system is required, which makes the system complex and expensive.

**semi-continuous** The third option is a hybrid system that combines the advantages (and the disadvantages) of continuous and periodical regeneration. Compared to periodical regeneration it will be more energy efficient because it requires less often ignition, but as ignition is sometimes required it will remain complex.

Catalytic soot oxidation is a great challenge because soot is solid and very immobile when deposited. Due to the immobility there is no mass transport and essentially no conversion. The lack of mass transport has been overcome by special means. Two methods are considered for application:
8.2. **MECHANISM OF LIQUID CATALYST BASED CATALYTIC FILTERS**

- The catalyst can be incorporated in the soot by means of catalytic fuel additives. This option is considered for some applications, but has as drawbacks that it should somehow be introduced to the fuel, and that additive ashes slowly plug the filter. Important advantages are that deactivation cannot occur and that low-sulfur diesel fuel is not required.

- A reactive intermediate can be formed that takes care of the mass transport: upstream of the filter $O_2$ can react with NO to the more reactive $NO_2$ molecule, which will react with the trapped soot. The dependency on $NO_x$ is the main drawback of the method: if the $NO_x$ content is lowered in future engines then the method might not work anymore.

**Research goal**

The lack of mobility of soot makes the development of a filter with catalyst coating very difficult. There exists much interest in such a device because in theory it is simple and adequate: it filters the soot and at the same time oxidizes it continuously with $O_2$.

It is occasionally cited that a catalytic filter might actually work, because when the catalytic coating is intensively mixed with the soot (known as tight contact) a high oxidation rate at a very low temperature is possible. A hypothesis was formulated that said that a catalytic filter can only work when it creates *in-situ* tight contact, and the idea was that a liquid catalyst could do the trick by wetting of the soot. The hypothesis and idea was verified during this Ph.D. study. The two main questions to be answered were:

- Does a liquid oxidation catalyst establish tight contact? Or more general: What is the mechanism of a liquid soot-oxidation catalyst?

- Can a liquid oxidation catalyst be applied in a practical catalytic filter?

**8.2 Mechanism of liquid catalyst based catalytic filters**

During the development of the liquid catalyst based catalytic filter much details were revealed about its functioning. Obviously, the overall performance of the catalytic filter depended on the individual performances of the filter and the catalyst. It is less obvious that these depend strongly on each other.

**Catalytic oxidation mechanism**

The choice for a liquid soot-oxidation catalyst was based on the idea that it could create a tight physical contact with the soot, a situation for which it was hypothesized that it would be beneficial for the catalyst’s performance. It was, however, discovered early on that the liquid catalyst had a low affinity for the soot: it formed immobile droplets on top of the soot. This means that there could be no question of in-situ tight contact formation. This finding was verified by comparing samples of catalyst and soot that were prepared by mixing with a spatula (i.e. loose contact) and by mixing in a ball mill (i.e. ex-situ tight contact).
And indeed, the tight contact sample was more reactive, in fact the temperature difference between tight and loose contact oxidation remained as large as for solid catalysts.

Despite the absence of in-situ tight contact formation, the liquid catalysts showed a relatively high activity. It was already suggested in literature that catalysts that have a loose physical contact might only come into effect when they can create spillover oxygen. This hypothesis was verified for the liquid catalysts by analyzing the kinetic data which was collected during the TPO analysis of the catalytic oxidation of soot. The spillover mechanism has two main characteristics: (1) spillover catalysts are known to be able to accelerate over a distance the oxidation of carbonaceous materials, and (2) the catalyst does not participate in the actual reaction, which is, therefore, similar to the non-catalytic reaction. The kinetic data of the liquid catalysts was consistent with these characteristics. The dependency of the reaction rate on the soot concentration was of a first order. In other words the rate of the catalytic reaction does not depend on the thickness of the soot layer present in the catalytic filter. This means that the catalyst can accelerate soot oxidation over a distance, which is an important feature of spillover oxidation. With the first order dependency on the soot concentration in mind a simple kinetic model equation was formulated

\[ r = k' \cdot e^{-\frac{E_a}{RT}} \cdot (1 - \xi) \]  

which described the TPO curves of the catalytic and non-catalytic oxidation of Printex U synthetic soot well. For both catalytic and non-catalytic oxidation reactions identical activation energies were found, which can be interpreted as evidence for an unchanged reaction mechanism. This is also a feature that fits the interpretation of spillover oxidation. So, the role of the liquid catalyst is only to raise the concentration of oxygen adsorbed on the soot surface, which it does well according to tenfold increase of \( k' \) it causes.

