
Regeneration of Catalytic Diesel Particulate Filters

**J. Gieshoff, M. Pfeifer, A. Schäfer-Sindlinger,
U. Hackbarth and O. Teysset**

Automotive Catalysts Division, dmc² AG

C. Colignon, C. Rigaudeau and O. Salvat

PSA Peugeot Citroën

H. Krieg and B.W. Wencławiak

Department of Chemistry, University of Siegen

**Reprinted From: Diesel Exhaust Emission Control: Diesel Particulate Filters
(SP-1582)**

The appearance of this ISSN code at the bottom of this page indicates SAE's consent that copies of the paper may be made for personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay a \$7.00 per article copy fee through the Copyright Clearance Center, Inc. Operations Center, 222 Rosewood Drive, Danvers, MA 01923 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale.

SAE routinely stocks printed papers for a period of three years following date of publication. Direct your orders to SAE Customer Sales and Satisfaction Department.

Quantity reprint rates can be obtained from the Customer Sales and Satisfaction Department.

To request permission to reprint a technical paper or permission to use copyrighted SAE publications in other works, contact the SAE Publications Group.



GLOBAL MOBILITY DATABASE

All SAE papers, standards, and selected books are abstracted and indexed in the Global Mobility Database

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISSN 0148-7191

Copyright 2001 Society of Automotive Engineers, Inc.

Positions and opinions advanced in this paper are those of the author(s) and not necessarily those of SAE. The author is solely responsible for the content of the paper. A process is available by which discussions will be printed with the paper if it is published in SAE Transactions. For permission to publish this paper in full or in part, contact the SAE Publications Group.

Persons wishing to submit papers to be considered for presentation or publication through SAE should send the manuscript or a 300 word abstract of a proposed manuscript to: Secretary, Engineering Meetings Board, SAE.

Printed in USA

Regeneration of Catalytic Diesel Particulate Filters

J. Gieshoff, M. Pfeifer, A. Schäfer-Sindlinger, U. Hackbarth and O. Teyssset
Automotive Catalysts Division, dmc² AG

C. Colignon, C. Rigaudeau and O. Salvat
PSA Peugeot Citroën

H. Krieg and B.W. Wenclawiak
Department of Chemistry, University of Siegen

Copyright © 2001 Society of Automotive Engineers, Inc.

ABSTRACT

This paper will discuss a number of different matters relating to the regeneration of catalyst coated diesel particulate filters such as: impact of the catalyst on the soot ignition temperature, soot combustion rate and NO₂ generation.

If catalytic coatings prove to be sufficient compared to certain fuel additives they could be used in second generation diesel particulate aftertreatment systems. Examples will be shown on how catalytic diesel particulate filters ("DPF") can operate on a common rail passenger car diesel engine. Furthermore, an outlook is given on the future combination of particulate - and NO_x - emission control for diesel passenger cars.

INTRODUCTION

The mandated EURO IV and LEV II legislation in 2005/2007 for diesel passenger cars and the increasing concern about health effects of diesel exhaust emissions leads to numerous efforts to solve the issue of NO_x and particulates of diesel vehicles. As shown in a previous SAE paper, a first car manufacturer has started to tackle the particulates issue for passenger cars by using a diesel particulate filter system requiring a fuel additive[1]. This development is only the first step into the direction of ultra clean diesel vehicles. Since the mid 1980's, a lot of efforts were made to solve the particulate emission problem on diesel engines [2].

However, none of these measures were sufficient to solve the problem completely. Figure 1 gives an overview of the possibilities to reduce particulates by means of engine measures or by emission control technologies.

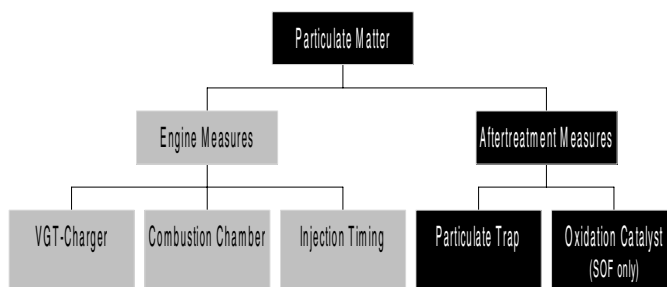


Figure 1: Possibilities for diesel particulate emission control

Diesel particulates can be filtered with a very high rate of efficiency. The major obstacle is the regeneration of the particulate filter [4]. Numerous papers were published that presented different soot ignition coatings [5]. Only a few technologies are in the market today whose main use is for heavy-duty applications. One of them applies a pre-catalyst to oxidize NO to NO₂ and to combust the collected soot with NO₂ [6]. It is well known that NO₂ oxidizes soot at temperatures in the range between 300°C and 400°C [7]. Notably, the broad application in passenger cars is limited due to its unfavorable temperature window for the particulate oxidation. In practice there is only one light duty vehicle currently available with a factory equipped DPF system using an additive to decrease the soot ignition temperature and to support the soot combustion process [1].

