

## CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub>

### A Potential Pt Replacement for NO<sub>x</sub>-Assisted Soot Oxidation Catalyst

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#### Abstract

Non-noble metal materials based on CeO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> have been studied in order to evaluate their potential as NO<sub>x</sub>-assisted soot oxidation catalysts. The final objective is to find a cheap material as substitute for Pt catalyst, normally applied in Continuously Regenerating Trapp (CRT), a commercial soot catalytic converter system. The catalytic activities were tested in flow reactor equipment both for NO oxidation and NO<sub>x</sub>-assisted soot oxidation. In testing the performance as NO oxidation catalyst, the reactor was filled only with catalyst. The feed gas used were 700 ppm NO, 10% O<sub>2</sub> and Argon as gas balance. In the investigation of the activity as NO<sub>x</sub> assisted soot oxidation catalyst the reactor was filled with soot bed placed downstream of the catalyst bed. Similar experiments were carried out with commercial Pt catalyst for comparison.

The catalysts were found to be significantly active in the oxidation of NO but the activity was lower than that of the commercial Pt catalyst. Produced NO<sub>2</sub> reaches thermodynamic equilibrium at 620 K and above. In NO<sub>x</sub>-assisted soot oxidation experiment, NO<sub>2</sub> generated in the first bed enters the soot bed in which NO<sub>2</sub>-soot reaction takes place. Isothermal experiment at 625 K showed that the reaction rate is comparable with that of Pt catalyst. This can be explained as follow. It is generally accepted that, NO<sub>x</sub>-assisted soot oxidation rate is mainly influenced by the amount of NO<sub>2</sub>. Since at 625 K, both with our catalyst and the commercial Pt catalyst, the

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amount of  $\text{NO}_2$  has reached equilibrium, it is reasonable that the oxidation rates are comparable. Therefore, the  $\text{CeO}_2\text{-Mn}_2\text{O}_3$  based catalyst is a potential Pt replacement to be used in the CRT's  $\text{NO}_x$ -assisted soot oxidation catalyst.

**Increased  $\text{NO}_x$ -assisted soot oxidation rate by Ce-Mn catalyst generated 'active oxygen'** ~~Base metal in the catalysis of soot oxidation~~  
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## 1. Introduction

Due to Environmental and health effects of diesel soot and the pressure to comply with the emissions regulations, reduction of diesel soot emission has gained a lot of attention. It is not surprising that efforts to reduce the emissions are ongoing and remain a challenging topic. One of the reduction strategies is to employ a diesel after-treatment system onto the exhaust. Soot trapping followed by oxidation with the highly reactive  $\text{NO}_2$  is an example and the basis of the so-called Continuously Regenerating Trap (CRT) [1] and the TU Delft filter [2]. These filter systems contain a platinum catalyst upstream of a soot trap. The main differences are as follows. In the CRT system Pt is loaded on a flow-through monolith, while in the TU Delft filter Pt catalyst is loaded on ceramic foam. In the CRT system the Pt coated flow-through monolith functions only as  $\text{NO}_2$  generator, no soot trapping or soot oxidation is aimed for. In the TU Delft filter a Pt/ceramic foam catalyst is designed as a multifunctional reactor that functions not only as  $\text{NO}_2$  generator but also as soot filter; a specific advantage is that  $\text{NO}_2$  is used catalytically, viz. every  $\text{NO}_2$  is used more than once. In both systems  $\text{NO}_2$  is generated that passes through the wall-flow monolith where it reacts with the trapped soot.

To deal with

### ~~A BRIEF SURVEY ON THE CATALYSIS FOR THE OXIDATION OF DRY DIESEL SOOT~~

~~In the last two decades, a number of materials have been explored as catalysts for diesel soot oxidation. The fact that in diesel exhaust  $\text{O}_2$  is available excessively (4-10%), has influenced the development of catalyst for the oxidation of soot. The study for the catalyst was initially focused on the direct contact between catalyst and soot in order to decrease the C- $\text{O}_2$  reaction temperature, which is generally, above 800 K for the non-catalytic soot oxidation. Furthermore, the catalytic oxidation of soot is slow,~~

since the solid soot particles are large and, when deposited, immobile. They cannot penetrate into the catalyst's micro pores or meso pores where catalytic processes usually take place. Soot oxidation takes place mainly on the filter walls of the particle filter where the catalyst has been deposited.

A good way of improving the quality of induced self supporting regeneration of a particle filter is to increase the reactivity of soot with a built in metal catalyst. Such a catalyst can be incorporated during the soot formation process. Blending a stable organo metallic additive into the fuel (typically 10-100 ppm) is the most convenient method. These catalytic fuel additives are also known as fuel borne catalysts and result in quasi-continuous regeneration [51].

