

# THE DEVELOPMENT OF CATALYTIC DIESEL PARTICULATE FILTER; (SOOT OXIDATION UTILIZING EXHAUST NO<sub>x</sub>)\*

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**Summary:** Increasing concerns on health effect and pressure to fulfill the emission regulation of noticeable diesel emission, soot, urge the development of diesel after-treatment systems. This stimulates the development of both catalyst and filter material. Latest development at TU Delft emphasizes on the development of catalytic filter by utilizing exhaust NO<sub>x</sub>. Two standard soot catalytic filter configurations and a so-called TUD catalytic filter have been investigated. The Pt/SiC foam catalyst upstream of soot configuration showed the lowest NO<sub>2</sub>-slip, but on the other hand the lowest soot oxidation rate. In the configuration where soot was loaded on Pt/ceramic foam, a higher soot oxidation rate but also higher NO<sub>2</sub>-slip was observed. An improvement on the utilisation of NO<sub>2</sub> has been observed in the TUD designed catalytic filter, verified by decreasing NO<sub>2</sub>-slip and increasing soot oxidation rate.

## 1. Introduction

Diesel engines with its popularity of compression-ignition principle and fuel economy potentially contributes to some atmospheric environmental problems. The engine emits specific pollutants that are hazardous for human health, e.g. carbon monoxide, hydrocarbons, soot, SO<sub>x</sub>, and NO<sub>x</sub> [1]. The visible sooty diesel exhaust has come under significant pressure, resulting in more stringent emission regulations all over the world. Starting in 1987 in California USA, and in 1992 in Europe the emission of diesel engine have to adjust to the standard. In ASEAN countries, the so-called EURO II standard, effected in Europe in 1996, will be effected in 2003. Some of the countries, Singapore and Thailand, have complied to this regulation earlier [2].

The most promising technique of soot reduction is particulate capture followed by catalytic combustion. Molten salt catalyst is one of the catalysts materials developed at TU

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Delft. Under simulated laboratory conditions, molten salt catalyst appeared to be promising and showed a comparable activity as commercially available catalytic fuel additives [3].

The oxidation of diesel soot with  $\text{NO}_2$  is another option.  $\text{NO}_2$  can be produced from exhaust  $\text{NO}_x$ , which subsequently oxidises soot trapped on the filter. However, driven by legislation, a trend in the development and production of new vehicle is to decrease  $\text{NO}_x$  emission. The so-called primary measure consists of engine modifications, fuel modifications and intake air modifications can lead to a lower  $\text{NO}_x$  formation of about 30-60% [4]. The 60% reduction is, however, not enough to comply to  $\text{NO}_x$  standards as define in Euro IV and V. Nevertheless, the trend can have an impact on the performance of the technology relying on  $\text{NO}_x$  in exhaust gas stream.

As an implication of decreasing  $\text{NO}_x$  emission, for  $\text{NO}_x$  assisted after-treatment system to be more efficient, a better utilisation of  $\text{NO}_x$  has to be applied in such a way that  $\text{NO}$  produced from the reaction of soot with  $\text{NO}_2$  has to be recycled. We observed that a physical mixture of soot and platinum catalyst could lead to the occurrence of recycle reactions [5]. The recycle reactions might overcome a limited amount of  $\text{NO}$  in the exhaust stream. In this investigation we explore the possibility to utilise more efficient  $\text{NO}_x$ , in the filter configuration for the oxidation of soot. An advanced catalytic filter consisting of Pt/ceramic foam and a SiC membrane was designed. This expectedly improves the performance of standard catalytic filter containing only Pt/SiC foam. The utilisation of  $\text{NO}_2$  was also explored in the oxidation of metal activated diesel soot. A gas stream of  $\text{NO}+\text{O}_2$  is used and the catalyst is tested in a laboratory reactor. The influence of  $\text{H}_2\text{O}$  vapour was also taken into consideration.