**Filtration mechanism**

The main feature of a ceramic foam filter is its open structure, which enables the deposition of a high amount of catalyst without having the chance on blockage of the gas flow. This feature was an important reason why it was chosen to use foam as test support for the liquid catalyst.

Despite the straightforward design of the filter an encouraging mass filtration efficiency of 35% was measured, which can be a good basis for the further optimization of the filter design. Parameters that can be optimized are the interstitial gas velocity by applying a smart geometry, the pore topology, and the surface roughness.

The major difference of a foam filter in comparison with a wall-flow monolith is that soot can be reentrained from the foam when the flow gets restricted by high amounts of deposited soot. For continuous regeneration this does not have to be a disadvantage when the soot oxidation rate is high enough to avoid such a high soot loading. For periodical regeneration the reentrainment mechanism can be a major drawback because regeneration must be often initiated to avoid reentrainment, and the pressure drop increase will only be moderate which makes it difficult to use it as a diagnostic tool. Because the pressure drop cannot be used for diagnostic purposes, the history of driving behavior collected in the engine management system might be an alternative controlling measure.
Overall mechanism

The performance of a catalytic foam filter is best described by four processes: deposition, penetration, reentrainment, and oxidation. Figure 8.1 shows an illustration of the overall mechanism. It works as follows: (1) a part of the soot deposits on the filter surface and (2) a part penetrates the filter; (3) a part of the deposited soot is oxidized by the catalyst and (4) a part reentrays the gas flow. It can be concluded that an optimal foam filter should have essentially no penetration and reentrainment. In contrast to penetration, reentrainment is not solely influenced by the filter design: it can be controlled by bringing the deposition rate in equilibrium with the oxidation rate by applying an oxidation catalyst. A complicating factor in the overall design is the spillover oxidation mechanism! The spillover mechanism requires a high soot loading for a high oxidation rate, which contradicts with the requirement of a low loading for minimizing reentrainment from the foam filter.

Figure 8.1: Schematic illustration of the mechanism of a Cs$_2$SO$_4$-V$_2$O$_5$/catalytic foam filter.
8.3 The application of a liquid soot-oxidation catalyst

The idea of the application of a liquid material in an exhaust pipe was received with quite some skepticism. Despite the skepticism no problems were encountered with the liquid catalysts when a proper support was applied. In no case it was found that catalyst trickled out of a catalytic filter or was adsorbed by the canning mat. The concept itself might, therefore, work if the catalyst would not fail due to other characteristics.

Activity The liquid catalyst was designed to create tight contact with deposited diesel soot in order to enable continuous regeneration at low temperatures. The catalyst turned out to be more reactive than its solid counterparts and as reactive as the cerium catalytic fuel additive. However, extremely low operation temperatures were not found because the catalyst failed to create tight contact. The applicability of the catalyst depends on the engine type:

passenger cars The catalyst is not adequate for continuous regeneration strategies in passenger cars, because the minimum operation temperature of the liquid catalyst is estimated to be in the range of 350 to 400°C, while current passenger cars average exhaust gas temperatures which are much lower than that.

trucks and busses Trucks and busses have higher exhaust temperatures which is beneficial for continuous regeneration, but on the other hand they emit higher soot concentrations. Fortunately, the size restrictions for the filter are less strict which means that lower space velocities can be applied which will be beneficial for the performance. The minimum operation temperature of a catalytic filter is also estimated to be in the range of 350 to 400°C which is approximately 50°C higher than for alternatives that use NO₂ for oxidation. The higher operation temperature compared to the alternatives means that there is a higher chance on inadequate regeneration for which should be compensated by incorporation of a periodical regeneration strategy which will raise the overall complexity of the system. This can be an important drawback.