Some catalysts can oxidize soot without having intimate physical contact. They catalyze the formation of a mobile compound ( $\text{NO}_2$ ,  $\text{O}_{\text{ads}}$ , etc.) that is more reactive than  $\text{O}_2$ . 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;  $\text{NO}_x$ -aided gas phase mechanism and spill-over mechanism.

Cooper and Thoss [54] patented a way of using gas phase  $\text{NO}_2$  as an activated mobile species for soot oxidation ( $\text{NO}_x$ -aided gas phase mechanism) in combination with a filter device. The reaction of  $\text{NO}_2$  with carbon material was published as early as 1956 [55]. They proposed that  $\text{NO}_2$  accelerates soot combustion:



Some catalysts can dissociate oxygen and transfer it to the soot particle, where it reacts as if it were in a non-catalytic reaction. This mechanism is known as the spill-over mechanism [ ].

Some examples exist that show that contact is not prerequisite in this type of reaction. For instance, Baumgarten and Schuck [56] 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 spill-over. Baker and Chludzinski [57]

~~showed that  $\text{Cr}_2\text{O}_3$  could accelerate edge recession of graphite while being motionless. Mul et al. [30] showed with a labelled oxygen study that spill over and redox oxidation can occur simultaneously. They discussed that the dominating mechanism will depend on the degree of physical contact between the catalyst and soot.~~

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In an attempt to increase the oxidation rate with  $\text{NO}_2$ ,  $\text{CeO}_2$  catalysts had been evaluated in a CRT-like bed reactor where miniaturisation of the CRT was employed. In that study, a quartz reactor was filled with two separate beds, a soot bed placed downstream of a Pt/alumina bed. The soot bed contains soot physically mixed with  $\text{CeO}_2$  catalyst in a so-called a 'loose contact' procedure. In that experiment, so-called 'active oxygen' was proposed as active specie that accelerates the oxidation rate. Recently, using labeled oxygen the creation of active oxygen was studied in an advance TAP reactor [ ]. It was shown that at 400 C active oxygen is also thought to be responsible

In this present paper, a study to find an alternative to find a cheaper material as substitute for Pt catalyst, normally applied in Continuously Regenerating Trapp (CRT), a commercial soot catalytic converter system is described. This include catalyst screening and catalytic testing as NO oxidation and  $\text{NO}_x$ -assisted soot oxidation.

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## 2. Experiments

### Catalyst Preparation and Characterization

#### a. Materials

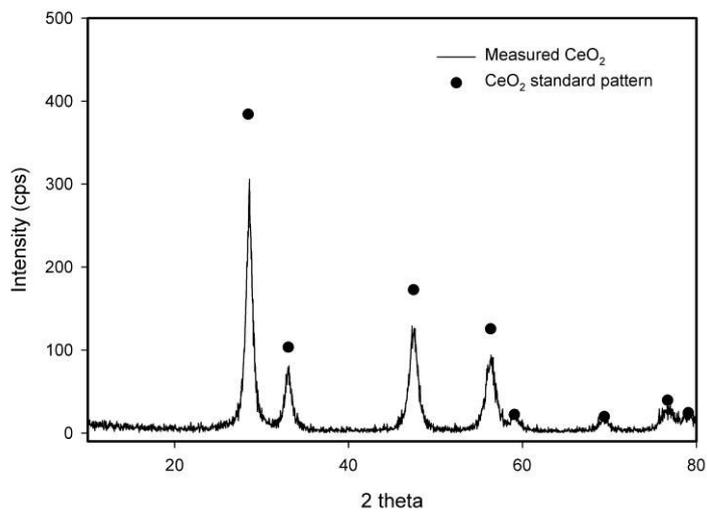
CeO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> catalysts were used in this study. The catalyst were prepared by incipient wetness impregnation on 63 to 100 μm γ-alumina (AKZO Nobel 003-1.5e) from those nitrate precursors. Catalysts content and those specific surface area are presented in Table 1. A Pt/alumina catalyst was obtained from Engelhard Corp. USA. The BET specific surface area of the catalysts were measured by Quantachrome Autosorb-6B. The model soot used is Printex-U. This model soot was proven to be an appropriate model for the NO<sub>2</sub>-soot based reaction [11].

Table 1.

<u>Sample</u>	<u>Catalyst Content</u>	<u>S<sub>BET</sub> (m<sup>2</sup>/g)</u>
<u>CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub></u>	<u>15%</u>	<u>111 ± 3</u>
<u>Mn<sub>2</sub>O<sub>3</sub>//Al<sub>2</sub>O<sub>3</sub></u>	<u>15%</u>	<u>103 ± 2</u>
<u>CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub></u>	<u>15%</u>	<u>100 ± 2</u>
<u>PtO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub></u>		

The powder diffraction pattern of the catalysts samples are shown in Figure 1. The pattern shows that the sample contains only CeO<sub>2</sub> phase.

