

An optimal usage of NO_x in a combined Pt/ceramic foam and a wall-flow monolith filter for an effective NO_x-assisted soot oxidation

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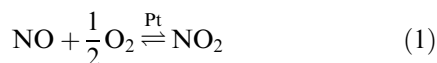
An NO₂-assisted soot oxidation based filter candidate consists of Pt-coated ceramic foam in combination with a wall-flow monolith is proposed to acquire for an optimal usage of exhaust NO_x. The configuration is designed to operate as deep bed filtration on Pt/ceramic foam and surface filtration on the wall-flow monolith. The oxidation of soot by NO₂ takes place by multi-cycle reaction in Pt/ceramic foam and by the normal CRT on the wall-flow monolith. The filter performs with a higher oxidation rate and a lower NO₂-slip.

KEY WORDS: CRT system; diesel filter; NO₂; NO_x; soot oxidation.

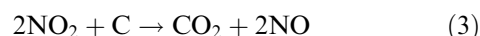
1. Introduction

A growing concern on health effect and demand to fulfil the emission regulation of noticeable diesel emissions, soot, urges the development of after-treatment systems. This stimulates the development both of diesel particulate filter (DPF) and of the invention of catalytic materials for the oxidation of trapped diesel soot. Molten salt catalyst had been proposed as a promising catalyst for the oxidation of diesel soot [1]. The superiority of this catalyst is thought to be its capability to establish a tight contact with the soot particle under practical conditions. The oxidation of soot with this catalyst is mainly based on the C—O₂ reaction. The temperature window for this type of catalytic oxidation is just above 600 K, which is in general relatively high in comparison with the average temperature of the diesel exhaust gas stream.

Another way to oxidise soot is to use C—NO₂ reaction. NO₂ can be obtained from the oxidation of NO, which is the main NO_x component in diesel exhaust gas. One of the soot oxidation systems based on C—NO₂ reaction is the so-called Continuously Regenerating Trap (CRTTM) system. This diesel after-treatment system claims to control particulate matter, as well as hydrocarbons (HC) and CO, with over 90% efficiencies and 700,000 km distance durability [2]. The CRT is composed of diesel oxidation catalyst installed upstream of a wall-flow monolith diesel soot filter. The main role of the oxidation catalyst is to convert engine out NO into NO₂. This NO₂ is essential to oxidise soot trapped on the wall-flow monolith. The chemical reactions, which take place in the system, are:



The carbon oxidation is also possible through the following stoichiometry:



For a reliable CRT technology, besides temperature windows for NO₂ formation and C—NO₂ reaction, a sufficient amount of NO_x is required. Assuming 50% NO_x is converted to NO₂ and the oxidation occurs through reaction (2), it can be calculated that the NO_x to soot ratio of at least 8, in mass base, is required [3]. Therefore, this technology is applicable in exhaust stream that contains relatively high amount of exhaust NO_x such as in those of heavy-duty diesel vehicle. Considering trend of decreasing engine out NO_x, a system with an optimal usage of NO_x should be employed. The produced NO₂ that is not reacted with the trapped soot is called NO₂ slip. Since the smell of NO₂ is rather unpleasant, the emission of the so-called NO₂ slip should be minimised.

1.1. Filter configurations base on NO₂-soot reaction

In this study the laboratory performance of the CRT-like system (the separated system) was compared with the so-called integrated system and *TU Delft filter* configuration using NO + O₂ as reactant gas. Instead of currently applied flow-through monolith as diesel oxidation catalyst Pt loaded ceramic foam catalyst was used in this present study. Soot is distributed in several ways to simulate possible soot trapping that might take place in a filter. In the CRT system soot is trapped only on the wall of the wall-flow monolith filter. To represent this configuration in the separated system, the soot particles were loaded only on the wall-flow monolith placed downstream of Pt/ceramic foam. To represent the situation of using only Pt/ceramic foam as a catalytic filter in the integrated system, soot was loaded onto the

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Pt/ceramic foam. The so-called *TU Delft filter* is composed of Pt/ceramic foam placed upstream of a wall-flow monolith. This filter configuration is designed to perform two stages of filtration *viz.* deep bed filtration on the Pt/ceramic foam and surface filtration on the wall-flow monolith. Therefore, soot was partly loaded on Pt/ceramic foam and partly on the wall-flow monolith.