Large diesel engines MW-range diesel engines for powering large ships and for the generation of electricity have relatively high and constant exhaust temperatures which is beneficial for continuous regeneration. However, the engines emit very high particulate matter masses (100 times (!) higher than light-duty engines) of which a large fraction consist of inorganic materials (which is a problem by itself). Due to the high particulate concentration a very large catalytic filter of several cubic meters will be required to reach an acceptable operation temperature of approximately 375°C. Fortunately, the size restrictions for this engine type is not very strict.

Selectivity The liquid catalyst accelerates the oxidation of soot. It does not accelerate the oxidation of CO and hydrocarbons, which means that precious metal catalysts are still required.
8.4. OUTLOOK

Stability of the catalytic filter  Despite the promising activity of the current catalyst formulations, their stability is not promising. There are two problems: (1) the hydrothermal stability is low which means that in due time, especially with temperature excursions, catalyst compounds will be emitted into the environment and the oxidation activity will drop dramatically. (2) The catalyst might be destroyed in the case of condensation of water. Another potential problem are the very high amounts of ashes that are present in the exhaust gas of some heavy-duty engines. These ashes might cause various problems, amongst others catalyst deactivation, filter plugging, and filter deterioration.

During the start of the project there was some skepticism regarding negative interactions between the liquid catalyst and the ceramic filter that would cause deterioration of the ceramic. Fortunately, it can be very well controlled by carefully selecting the appropriate filter composition.

Foam filters  During the study ceramic foam was used as a tool to test the catalyst. No optimization of its performance was conducted as it was not the goal of the study. Despite its unoptimized form an initial filtration efficiency of 35% was found. Probably this value can be raised by further optimization, and in combination with an adequate catalyst, an acceptable catalytic filter might be produced. However, the use of a liquid catalyst was the original motivation to use foam as filter. When there is no adequate catalyst formulation there is not much motivation for using a foam filter, because the wall-flow monolith is still the superior filter. An exception might be to use a precious metal coated ceramic foam (placed in front of a wall-flow monolith) for improving the performance of regeneration with the aid of NO₂.

Alternatively monolith filters with a low catalyst loading might be a promising option for periodical regeneration strategies. The catalyst should be very robust because very high temperatures have been reported for periodical regeneration.

8.4  Outlook

It is expected that filters will be introduced on a large scale in a few years time. The chosen catalytic regeneration technology will depend on the engine and vehicle type. For passenger cars periodical catalytic regeneration currently looks like the best option because the average exhaust temperatures are too low for the other alternatives. For heavy-duty engines it is difficult to assess which technology will be applied, because there is a wide variety of engine applications. It is most likely that different ones will be used depending on the application and engine technology.

It is expected that a liquid catalyst will not play a crucial role in these developments because no evidence was found that the liquid state is absolutely necessary. On the other hand it has been shown that a catalytic filter that uses solely O₂ for oxidation can be as reactive as for instance the commercially applied Ce fuel additive. Therefore, there is some potential for this type of catalytic filters. The potential depends on the chosen engine type and regeneration strategy. For continuous regeneration for some heavy-duty applications
the activity might be adequate, but it is felt that the operation temperature is still a bit on the high side. A semi-continuous regeneration strategy might be more promising. It is not known how the catalyst will operate in such a regeneration type. Compared to the cerium fuel additive it is not mixed within the soot, because of which it is uncertain if it can help with sustaining the short and fast regeneration reactions that can occur in semi-continuous type of regeneration.