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**Figure 1.** Powder diffraction pattern of CeO<sub>2</sub> sample

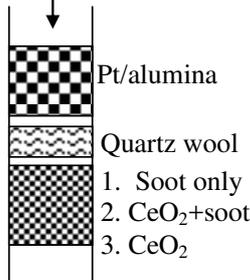
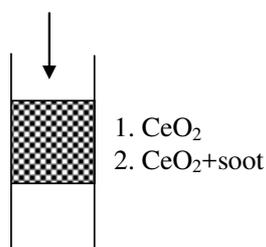
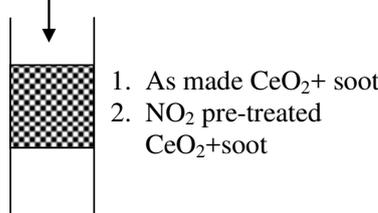
#### Activity test

The catalytic activities were tested in flow reactor equipment both for NO<sub>x</sub> oxidation and NO<sub>x</sub>-assisted soot oxidation. The flow reactor equipment is schematically presented in Figure xx. The flow reactor equipment described in [11] was used to examine the influence of CeO<sub>2</sub> in NO<sub>2</sub>-assisted soot oxidation. A quartz reactor with 6 mm inner diameter was filled with two separate beds, a soot bed placed downstream of a Pt/alumina bed. Quartz wool was used to separate the two beds. The

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soot bed contains 20 mg soot physically mixed with 40 mg  $\text{CeO}_2$  and 400 mg SiC in a so-called a 'loose contact' procedure, while the Pt/alumina bed contains 40 mg 1% Pt/alumina mixed with 400 mg SiC. In another reactor 20 mg soot was mixed with 400 mg SiC and placed downstream of the Pt catalyst bed. Several reference experiments were also done for comparison. The samples were heated to 900 K at a heating rate of 0.6 K/min. Unless otherwise stated, the gas composition used is 700 ppm NO + 10%  $\text{O}_2$  with argon as balance gas. An NDIR and a NOx analyser are placed downstream of the reactor to analyse the reaction product.

**Table 1.** Reactor bed configurations for catalyst activity of soot oxidation and NO oxidation to  $\text{NO}_2$

Bed configurations	Aspects to observe:
<p>700ppm NO+10%<math>\text{O}_2</math></p>  <p>1. Soot only 2. <math>\text{CeO}_2</math>+soot 3. <math>\text{CeO}_2</math></p>	<p>1. <math>\text{NO}_x</math> assisted soot oxidation rate without <math>\text{CeO}_2</math></p> <p>2. <math>\text{NO}_x</math> assisted soot oxidation rate with <math>\text{CeO}_2</math></p> <p>3. Effect of <math>\text{CeO}_2</math> down stream Pt catalyst on the formation of <math>\text{NO}_2</math></p>
 <p>1. <math>\text{CeO}_2</math> 2. <math>\text{CeO}_2</math>+soot</p>	<p>1. Catalytic activity of <math>\text{CeO}_2</math> in the formation of <math>\text{NO}_2</math> without Pt catalyst</p> <p>2. Oxidation rate of <math>\text{CeO}_2</math>-soot</p>
<p>10% <math>\text{O}_2</math></p>  <p>1. As made <math>\text{CeO}_2</math>+ soot 2. <math>\text{NO}_2</math> pre-treated <math>\text{CeO}_2</math>+soot</p>	<p>Effect of <math>\text{NO}_2</math> pre-treated <math>\text{CeO}_2</math> on the oxidation rate of soot with <math>\text{O}_2</math></p>

Activity tests were designed to evaluate the catalysts performances in both NO oxidation and indirect soot oxidation catalysis. In NO oxidation, the catalysts were tested both as a single bed and as a second bed placed downstream of Pt catalyst in the flowing NO and O<sub>2</sub> gas mixture. In the single bed configuration, the activity of the catalyst is entirely measured. In the configuration where the catalyst was placed downstream of Pt catalyst, the oxidation of NO to NO<sub>2</sub> is mainly due to Pt catalyst. Locating the catalyst bed down stream of Pt catalyst strives for evaluating its (synergetic) influence on Pt catalysed conversion of NO to NO<sub>2</sub>.