This paper demonstrates the capabilities of catalytic diesel particulate filter coatings for oxidative removal of diesel particulates. Catalytic coatings were categorized according to their potential to reduce soot ignition temperatures. Furthermore, the paper describes the impact of O₂ and NO₂ on passive regeneration of passenger car diesel particulate filters. Finally, the NO₂ impact on active regeneration is discussed and an

SOOT IGNITION COATINGS

Beginning in the mid 1980's many attempts have been made to develop materials which are able to lower the soot ignition temperature. None of the materials proved to be sufficient to lower the soot combustion temperature significantly except the so-called molten salts, such as the ones based on vanadia-containing compounds [8]. This class of compounds seemed to show promise, but recent investigations have shown some problems associated with these materials [9].

TGA AND DSC EXPERIMENTS – Most investigations into soot ignition temperatures start with thermogravimetric analysis (TGA) or differential scanning calorimetric (DSC) experiments. Usually a well-defined artificial soot like Printex U (Degussa-Hüls AG) is used. The advantage in using artificial soot relates to the fact that this type of material does not contain any soluble organic fraction thus providing a well-defined starting point for all the tests. Soot collected from engines does not always have a defined SOF content. The concentration depends greatly on the sampling procedures. Figure 2 gives an example for TGA tests with Printex U. Tests were performed in a mixture of 10% oxygen diluted in nitrogen in a temperature range between 25°C and 1000°C. The gas flow rate was adjusted to 50 ml/min with the temperature ramp 20°C/min.

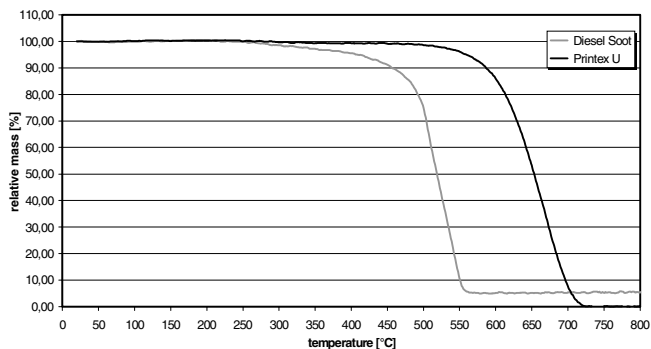


Figure 2. Soot combustion of Printex U and diesel soot in TGA experiments.

The soot combustion with Printex U starts at about 520°C and finishes at around 720°C. The curves are very reproducible. The soot ignition temperature is defined as the temperature at 50% soot combustion. The ignition temperature of diesel soot without any catalyst is usually 100°C lower than Printex U.

A concept has been proposed that by mixing certain materials with soot lead to either a change in the onset of the combustion or in an increase of the soot combustion rate [10]. A significant decrease of soot ignition temperature is only observable with a certain class of compounds which improves the contact

between soot and active catalyst material. Figure 3 shows an example of TGA with $K_4V_2O_7$.

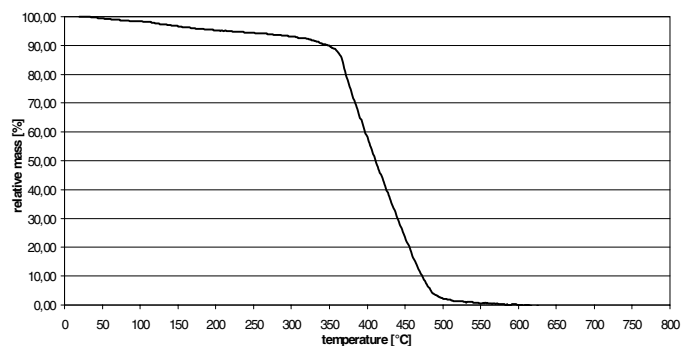


Figure 3: Impact of $K_4V_2O_7$ as catalytic material on soot ignition temperatures of Printex U

$K_4V_2O_7$ belongs to the class of molten salts which begin to liquefy before soot combustion starts. There are other materials with similar properties but they do not exhibit the same behavior. Table 1 lists these materials.

Table 1: Decrease soot ignition temperature (50% conversion) for different catalyst materials.

Material	Printex U [°C]	Diesel Soot [°C]
$K_4V_2O_7$	- 190	- 100
V_2O_5	- 100	- 10 ~ 20
Ce-Mn-Ag mixed oxide/Pt	- 60	- 20
$Ag_2V_2O_6$	- 10 ~ 20	none
CeO_2 /Pt	- 10	none
MnO_2 /Pt	none	none

As the list in Table 1 exemplifies, the most active compounds contain vanadium. V_2O_5 formation of vanadia salts at elevated temperatures up to 600°C during soot combustion was found. Oxygen storage material like ceria just increases soot combustion rate, but reduction of the soot ignition temperature is not observable.