8.5 Recommendations

It remains to be seen if catalytic filters that solely use $O_2$ will play a role in future developments. Additional research is required. The research should focus on two different regeneration strategies:

**continuous regeneration** The creation of tight contact in a catalytic filter remains in theory the best option for continuous regeneration at very low temperatures. However, in practice it seems not feasible: a liquid catalyst does not work, and the application of a ball-mill type of contacting device is no option. Therefore, loose contact seems to be the only option. The rate of loose-contact soot oxidation is controlled by the concentration of carbon-oxygen complexes present on the soot surface. Whether further improvements compared to the current catalyst are possible will depend on saturation level of carbon-oxygen complexes on the soot surface. If the surface can further be saturated or even oversaturated then further optimization should be possible. Therefore, it is recommended to investigate the degree of saturation, and how it should be maximized.

**periodical regeneration** Periodical regeneration was not studied here. However, the technique is at the moment put into practice for passenger cars. Current systems use catalytic fuel additives, but filter plugging and a costly fuel additive dosing system have been mentioned as important drawbacks. A filter with a catalytic coating will not have these drawbacks. It is recommended to investigate the potential of such a filter for periodical regeneration. It will be essential to elucidate the catalytic mechanism of periodical regeneration because it could be different from continuous regeneration. To start with it should be investigated if there are major differences between the mechanisms of catalytic coatings and catalytic fuel additives, and the study should include both the effects of the catalyst before regeneration where $NO_2$ can play an important role and during regeneration where it is expected that only $O_2$ plays an important role.

It should be noted that there remains the alternative of adapting the exhaust temperature to the operation range of current catalyst technologies. It is recommended to perform a case study to the possibilities. It is very well possible that for some engine types some insulation and the fitting of the catalytic filter closer to the exhaust manifold will make some of the current catalyst technologies more feasible.
Appendix A

Calculation of chemical equilibrium between NO, O₂, and NO₂

The equilibrium between NO and NO₂ was calculated for the following conditions: 500 ppm NOₓ and 10 vol % O₂ at 1 bar.

\[ \text{NO} + 0.5\text{O}_2 \leftrightarrow \text{NO}_2 \]  \hspace{1cm} (A.1)

For \( P_0 \) is 1 bar the equilibrium is calculated as follows:

\[ K(T) = \frac{x_{\text{NO}_2}^{\nu_{\text{NO}_2}}}{x_{\text{NO}}^{\nu_{\text{NO}}}x_{\text{O}_2}^{\nu_{\text{O}_2}}} \left( \frac{P}{P_0} \right)^{\nu_{\text{NO}_2} - \nu_{\text{NO}} - \nu_{\text{O}_2}} \]  \hspace{1cm} (A.2)

where \( K(T) \) is the equilibrium constant, \( x \) are mole fractions, and \( \nu \) stoichiometric coefficients. For \( \nu_{\text{NO}} \) is 1, \( \nu_{\text{O}_2} \) is 0.5, \( \nu_{\text{NO}_2} \) is 1, and \( P \) is 1 bar the equation will read as follows:

\[ K(T) = \frac{x_{\text{NO}_2}}{x_{\text{NO}}^{0.5}x_{\text{O}_2}} \]  \hspace{1cm} (A.3)

The concentrations are calculated by replacing in Equation A.3 \( x_{\text{NO}_2} \), \( x_{\text{NO}} \) and \( x_{\text{O}_2} \) with

\[ x_{\text{NO}_2} = y \]  \hspace{1cm} (A.4)

\[ x_{\text{NO}} = 500 \cdot 10^{-6} - y \]  \hspace{1cm} (A.5)

\[ x_{\text{O}_2} = 0.1 - 0.5y \]  \hspace{1cm} (A.6)

and \( y \) is calculated by

\[ y = \frac{K(T) \cdot 500 \cdot 10^{-6} \cdot 0.1^{0.5}}{1 + K(T) \cdot 0.1^{0.5}} \]  \hspace{1cm} (A.7)

Equation A.7 was calculated for different temperatures. The equilibrium constants \( K(T) \) were calculated by the van 't Hoff equation:

\[ K(T) = e^{\frac{-\Delta G(T)\theta}{RT}} \]  \hspace{1cm} (A.8)
where $\Delta G(T)^\circ$ is the standard reaction Gibbs function calculated from the difference in the standard Gibbs function of formation ($\Delta G_f^\circ$) of the reactant and products in Equation A.2. Table A.1 shows the data and results of the equilibrium calculation, data from 1.