As mentioned the catalysts were, furthermore, tested as indirect soot oxidation catalysts, which means the role of catalyst is to provide soot oxidation active species such as NO<sub>2</sub> or 'active oxygen' as a result of catalyst O<sub>2</sub>, catalyst NO, or catalyst-NO<sub>2</sub> interactions. As in NO oxidation experiments, tested catalysts are put in both single bed and as a second bed downstream of Pt catalyst. Table 1 summarise the activity test experiments.

<u>Catalysts Bed Configuration</u>	<u>Experiments</u>		
	<u>NO oxidation</u>	<u>Soot Oxidation</u>	<u>Isothermal</u>
<u>NoCat</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Ce5%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Ce10%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Ce15%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Mn15%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Co15%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Ce-Mn10%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Ce-Mn15%</u>	<u>✓</u>		<u>✗</u>
<u>Pt No-Cat</u>	<u>✓</u>	<u>✓</u>	<u>✓</u>
<u>Pt Ce10%</u>	<u>✓</u>	<u>✓</u>	<u>✗</u>
<u>Pt Ce15%</u>	<u>✓</u>	<u>✓</u>	<u>✓</u>
<u>Pt Co15%</u>			
<u>Pt Mn15%</u>			
<u>Pt</u>	<u>✓</u>	<u>✓</u>	<u>✓</u>

<u>Ce-Mn10%</u>			
<u>Pt</u> <u>Ce-Mn15%</u>			<u>Y</u>

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### 3. Results

To determine catalyst reduction temperature and to get indications of active catalyst, Temperature Programmed Reduction (TPR) analysis was carried out to Mn, Co, and Ce Mn-Ce catalysts. The catalysts TPR profiles are shown in Figure 3.3. CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> mixed oxide shows the lowest reduction temperature, followed by Mn<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>. It was anticipated that reduction temperature would be related to the activity

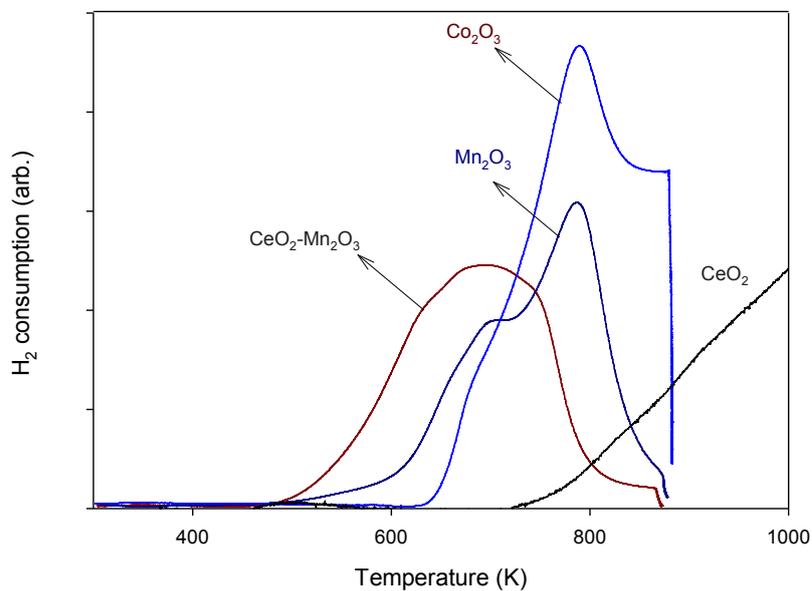


Figure 3.3 Temperature Programmed reduction of the prepared catalyst with Xx ml/min flowing H<sub>2</sub>, temperature programmed of aa K/min

### 3. Catalysts Activity in NO oxidation to NO<sub>2</sub> and PM Oxidation

The activity of the prepared catalysts in the oxidation of NO to NO<sub>2</sub> is shown in Figure 3.4. The solid curve (thermodynamic) shows the maximum NO<sub>2</sub> concentration based on thermodynamic equilibrium calculation. It is shown that the thermodynamic stability of NO<sub>2</sub> is a function of temperature at

gas phase equilibrium for 700 ppm NO and 10% O<sub>2</sub>. The curve indicates the maximum NO<sub>2</sub> concentration that can be formed at the specified temperature.