A major disadvantage of TGA and DSC experiments was the test set-up does not represent the situation of wall flow particulate filters. The experiments are usually performed in small crucibles. In reality, the catalyst material is coated as a layer on the inner surface of the wall flow filter and a soot layer builds up on the top of catalyst. The exhaust gas passed these layers while flowing through the surface filter. In TGA and DSC experiments the gas does not flow through the sample mixture. Powder reactor experiments were designed to better represent actual conditions in wall flow filters but these tests also do not correlate completely to engine bench measurements with wall flow filters.

POWDER REACTOR TESTS – The powder reactor tests were performed with a mixture of Printex U and the catalyst material at a mass-ratio of 2:3. The model gas flows over the mixture deposited on a quartz filter. The tests reported here were also performed in a mixture of 10 vol.-% oxygen in nitrogen. The gas flow rate was set to 50 ml/min at standard conditions. The temperature ramp was 10°C/min, the temperature range was between 25°C and 800°C.

During these experiments, the soot combustion progress was monitored by mass spectrometry. The start of the soot combustion was determined when the oxygen signal (mass 32) started to drop. The soot ignition temperature was defined as the maximum of the CO₂ formation curve (mass 44). Figure 4 shows the soot combustion curves for different materials evaluated during the powder reactor experiments.

Table 2: Soot ignition temperatures determined by Powder Reactor tests

Material	Printex U [°C]	Diesel Soot [°C]
w/o catalyst	536	478
K ₄ V ₂ O ₇	398	372
V ₂ O ₅	476	433
Ag ₂ V ₂ O ₆	512	458
CeO ₂	505	453
CeO ₂ /Pt	525	450

As shown in Table 2, only the molten salt decreases the soot ignition temperature significantly. This confirms the TGA and DSC results. The observed soot ignition temperatures come closer to values observed for diesel soot in engine experiments. One important observation presents a drawback for materials based on molten salts such as K₄V₂O₇. As mentioned above, under reducing conditions such as the one occurring locally during soot combustion, vanadia formation was observed in the crucibles of the TGA and DSC experiments. Notably, Ag₂V₂O₆ decomposes into vanadia and metallic silver at temperatures below 600°C as shown in Figure 5. Decomposition of vanadia salts may pose limitations to their use in soot ignition catalysts. During filter regeneration temperatures up to 1000°C inside the trap were observed in engine test experiments.

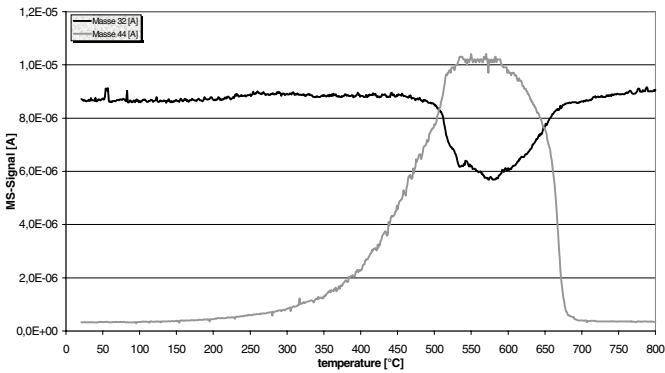


Figure 4. Soot ignition temperature when using catalyst components with Printex U in powder reactor tests

The soot combustion temperature for both types of soot decreases significantly and approaches the level of diesel soot in engine tests. The lowest soot combustion temperature was again observed with potassium vanadate while ceria and mixtures of Pt and ceria had almost no impact on soot combustion temperatures [9].

The results of these powder reactor tests are summarized in Table 2.

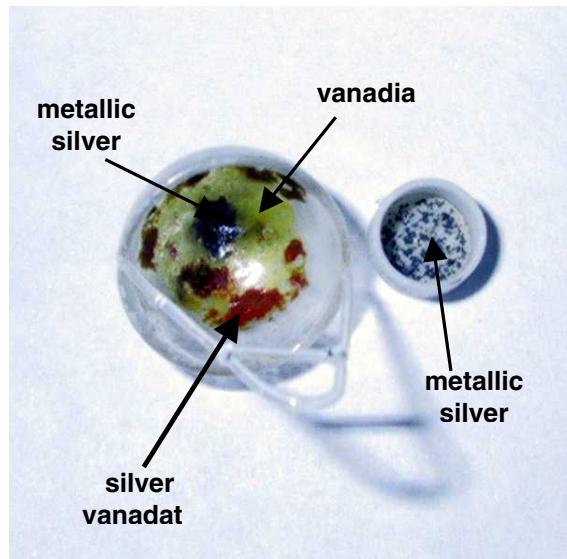


Figure 5: Vanadia and metallic silver formation during TGA and DSC tests.

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.