Table A.1: Thermochemical properties of NO, NO$_2$, and O$_2$, and calculated chemical equilibrium concentrations of NO and NO$_2$ as function of temperature.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta G_f^\circ$ NO (J/K/mol)</th>
<th>$\Delta G_f^\circ$ NO$_2$ (J/K/mol)</th>
<th>$\Delta G_f^\circ$ O$_2$ (J/K/mol)</th>
<th>$\Delta G(T)^\circ$ (J/K/mol)</th>
<th>$K_{eq}$</th>
<th>NO (ppm)</th>
<th>NO$_2$ (ppm)</th>
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<td>27020</td>
<td>-38911</td>
<td>-61543</td>
<td>-35160</td>
<td>1.33 $\cdot 10^6$</td>
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<td>500</td>
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<td>5471</td>
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<td>-82520</td>
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<td>4.19 $\cdot 10^3$</td>
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<td>500</td>
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<tr>
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<td>-115625</td>
<td>-126639</td>
<td>-12510</td>
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<td>398</td>
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Appendix B

Statistics of compressive strength tests

**Determination of normality**  Most statistical procedures are based on the assumption that the population distribution of the measured samples is of a specified type. An effective way to verify a probability distribution is to construct a *probability plot* \(^1\). If the distribution on which the plot has been based is correct then the points in the plot fall close to a straight line. The construction of a probability plot is started by ordering the measured values from smallest to largest and then by dividing them in sample percentiles:

\[
100(i - 0.5)/n
\]

(B.1)

where \(i = 1, 2, \ldots, n\) and \(n\) is the total number of measured values. So, for instance, the 90th percentile separates the highest 10% from the lowest 90%. Because the normal distribution is the most frequently occurring population distribution in physics and chemistry it is logical to verify if the distribution of the determined compressive strengths is normal. Figure B.1 shows the standard normal curve which can be used as reference distribution. If we use the 90th percentile again as example, then we can find it in Figure B.1, where the shaded region has a surface area of 0.900, the accompanying value on the x-axis is called the \(z\)-percentile. The different areas and accompanying \(z\)-percentiles can be found in the different statistics text books and in many other scientific table books \(^2\). A normal probability plot is constructed by plotting the measured compressive strengths as function of their \(z\)-percentile.

Figure B.2 shows the normal probability plots of compression tests of Section 6.2.1. The points in the plots fall approximately close to a straight line, because of which it is reasonable to assume that the population distribution of the measured compression strengths is normal.

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but unknown values $\mu$ and $\sigma$. In order to use the normal distribution for calculation of the confidence interval of $\bar{x}$, $\sigma$ must be known. In most cases $\sigma$ will be unknown and an alternative method should be used to calculate a confidence interval. The confidence interval of $\bar{x}$ can be calculated using the family of $t$ distributions when it is known (by for instance the construction of a probability plot) that the samples $x_1, x_2, \ldots, x_n$ have a normal distribution. The advantage of using a $t$ distribution is that it is only controlled by the number of degrees of freedom $\nu$, which equals $n - 1$, and not by $\sigma$. The $t$-values corresponding to different $\nu$'s and probabilities $(1 - \alpha)$ can be found in a $t$ table and are called the $t$ critical values $t_{\alpha, \nu}$. $t$ tables can be found in different statistics text and table books. The $100(1 - \alpha)\%$ confidence interval can be calculated using:

$$\left( \bar{x} - t_{\alpha/2, \nu} \cdot \frac{s}{\sqrt{n}}, \bar{x} + t_{\alpha/2, \nu} \cdot \frac{s}{\sqrt{n}} \right)$$ (B.2)