2. Experimental

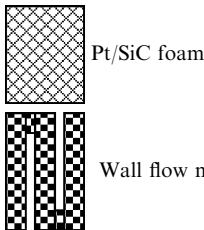
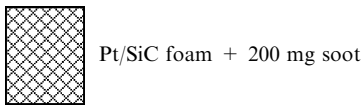
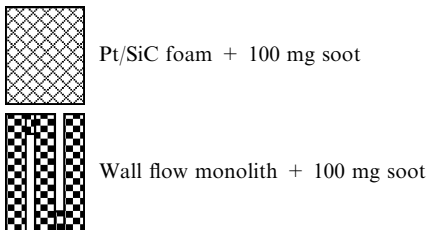
Pt/ceramic foam catalyst was prepared by incipient wetness impregnation of SiC foam (20 ppi, Porvair Advanced Material). 240 mg Pt(NH₃)₄·Cl₂·H₂O (Engelhard) was dissolved in 2.5 cm³ de-mineralised water and used as catalyst precursor solution. The impregnated foam was dried in 353 K in an oven for 2 h and, subsequently, calcined at 725 K for 2 h. This preparation method resulted in about 1.5 w% platinum content, as confirmed by XRF analysis. A 30 mm length SiC 100 cpsi flow-through monolith (NOTOX) with a mean grain size of 55 μm and 2 mm wall thickness was used to prepare the wall-flow monolith. The alternate monolith channels were blocked by ceramic glue compatible to SiC material (Ceramabond 503 Aremco product).

The soot oxidation experiments were performed in flow-reactor equipment. The feed gas is NO with Argon

as balance gas. The gas stream is fed to the vaporiser, where water can be injected. Oxygen is introduced just in front of the reactor to minimise the oxidation of NO to NO₂ before the reactant gas enters the reactor. Only up to 3% NO to NO₂ conversion is observed. The diameter of the reactor tube is 25 mm. A Hartman & Braun Uras 10E non-dispersive infra-red analyser (NDIR) is used to analyse CO, CO₂, NO, and SO₂. A NO_x analyser, CLD 700 EL ht (Eco physics), is placed downstream of the NDIR to analyse NO and NO₂. For the temperature programmed oxidation experiments, the sample was heated to 773 K with 0.2 K/min, followed by 1.5 K/min to 900 K and kept there for 1 h to verify the mass balance, which is normally in the range of 95–105 wt%.

Printex-U, a model soot, was deposited on the ceramic foams and the monolith by immersing the foam or the monolith into n-heptane dispersed soot (1.5 g/50 mL) for about 2 min followed by drying in 353 K oven. The procedure was repeatedly done until desired soot loading was obtained. For integrated system 200 mg soot was loaded on Pt/ceramic foam. The same amount of soot was loaded on the wall flow monolith in the separated system. For experiment with TU Delft filter, the 200 mg soot was equally distributed (100 mg on Pt ceramic foam and 100 mg on wall-flow monolith). The gas composition used was NO (typically 700 ppm)

Table 1
Schematic filter configurations and soot distributions on the filters for the oxidation experiment in the flow reactor

Catalytic filter configurations	Filter scheme and soot distribution	Gas compositions
1. Separated system	NO + O ₂ 	(1) 700 ppm NO + 10%O ₂
2. Integrated system	NO + O ₂ 	(1) 700 ppm NO + 10%O ₂
3. TUD filter	NO + O ₂ 	(1) 700 ppm NO + 10%O ₂ (2) 700 ppm NO + 10%O ₂ + 3%H ₂ O

and O_2 (typically 10 vol%) in Ar (gas balance). For experiment with water, 3 vol% water is injected. The gas hourly space velocity (GHSV) is set to be 65,000 L/L h. The soot distribution on the filter and the filter scheme are summarised in table 1.

3. Results and discussion

In figure 1, the $\text{CO} + \text{CO}_2$ emissions of the *TU Delft filter* configuration plotted as a function of temperature is presented together with the separated (CRT-like) system and the integrated system. As the amount of the total soot was kept constant and the same heating rate was applied, the $\text{CO} + \text{CO}_2$ emissions reflect the oxidation rate of each system. The NO_2 that is generated under these conditions is included in this figure. These data have been measured in a separate experiment in the absence of soot and are referred to as the 'base case

NO_2 '. In the separated system, figure 1a, it can be seen that NO_2 is generated by the system and reaches thermodynamic equilibrium already at 550 K. Despite the significant amount of NO_2 around 500 K, the generation of $\text{CO} + \text{CO}_2$ takes place at a somewhat higher temperature. Furthermore, only part of NO_2 is consumed in $\text{C}-\text{NO}_2$ reaction. This is assigned as NO_2 slip. The separated system configuration favours only for the so-called one stage reaction, which means that NO_2 is used to oxidise soot for one time. As a result the amounts of $\text{CO} + \text{CO}_2$ produced are almost the same as the amount of NO_2 produced. This system mimics the operation of the CRT system.