## 2. Experimental

The experiments were performed in the flow reactor equipment described elsewhere [6,7]. A 25 mm diameter quartz reactor was used with a constant gas flow of 1000 ml/min. A gas mixture containing  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  was used with Argon as a gas balance. A heating rate of 0.2 K/min was applied for the temperature programmed oxidation, while isothermal reaction was performed at 575 K.

Before each experiment, about 200 mg ( $\pm 10\%$ ) soot was loaded on the catalyst formulation. The catalysts tested are Pt/SiC foam (25 mm diameter and 30 mm length) and an integrated Pt/SiC foam and SiC membrane (20 mm diameter and 30 mm length Pt/SiC

foam in SiC membrane cylinder), this referred as TUD catalytic filter. The soot sample is Printex-U, a model soot. Three catalyst configurations are investigated. These are Pt/SiC foam upstream of soot bed (referred to as separated system), soot loaded on Pt/SiC foam (referred to as integrated system), and a combination of Pt/SiC foam and SiC membrane at which soot was loaded on foam only and both on foam and membrane.

Pt/SiC foam catalyst was prepared by incipient wetness impregnation. The reaction effluent gases, CO, CO<sub>2</sub>, NO, and SO<sub>2</sub> were measured with a Hartman & Braun URAS 10 Non Dispersive Infra Red Analyser. A NO<sub>x</sub> analyser is incorporated to analysed NO and NO<sub>2</sub>. Based on the flow and the concentration of CO+CO<sub>2</sub> produced, the soot oxidation rate was calculated together with the mass balanced.

### 3. Result and Discussion

#### 3.1. Basic utilisation of NO/O<sub>2</sub>-Pt/ceramic foam system

Figure 1 demonstrates that soot oxidation can take place either with O<sub>2</sub> or with NO<sub>2</sub>. When soot was loaded on Pt/SiC foam and O<sub>2</sub> was used as reactant gas, significant soot oxidation rate with O<sub>2</sub> can only take place at relatively high temperatures (650 to 750 K). When NO+O<sub>2</sub> was introduced into the system, the production of NO<sub>2</sub> over platinum catalyst can take place, which then followed by soot oxidation with NO<sub>2</sub>. Both NO<sub>2</sub> production and soot oxidation can occur at relatively low temperatures (starting at 500 K).

By using NO+O<sub>2</sub> as feed gas, two configurations of platinum-soot give rise to a contrast oxidation profile. In the separated system Pt/SiC foam functions as NO<sub>2</sub> generator. NO<sub>2</sub> produced then enters the next ceramic foam loaded with soot at which soot oxidation with NO<sub>2</sub> occurs. In this circumstances, NO is re-produced, but it is not used any further. This is a miniaturisation of commercial Continuously Regenerating Trap (CRT) technology.

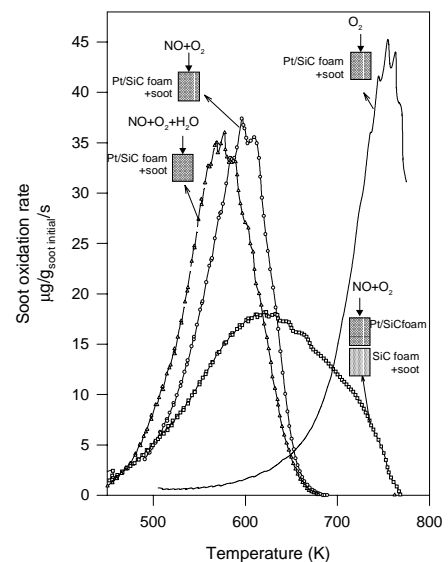


Figure 1  
Effect of gas composition and catalyst configuration on soot oxidation rate;  
Temperature programmed oxidation heating rate of 0.2 K/min

In the integrated system, platinum catalyst and the soot particles are randomly distributed. As a result, NO reproduced from soot oxidation with NO<sub>2</sub> can go through the reaction cycle and possibly to oxidise soot multiple time. This explains that the oxidation rate of soot loaded in Pt/ceramic foam is higher than that in Pt/ceramic foam upstream of soot configuration.