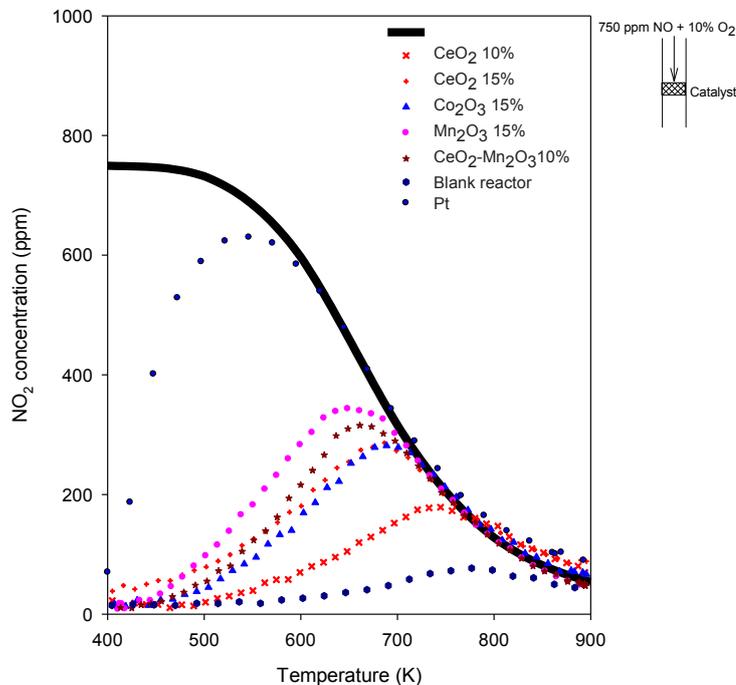


Figure 3.4 Catalyst activity in NO oxidation to NO<sub>2</sub> by Platinum catalyst and prepared non-noble metal catalysts with 700 ppm NO and 10% O<sub>2</sub>, heating rate of 1.5 K/min.

The activity of Pt catalyst to NO oxidation can be observed already at 400 K, whereas, the activity of prepared catalysts is observed at 500 K and above. Furthermore, compared to Pt catalyst, prepared catalyst has a very low activity. Around 600 K, the activity of Mn<sub>2</sub>O<sub>3</sub> catalyst reaches thermodynamic equilibrium. CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> requires a bit higher temperature. The rest of the catalysts reach equilibrium at 700 K and above. However, at the experimental conditions, thermodynamic equilibrium is reached by thermal reaction at much higher temperature, above 850 K.

### C. NO<sub>2</sub> assisted soot oxidation by non-noble metal catalyst

To evaluate the potential of the catalyst as replacement for Pt catalyst in the CRT system, experiments were carried out in a reactor in which

prepared catalysts were placed upstream of soot bed. For comparison, experiment with Pt catalyst was also carried out for comparison. The results are shown in Figure xx where soot oxidation rate is plotted as a function of conversion. Apparently that the oxidations rates are comparable.