In figure 1b, the performance of the integrated system is presented. The production of $\text{CO} + \text{CO}_2$ from the soot oxidation at 550–625 K is significantly higher than the base case NO_2 . According to stoichiometry of reaction (2), it can be estimated that if all NO_2 produced reacts with carbon, the amount of $\text{CO} + \text{CO}_2$ will not exceed the total amount of NO_2 as in the separated system. As shown in figure 1b, even most of NO_2 is emitted as NO_2 slip, but for example at 560–650 K the amounts of $\text{CO} + \text{CO}_2$ is much higher than the base case NO_2 . Note that in this temperature window soot oxidation with oxygen can be excluded. In the integrated system, soot particles are randomly distributed along the Pt/SiC foam. The random distribution of soot and platinum particles as well as the SiC foam structure is favourable for the multiple usage of NO. The foam texture that consists of large cells enhances turbulence and produces good mixing [4,5]. These stimulate the occurrence of recycle reaction like the multiple NO_2 -soot reaction in the integrated system.

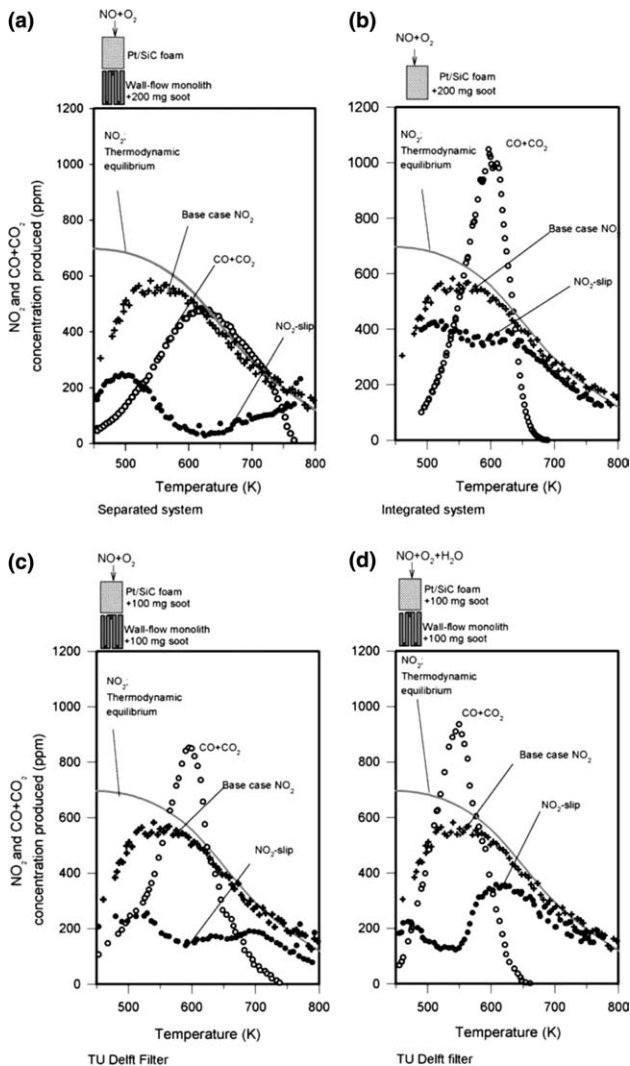


Figure 1. $\text{CO} + \text{CO}_2$ and NO_2 slip emissions from: (a) separated system, (b) integrated system, (c) *TU Delft filter* without water and, (d) *TU Delft filter* with water. The base case NO_2 was measured in separate experiments.

3.1. *TU Delft filter*

As shown in the previous section, using Pt/ceramic foam alone as a filter candidate, the integrated system, has a potential drawback since the significant amount of NO_2 slip emission is observed. Furthermore, the application of ceramic foam as diesel filter will result in relatively low filtration efficiency. Although 40–70% efficiencies can be observed [6,7], the geometry and test conditions strongly affect the efficiencies. Furthermore, decreasing efficiency is observed due to the soot re-entrainment [8].