The explanation becomes clear when the base case NO<sub>2</sub>, NO<sub>2</sub>-slip, and CO+CO<sub>2</sub> produced from the reaction systems are compared, as shown in Figure 2. The base case NO<sub>2</sub> describes the concentration of NO<sub>2</sub> that is generated under these conditions and measured in a separate experiment. NO<sub>2</sub>-slip is the amount that does not react with soot.

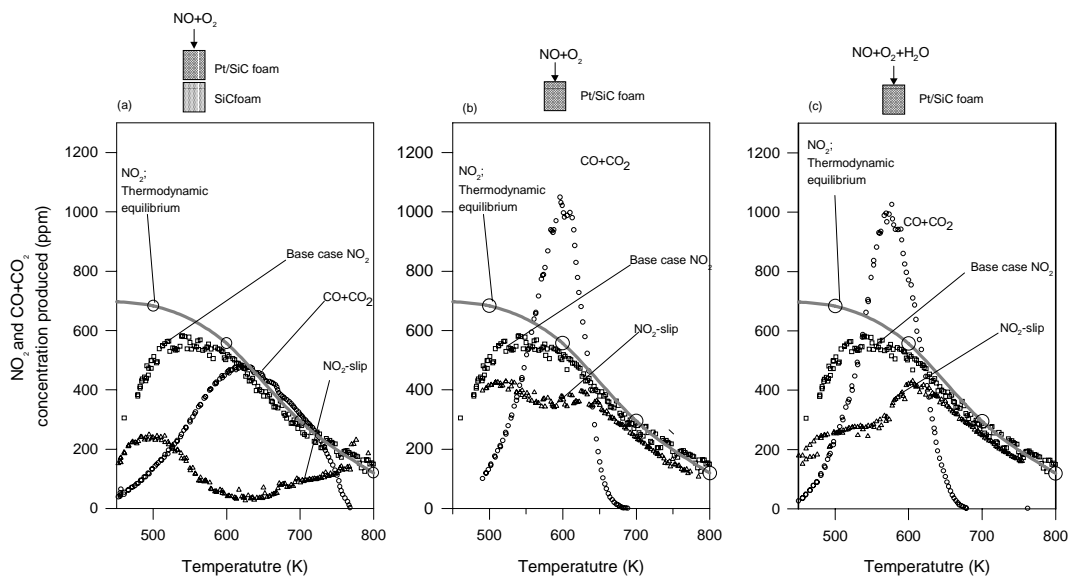
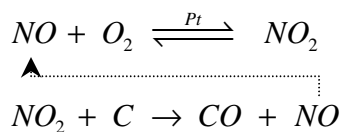


Figure 2  
NO<sub>2</sub>-slip and the production of CO+CO<sub>2</sub>  
from different catalyst configurations and gas compositions

The low amount of NO<sub>2</sub> slip in the separated system indicates that most NO<sub>2</sub> is consumed to oxidise soot, and to re-produce NO. In the integrated system, the amount of NO<sub>2</sub>-slip is higher. This is due to the occurrence of recycle reaction of NO to NO<sub>2</sub> coupled with soot oxidation



The recycle reaction is favourable in the ceramic foam structure as the mega porosity/pore tortuosity of the foam structure enhance the turbulence in gas flowing through the foam, produces better mixing, and transport [8] like soot oxidation.

The light off temperature of soot oxidation becomes lower when 3% H<sub>2</sub>O is fed to the gas stream, as also shown in Figure 1. Cooper and Thoss [9] proposed that the increased in soot oxidation rate by water addition possibly due to the facilitation of NO<sub>2</sub> adsorption on the active site of the soot particles. At low temperature regime, the amount of NO<sub>2</sub>-slip is less than the system without water, if one compare Figure 2b with 2c. The presence of water, therefore, might help the adsorption of NO<sub>2</sub> on the soot surface. Adsorbed NO<sub>2</sub> can then initiate soot oxidation at lower temperature. As a result with the present of water the onset temperature in soot oxidation is lower. Although still not clear, the other possible explanation is that water takes a role in the decomposition of surface oxygen complexes (SOC's), a presumed intermediate in the oxidation of soot.