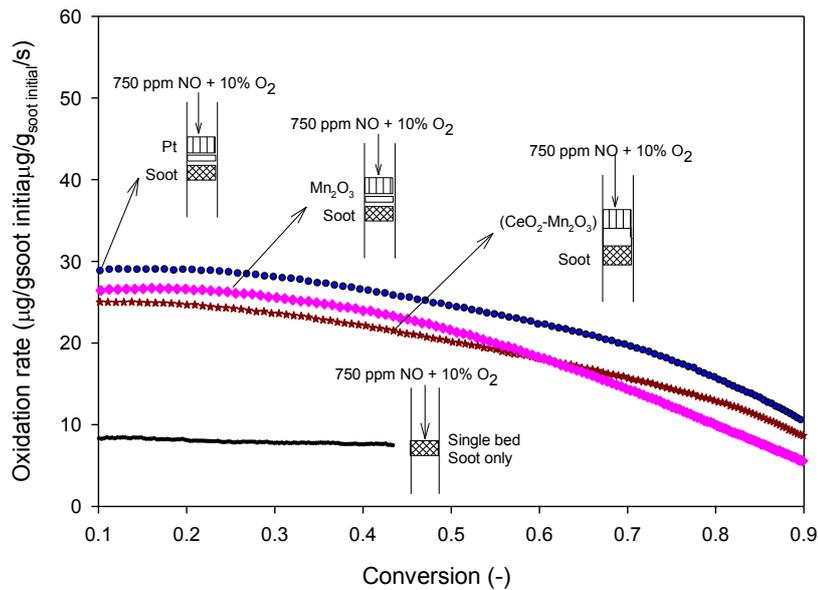


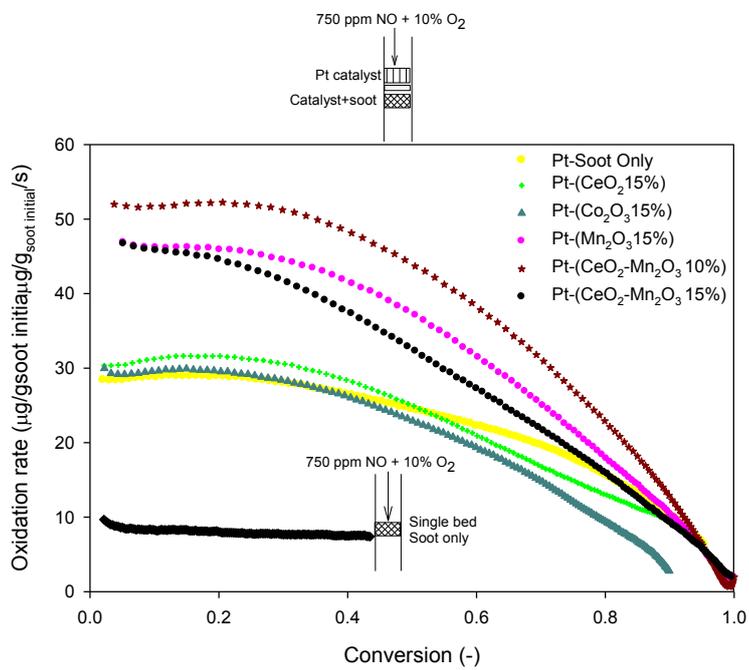
Figure 3.7 Catalysts activity in soot oxidation, isothermal experiment at 620 K in flowing 700 ppm NO and 10% O<sub>2</sub>. The catalysts and soot are placed in separate beds

Instead of producing NO<sub>2</sub>, non noble metal catalyst can also have a role to accelerate soot oxidation with NO<sub>2</sub>. This had been proven by CeO<sub>2</sub> catalyst [ ]. To evaluate this role, soot oxidation rate of non-noble metal soot mixture placed downstream of Pt catalyst were measured. The results are shown in Figure 3.8. Onset figure emphasized different effect among the catalysts. It can be seen that Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> increase the oxidation rate the most.

To confirm the effect, the same configuration was tested in isothermal experiment. The results are shown in Figure 3.8. It is clearly shown that  $Mn_2O_3$  based catalysts increase the oxidation rate significantly.

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When non-noble metal catalysts were placed downstream of Pt catalyst, the formation of NO<sub>2</sub> is presented in Figure 3.5. It is clear that the present of non noble metal catalyst downstream of Pt catalysts slightly increase the amount of formed NO<sub>2</sub>. After NO<sub>2</sub> concentration has reached thermodynamic equilibrium all catalysts system result in the same amount of NO<sub>2</sub>

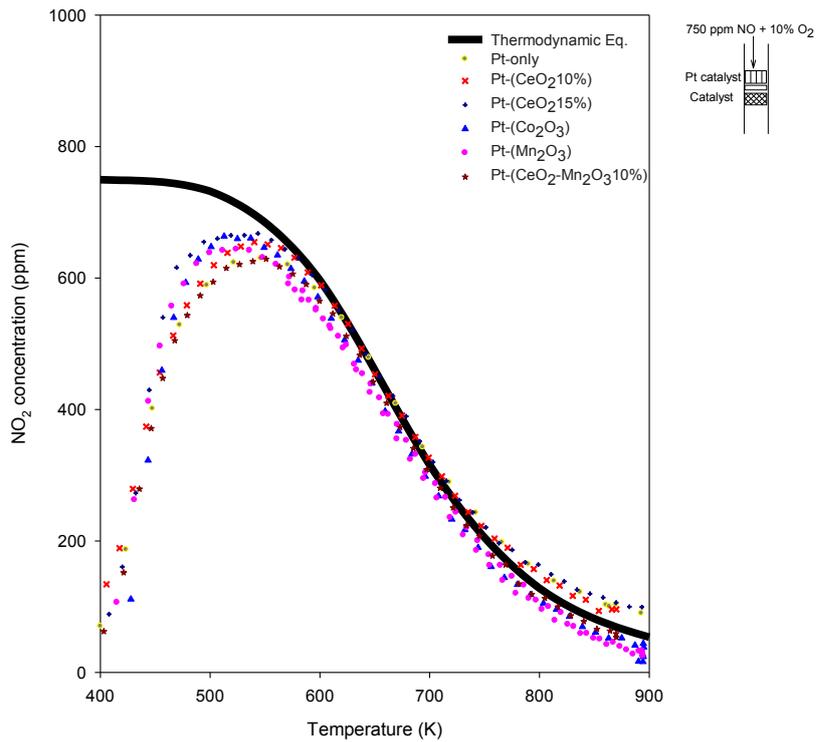


Figure 3.5 Formation of NO<sub>2</sub> with Pt catalysts and non-noble catalysts downstream Pt catalyst configuration

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Results

Catalysts activity in the oxidation of NO to NO<sub>2</sub>

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2. 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