A combination of Pt/ceramic foam and a wall-flow monolith, *TU Delft filter*, was then tested to explore the potential of the system to overcome the above mentioned limitations. In this configuration, Pt/ceramic foam is installed upstream of a wall-flow monolith. This configuration will fulfil the application of two types of filtration and the concept of utilising NO_2 slip. With respect to the filtration process the filter configuration should be capable to employ two stages of filtration, namely: deep bed filtration on the foam and surface filtration on the wall-flow monolith. At the same time,

two modes of soot oxidation reactions will operate. In Pt/ceramic foam NO oxidation to NO₂ and recycle reaction of NO₂-assisted soot oxidation take place, while part of NO₂ is released as NO₂ slip, and this NO₂ slip is, subsequently, used to oxidise trapped soot on a wall-flow monolith.

The concept of utilising NO₂ slip is demonstrated in figure 1c. The *TU Delft filter* shows an equivalent oxidation rate in comparison to the integrated system. The main gain of combining Pt/ceramic foam with a wall-flow monolith is the lower amount of NO₂ slip as clearly shown when comparing the amount of NO₂ slip with that of the integrated system, figure 1b. This lower NO₂ slip is clearly caused by C—NO₂ reaction in the wall-flow monolith.

It has to be noted that the amount of NO₂ slip is influenced by the amounts of soot loaded downstream of NO₂ generator. By comparing the NO₂ slip of the separated system to the *TU Delft filter*, figure 1a–c, it can be concluded that the lower NO₂ slip in the separated system is caused by the higher amount of soot loaded than that in the *TU Delft filter*. In the separated system 200 mg soot was loaded, while in the wall-flow monolith of *TU Delft filter* is 100 mg. Therefore, data presented in this work could not straight forward be compared to that of the CRT test data that shows about 20% NO₂ slip [9]. A similarity between *TU Delft filter* and the CRT system is that both system use NO₂ generated upstream of trapped soot to oxidised soot. The *TU Delft filter* might have, however, a better oxidation performance than the CRT system because in *TU Delft filter*, Pt/ceramic foam will act not only as multi-NO₂ generator, but also as a catalytic trap. This is not the case in Pt-catalysed flow-through monolith of the CRT system, which acts only as single NO₂ generator. As clearly shown in figure 1c, soot trapped in Pt ceramic foam is combusted with high oxidation rate due to the multiple usage of NO_x.

In the so-called CR + CSF, where platinum catalyst is coated on the DPF part of the CRT system, the multiple use of NO₂ is also claimed to occur [2]. Compared to *TU Delft filter* this system has only one trapping system, which is the catalysed DPF part, while in *TU Delft filter* both multi-NO₂ generator (Pt/ceramic foam) and the wall-flow monolith function as filter. The pressure drop of the *TU Delft filter* is not checked yet in this work. Taking into consideration that ceramic foam results in very low pressure drop, the pressure drop behaviour of the system would, however, be similar to that of wall-flow monolith system. Example of pressure loss of the DPF study in relation to soot loading is discussed in [10].

3.2. The influence of water

The influence of water has been long acknowledged to influence the oxidation of soot with NO₂ [11,12]. In this work, soot oxidation rate of *TU Delft catalytic filter*, when water is present, is also measured. The result is presented in figure 1d. It is clear that the oxidation rate

was enhanced while the NO₂ slip is lower than without water in the presence of soot at 550 K. Similar result was observed when the same experiment was done with the integrated system (not shown). The generally accepted explanation for the role of water is that water accelerates the decomposition of surface oxygen complexes (SOC's) as soot oxidation intermediates. This SOC's decomposition is generally accepted as a rate determining step in diesel soot oxidation reaction. This is, of course, beneficial in view of commercial application because about 2–10% water is always present in the exhaust stream.

4. Conclusions

1. For the NO_x-assisted soot oxidation diesel filter system, platinum-based catalyst can be installed upstream of the soot bed to account for the CRT operation. To account for higher oxidation rate through soot-NO₂ recycle reaction, soot should be trapped in such a way that it is randomly distributed with platinum catalyst such as in the case of soot loaded on Pt/ceramic foam. NO₂-assisted soot oxidation with Pt/ceramic foam resulted in high oxidation rate in the expense of high NO₂ slip.

2. An improvement in the use of NO₂ has been observed in the *TU Delft filter*. In this filter soot oxidation takes place in Pt/SiC foam through multiple NO₂-soot reaction and in wall-flow monolith filter with the CRT operation. The oxidation rate of *TU Delft filter* is about 90% of that of the integrated system with the benefit of lower NO₂ slip.

3. The presence of water is beneficial for the NO₂-soot reaction based diesel filter system.

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