Equality test The $t$ table can also be used to determine whether two estimated averages $\bar{x}$ and $\bar{y}$ with normal population distributions from a number of $m$ and $n$ experiments are equal or not. In order to do this $t$ and $\nu$ must be calculated, and a null ($H_0$) and alternative ($H_a$) hypothesis must be formulated:

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{s_x^2}{m} + \frac{s_y^2}{n}}}$$ (B.3)

$$\nu = \frac{\left( \frac{s_x^2}{m} + \frac{s_y^2}{n} \right)^2}{\frac{(s_x^2/m)^2}{m-1} + \frac{(s_y^2/n)^2}{n-1}}$$ (B.4)

$$H_0 : \bar{x} - \bar{y} = 0$$ (B.5)

$$H_a : \bar{x} - \bar{y} \neq 0$$ (B.6)
$t$ compares the measured difference between $\bar{x}$ and $\bar{y}$ with the variability $s_1$ and $s_2$ inherent in the data. $H_0$ may be rejected for either $t \geq t_{\alpha/2,\nu}$ or $t \leq -t_{\alpha/2,\nu}$. For instance, when a probability of 2.5% has been met, then there is a 2.5% chance that a $t$ value higher than $t_{0.025,\nu}$ will arise from random variation. Since the $t$ distribution is symmetric around a zero mean, there is also a 2.5% chance of obtaining a $t$ that is smaller than $-t_{0.025,\nu}$. Overall, $|t| \geq t_{0.025,\nu}$ is only met in 5% of the trials. When the difference between $\bar{x}$ and $\bar{y}$ is statistically significant then its confidence interval can be calculated with a confidence level of $100(1 - \alpha)\%$:

$$\bar{x} - \bar{y} \pm t_{\alpha/2,\nu}\sqrt{\frac{s_1^2}{m} + \frac{s_2^2}{n}}$$

(B.7)
Figure B.2: Normal probability plots of the uniaxial compressive strength of catalytic and non-catalytic ceramic foams as determined in Section 6.2.1: a, zirconia-toughened mullite; b, zirconia-toughened mullite with CsVO₃·MoO₃; c, zirconia-toughened mullite with Cs₂SO₄·V₂O₅; d, alumina; e, alumina with CsVO₃·MoO₃; and f, alumina with Cs₂SO₄·V₂O₅.
Appendix C

XRD analysis of destructive phases formed in catalytic foams

In Section 6.2.1 XRD experiments were performed on several samples: unsupported catalysts, Cs$_2$SO$_4$·V$_2$O$_5$ and CsVO$_3$·MoO$_3$; ceramic foams, alumina and zirconia-toughened mullite; catalytic foams, Cs$_2$SO$_4$·V$_2$O$_5$ alumina, CsVO$_3$·MoO$_3$ alumina, Cs$_2$SO$_4$·V$_2$O$_5$ mullite and CsVO$_3$·MoO$_3$ mullite. The measured X-ray diffractograms were systematically compared with reference diffractograms from the comprehensive Powder Diffraction Files (PDF) of the International Center for Diffractional Data (1998 version). Figures C.1, C.2, C.3, and C.4 show the diffractograms with identified reflections.

Unsupported catalysts  The analysis of the unsupported catalysts was very complex. The problems that were encountered were identical to the problems that Neeft $^1$ reported for the analysis of the CuKMo(Cl)/ZrO$_2$ catalyst. The wide range of possible stoichiometries of vanadium and molybdenum compounds caused that often reference data of such compounds only approximated the experimental data. In most cases reflections were found to fit certain reference compounds, but identification was not possible because some of the reference reflections were lacking.

Noncatalytic foams  The reflections in the diffractograms of the noncatalytic mullite and alumina foams were easy to identify with the PDF. Alumina matched the alumina reference diffractogram. Zirconia-toughened mullite matched zirconium silicate, zirconium oxide and mullite.

Catalytic foams  The diffractograms of the catalytic foams were less complex than those of the unsupported catalysts. The diffractograms of the catalytic mullite foams matched noncatalytic mullite. Apparently, no new phases were formed. This was not the case for the catalytic alumina foams. Their diffractograms also contained the reflections of pollucite (CsAlSi$_2$O$_6$) and aluminum phosphate (AlPO$_4$).