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fraction of diesel particulate matter would be discovered quickly. A catalytic device like the three-way catalyst for gasoline engines was seen as unreliable, since the onset temperature of around 800 K of the soot combustion catalysts of those days was too high for spontaneous regeneration [24]. The general regeneration strategy for non-catalytic oxidation has been to substantially load the trap with soot, ignite the soot by raising the temperature in the presence of available oxygen in the exhaust gas, 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 reaction. The mechanism is known as self-supporting flame propagation [25]. This type of regeneration can easily get out of control and damage the filter due to chaotic thermal runaways. The regeneration is influenced by many variables like temperature, oxygen concentration, deposited soot amounts, and mass gas flow rate. 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 without the intervention of the driver. Another problem was inadequate regeneration efficiency: Up to 35% of the soot can remain on the filter. This is undesirable because it will create a soot gradient build-up, which can lead, when finally ignited, to extremely high temperature gradients within the filter.

3. In the last two decades, a number of materials have been explored as catalysts for diesel soot oxidation. The fact that in diesel exhaust  $O_2$  is available excessively (4-10%), has influenced the development of catalyst for the oxidation of soot. The exploration for the catalyst was initially focused on the direct contact between catalyst and soot in order to decrease the C- $O_2$  reaction temperature, which is generally, as mentioned before, above 800 K for the non-catalytic soot oxidation. Furthermore, the catalytic oxidation of soot is slow, since the solid soot particles are large and, when deposited, immobile. They cannot penetrate into the catalyst's micro-pores or meso-pores where catalytic processes usually take place. Soot oxidation takes place mainly on the filter walls of the particle filter where the catalyst has been deposited.

4. —

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6. A. Direct Contact Diesel Soot Oxidation Catalysts

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8. The development of a direct contact soot oxidation catalyst is problematic, since it is difficult to realize a direct contact with the solid soot under real exhaust conditions. Inui and Otowa [26] and Löwe and Mendoza-Frohn [27] were among the first to realize that the contact of deposited soot on a catalytic filter is poor. Neef et al. [28,29] systematically investigated the effect of 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; they filtered diesel soot from an exhaust stream on a bed of catalyst particles and defined that as in situ contact. Combustion temperature differences as large as 200 K can be were found between loose and tight contact samples of one catalyst. It is clear that Neef et al. measured apparent activities that were a function of the intrinsic activity and the degree of physical interaction. They found that with the in situ samples, the combustion temperatures were similar to the combustion temperatures of the loose contact samples and concluded that the

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contact that arises during practical conditions is similar to loose contact as illustrated in Figure 6.

9. 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. [30] found that the type of contact controls the actual mechanism. They found that for  $V_2O_5$  and  $MoO_3$  a redox and spill-over mechanism occurs simultaneously in tight contact and discussed that whereas in loose contact, only the spill-over mechanism will occur. They expected that for soot oxidation in a catalytic filter, oxygen spill-over would be the predominant mechanism.
10. Watabe et al. [31] were 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 extensively investigated [28,29,32-42] because they exhibited high soot oxidation rates at low temperatures. The high activity was related to the mobility and volatility of the active copper oxy-chloride component of the catalyst [43]. Unfortunately, catalyst compounds evaporated during soot oxidation [32,39] and, therefore, the catalyst should had to be kept below 625 K at all times [39], which makes made the feasibility of the catalyst questionable [32]. This mobility probably explains why the stability of some of those reported catalysts was low. Querini et al. [44] stated that the high activity of  $Co/MgO$  and  $Co/K/MgO$  could be caused by enhanced catalyst mobility caused afforded by potassium. Badini et al. [40,45] reported that  $KCl:KVO_3$  and  $KI:KVO_3$  are active catalysts, but they also reported the emission of volatile components of the catalyst. Ahlström and Odenbrand [46] and Moulijn and co-workers [47-52] reported mobile catalysts that did not evaporate during soot oxidation. This type of liquid contact occurs in both laboratory test and pilot plant scale. These types of mobile materials, like  $Cs_2SO_4 \cdot V_2O_5$  (melting point of 647 K),  $CsVO_3 \cdot MoO_3$  (melting point of 650 K) and  $KCl:KVO_3$  (melting point of 760 K), demonstrate high activity in the for oxidation of soot [47-50]. This activity is primarily due to the in situ tight contact between soot and catalyst in its molten state. However, the stability of this type of liquid catalyst might be too low under severe exhaust conditions. Figure 7 shows the different types of contact, namely the solid catalyst, the mobile catalyst and the liquid catalyst are presented.
11. A good way of improving the quality of induced self-supporting regeneration of a particle filter is by to increase the reactivity of the soot with a built-in metal catalyst. Such a catalyst can be incorporated during the soot formation process. Blending a stable organo-metallic additive into the fuel (typically 10-100 ppm) is the most convenient method. These catalytic fuel additives are also known as fuel borne catalysts, and the type of regeneration as result in quasi-continuous regeneration [51].
12. Catalytic fuel additives are were 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 and, therefore, it is 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 defined as the balance temperature. Lepperhoff et al. [51] compared cerium, iron, and copper additives. They found the lowest balance temperatures for iron and copper,