### 3. 2. An advanced utilisation of NO<sub>2</sub> by means of filter configuration

Advanced NO<sub>2</sub> utilisation was observed in a TUD catalytic filter. By loading about 120 mg soot on SiC membrane and 80 mg on Pt/SiC foam, the performance of this catalyst configuration is tested. The result is compared to the experiment where only 80 mg soot loaded on Pt/SiC foam, but not on SiC membrane. The production of CO+CO<sub>2</sub> and NO<sub>2</sub> as a function of conversion at 575 K are compared and presented in Figure 3. Clearly that NO<sub>2</sub>-slip of the TUD designed filter is lower than the standard Pt/ceramic foam. This lower NO<sub>2</sub>-slip is accompanied by higher CO+CO<sub>2</sub> production.

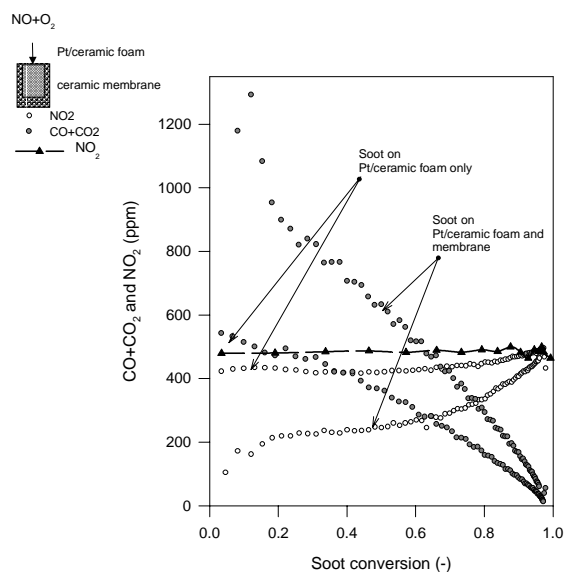


Figure 3  
Decreased NO<sub>2</sub>-slip and Increased of CO+CO<sub>2</sub> production by means of advanced filter configuration during isothermal soot oxidation at 575 K with 700 ppm NO and 10% O<sub>2</sub>

In the TUD filter, NO<sub>2</sub>-slip was decreased when soot was loaded on both Pt/SiC foam and SiC membrane. Compare to the NO<sub>2</sub>-slip when soot only loaded on Pt/SiC foam, 50% NO<sub>2</sub> slip can be utilised for additional soot oxidation. Experiment with soot loaded on both SiC foam and the membrane produced more CO+CO<sub>2</sub> and less NO<sub>2</sub>-slip than that of soot loaded only on Pt/ceramic foam only. This indicates that the reaction take place both in Pt/SiC foam by a multi-cycle mode, and on ceramic membrane utilising NO<sub>2</sub>-slip released from Pt/ceramic foam section. The increase in NO<sub>2</sub> production in both experiments reflected the decrease of soot remaining in the system. The less soot remains the less NO<sub>2</sub> consumed.

#### 4. Conclusion

The use of Pt/ceramic foam as NO<sub>2</sub> generator and reactor for the oxidation of soot tends to produce NO<sub>2</sub> as a secondary emission. In the separated system, the lowest NO<sub>2</sub>-slip but the lowest soot oxidation rate was observed. Meanwhile in the integrated system the higher oxidation rate but also higher NO<sub>2</sub>-slip can be produced. An improvement on the utilisation of NO<sub>2</sub> has been observed in the so-called TU Delft filter configurations, where soot was loaded on Pt/SiC foam placed in a SiC membrane at which soot was also loaded. The configuration gives rise to the highest soot oxidation rate and lowest NO<sub>2</sub>-slip.

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