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Figure C.1: XRD diffraction patterns of unsupported Cs₂SO₄·V₂O₅·CsSO₄·V₂O₅ supported by alumina foam, and alumina foam without catalyst.

APPENDIX C: XRD ANALYSIS OF CATALYTIC FOAMS
Figure C.2: XRD diffractograms of unsupported CsVO₃·MoO₃, CsVO₃·MoO₃ supported by alumina foam, and alumina foam without catalyst.
Figure C.3: XRD diffractograms of unsupported Cs$_2$SO$_4$·V$_2$O$_5$, supported by zirconia-toughened mullite foam and zirconia-toughened mullite foam without catalyst.

APPENDIX C: XRD ANALYSIS OF CATALYTIC FOAMS
Figure C.4: XRD diffractograms of unsupported CsVO$_3$·MoO$_3$, CsVO$_3$·MoO$_3$ supported by zirconia-toughened mullite foam, and zirconia-toughened mullite foam without catalyst.
APPENDIX C. XRD ANALYSIS OF CATALYTIC FOAMS
Samenvatting

Onderzoek naar de verwijdering van roetdeeltjes uit dieseluïtlaatgas wordt reeds 20 jaar gedaan. Het onderwerp is en blijft actueel omdat de milieuvorschriften van de overheid steeds meer aangescherpt worden. Het onderzoek heeft zich in twee richtingen verdeeld. Ten eerste is het mogelijk de uitstoot van roetdeeltjes te verlagen door het verbrandingsproces in de motor te verbeteren en ten tweede is het mogelijk de deeltjes nadat ze gevormd zijn met een filter af te vangen.

Autofabrikanten stellen hoge eisen aan de betrouwbaarheid van een auto en zijn daardoor altijd huiverig geweest voor het plaatsen van een filter in de uitlaatpijp omdat deze mogelijk kan verstoppen. Zij hebben er daarom hard aan gewerkt om aan de emissienormen te voldoen door hun dieselmotoren zooveel mogelijk te optimaliseren. Het lijkt er nu op dat de grenzen van motoroptimalisatie zijn bereikt en het wordt voor de autofabrikanten noodzakelijk om het plaatsen van een filter te overwegen omdat zij anders binnen vijf jaar niet meer aan de emissienormen kunnen voldoen.

Er zijn de afgelopen 20 jaar veel mogelijkheden ontwikkeld om het verstoppen van de filter te voorkomen. Het nadeel van veel van deze technieken is dat ze niet betrouwbaar of niet breed toepasbaar zijn. Er bestaat een type filter dat in theorie wel aan deze twee eisen voldoet, namelijk het katalytisch filter. Dit is een filter waarop zich een verbrandingskatalysator bevindt. Deze katalysator is een stof die ervoor zorgt dat een roetdeeltje dat ermee in aanraking komt spontaan ontbrandt zonder dat de katalysator zelf wordt verbruikt. Dit type filter wordt sinds 1990 aan de Technische Universiteit in Delft onderzocht. Er werd echter ontdekt dat de toepasbaarheid gering is vanwege het slechte contact tussen roet en de katalysator. Het is namelijk zo dat roet een vaste stof is en wanneer het neerslaat in een filter op een plek waar zich geen katalysatordeeltje bevindt dan ontbrandt het ook niet. Een belangrijke aanbeveling van het voorgaande onderzoek was om het probleem op te lossen door de mobiliteit van de katalysator te verhogen. Deze aanbeveling werd overgenomen en een onderzoek werd opgestart in 1996 waarvan u nu het resultaat in handen heeft.