which were to be 625 K. Jelles et al. [52] measured balance temperatures for different mixed additives to discover whether synergetic effects could play a role. They found that after some time of running on low concentration fuel additive combinations, there was a dramatic reduction in balance temperature reduction. The reduced balance temperature was explained as follows: Platinum, which was deposited on the monolith, catalyzes the oxidation of NO to NO<sub>2</sub>. NO<sub>2</sub> subsequently reacted with the fuel additive catalysed catalyzed soot. The enhanced activity was is explained by assuming that each NO<sub>x</sub> molecule is used many times, as is illustrated in Figure 8.

13-

14. Figure 9 shows a reaction scheme of the proposed mechanism of the oxidation of soot by using platinum cerium fuel additive. A Road trial of the mixed catalysts showed that not only the regeneration of the filter was altered but also the so was fuel combustion. The fuel efficiency increased by 5-7% and, at the same time, a decrease of the produced particulate mass of 10-25% was observed.

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16. Figure 10 shows the influence of various after treatment configurations for fuel additives on the balance temperature. The balance temperature is the lowest temperature where soot mass conversion rate is in equilibrium with the soot deposition rate [52,53]. If the wall flow monolith is partially replaced with platinum catalysed catalyzed ceramic foam, the lowest balance temperature of 550 K for a diesel fuel containing up to 500 ppm sulfur was is observed [52]. It should be noted that the reported balance temperature strongly depends on several factors such as: particulate matter loading, trap volume, trap materials, trap pore size, additive concentration, oxygen concentration, engine type, and engine load.

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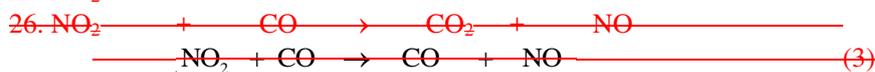
## 19. B. Indirect Contact Catalysts for Diesel Soot Oxidation

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21. Some catalysts can oxidize soot without having intimate physical contact. They catalyze the formation of a mobile compound ( $\text{NO}_2$ ,  $\text{O}_{\text{ads}}$ , etc.) that is more reactive than  $\text{O}_2$ . 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;  $\text{NO}_x$ -aided gas phase mechanism and spill-over mechanism.

22. Cooper and Thoss [54] patented a way of using gas phase  $\text{NO}_2$  as an activated mobile species for soot oxidation ( $\text{NO}_x$ -aided gas phase mechanism) in combination with a filter device. The reaction of  $\text{NO}_2$  with carbon material was published as early as 1956 [55]. They proposed that  $\text{NO}_2$  accelerates soot combustion:

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27. —

28. Some catalysts can dissociate oxygen and transfer it to the soot particle, where it reacts as if it were in a non-catalytic reaction. This mechanism is known as the spill-over mechanism (Figure 11).

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30. Some examples exist that show that contact is not prerequisite in this type of reaction type. For instance, Baumgarten and Schuck [56] 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 spill-over. Baker and Chludzinski [57] showed that  $\text{Cr}_2\text{O}_3$  could accelerate edge recession of graphite while being motionless. Mul et al. [30] showed with a labelled oxygen study that spill-over and redox oxidation can occur simultaneously. They discussed that the dominating mechanism will depend on the degree of physical contact between the catalyst and the soot.

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32. Another indirect contact catalysis phenomenon can be concluded from the so-called 'active oxygen' creation [ ]. Active oxygen was indicated when soot-CeO<sub>2</sub> catalyst mixture was placed downstream of platinum catalyst with NO and oxygen as feed gas. Active oxygen acts similarly with that of  $\text{NO}_2$ . Furthermore, the postulated specie is more active in the oxidation of soot than that of oxygen.

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34. This experiment evaluate the potential of base metal catalyst in the acceleration of soot oxidation in the presence of NO and  $\text{O}_2$ , the performance of several base metals in the oxidation of NO to  $\text{NO}_2$  and in the acceleration of soot oxidation with  $\text{NO}_2$ .

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### 36. 2. Experiments

37. Base metal catalyst was prepared by

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Feldfunktion geändert

Feldfunktion geändert

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43. Prepared catalyst was then tested in NO oxidation and soot oxidation experiments.  
The catalyst was packed in two different configurations

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45. 3. Results

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51. 4. Discussion