In dit proefschrift wordt de katalytische verbranding van roetdeeltjes door middel van een vloeibare katalysator behandeld. Het idee achter een vloeibare katalysator is dat het door middel van bevontiging het contact met het roet kan bevorderen en daarmee de werking van een katalytisch filter. Het onderzoek werd in samenwerking met Europese dieselmotorfabrikanten gedaan en is toepassingsgericht. Een groot deel van de totale ontwikkeling van een katalytisch filter is doorlopen. Er is begonnen met simpele poeders en geëindigd met een prototype, vandaar de ondertitel van het proefschrift "From powder to prototype".
Informatie in wetenschappelijk literatuur kan een grote bijdrage leveren aan onderzoek. Een goed overzicht van de literatuur kan overbodig werk voorkomen en vergroot het inzicht in de eigen experimenten. Hoofdstuk 1 geeft een overzicht van de wetenschappelijke literatuur. Er wordt kort beschreven wat roet is en hoe de emissie daarvan gereguleerd wordt. Een uitgebreid overzicht wordt gegeven van de technologie van roetverwijdering uit uitlaatgas waar veel gebruik wordt gemaakt van resultaten van wetenschappelijk onderzoek en voorbeelden uit de praktijk. Belangrijke conclusies van dit hoofdstuk zijn dat het onderwerp zeer complex is, en dat de reeds ontwikkelde technologieën beperkingen hebben waardoor het niet duidelijk is voor welke oplossingen de industrie in de toekomst zal kiezen.

Een belangrijk deel van het onderzoek bestond uit het samenstellen van de bestanddelen van een katalytische filter. In Hoofdstuk 3 worden vloeibare katalysatoren gemaakt en wordt onderzocht hoe ze werken. In Hoofdstuk 4 worden dragers voor de vloeibare katalysatoren onderzocht. Zo’n drager is erg belangrijk omdat die moet voorkomen dat de katalysator de uitlaatpijp uitstroomt. In Hoofdstuk 5 wordt de bereiding van katalytische filters onderzocht en wordt met behulp van een case-studie onderzocht hoe de katalysator zich in het echt zal gedragen. De belangrijkste conclusies van deze hoofdstukken zijn dat vloeibare katalysatoren niet in staat zijn het roet te bevochtigen. Toch is de katalysator in staat om roet te oxideren en wel door middel van een zogenaamd 'spillover' mechanisme. De werking van dit mechanisme bleek zo goed te zijn dat de katalysator zich in het laboratorium kon meten met een van zijn concurrenten, namelijk het zogenaamde cerium katalytisch brandstofadditief. De case-studie wees echter uit dat het moeilijk zal worden om met de katalysator een filter constant schoon te houden omdat zijn werkingstemperatuur nog steeds te hoog is. Een nadelige bijkomstigheid van het gevonden 'spillover' mechanisme is dat het mogelijk wordt geacht dat het bij lage temperaturen niet zal kunnen werken wat verdere verbeteringen aan de katalysator moeilijk zal maken.

In Hoofdstukken 6 en 7 werden de katalytische filters onder praktijkcondities getest. Het bleek dat de katalysator in staat was om roet om te zetten, zelfs beter dan in de case-studie was voorspeld. Helaas ging de kwaliteit van de katalysatoren achteruit wanneer zich hoge temperaturen met stoom voordeden in het uitlaatgas.

De resultaten van dit proefschrift geven geen aanleiding om vloeibare katalysatoren toe te passen. De aanwezigheid van een vloeibare fase lijkt niet noodzakelijk en wordt daarom niet aangeraden. Toch bleek wel mogelijk te zijn om roet met behulp van een katalysator te oxideren wanneer er weinig contact tussen beiden aanwezig is. Er wordt echter gedacht dat hele lage onbrandingstemperaturen moeilijk te realiseren zijn, aangezien het spillover mechanisme mogelijk weinig ruimte geeft voor optimalisatie. De beste weg naar een verbeterde werking van een katalytisch filter blijft het verbeteren van het contact tussen het roet en de filter. Nu echter is gebleken dat een vloeibare katalysator deze weg niet mogelijk maakt, zal het moeilijk zijn om deze weg verder te volgen.
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Publikatielijst


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Curriculum Vitae
