

Increased NO<sub>x</sub>-assisted soot oxidation rate by Ce-Mn catalyst generated 'active oxygen' Base metal in the catalysis of soot oxidation  
(What possibly it's role)

## 1. Introduction

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 O<sub>2</sub> 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-O<sub>2</sub> 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 (NO<sub>2</sub>, O<sub>ads</sub>, etc.) that is more reactive than O<sub>2</sub>. 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<sub>x</sub>-aided gas-phase mechanism and spill-over mechanism.

Cooper and Thoss [54] patented a way of using gas-phase NO<sub>2</sub> as an activated mobile species for soot oxidation (NO<sub>x</sub>-aided gas-phase mechanism) in combination

with a filter device. The reaction of NO<sub>2</sub> with carbon material was published as early as 1956 [55]. They proposed that NO<sub>2</sub> 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 Cr<sub>2</sub>O<sub>3</sub> 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.

In an attempt to increase the oxidation rate with NO<sub>2</sub>, CeO<sub>2</sub> catalysts had been evaluated in a CRT-like bed reactor. 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 CeO<sub>2</sub> 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 also thought responsible

In this present paper,

## 2. Experiments

### Catalyst material

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#### Activity test

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

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### 3. Results

BET Surface area of the selected prepared catalysts are shown in Table 2. The specific surface areas have a value around 100 m<sup>2</sup>/g with some minor differentiation. The total pore volume is also rather comparable, as is the pore size distribution.

Table 2. BET specific surface area of the selected prepared catalysts

<u>Sample</u>	<u>S<sub>BET</sub> (m<sup>2</sup>/g)</u>	<u>total pore volume* (cm<sup>3</sup>/g)</u>	<u>Max pore size (nm)</u>
<u>Co<sub>2</sub>O<sub>2</sub> 15%</u>	<u>96 ± 2</u>	<u>0.19</u>	<u>5.4</u>
<u>CeO<sub>2</sub>15%</u>	<u>111 ± 3</u>	<u>0.19</u>	<u>4.9</u>
<u>Mn<sub>2</sub>O<sub>3</sub> 15%</u>	<u>103 ± 2</u>	<u>0.21</u>	<u>5.3</u>
<u>CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> 10%</u>	<u>107 ± 2</u>	<u>0.20</u>	<u>4.9</u>
<u>CeO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> 15%</u>	<u>100 ± 2</u>	<u>0.18</u>	<u>5.2</u>

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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

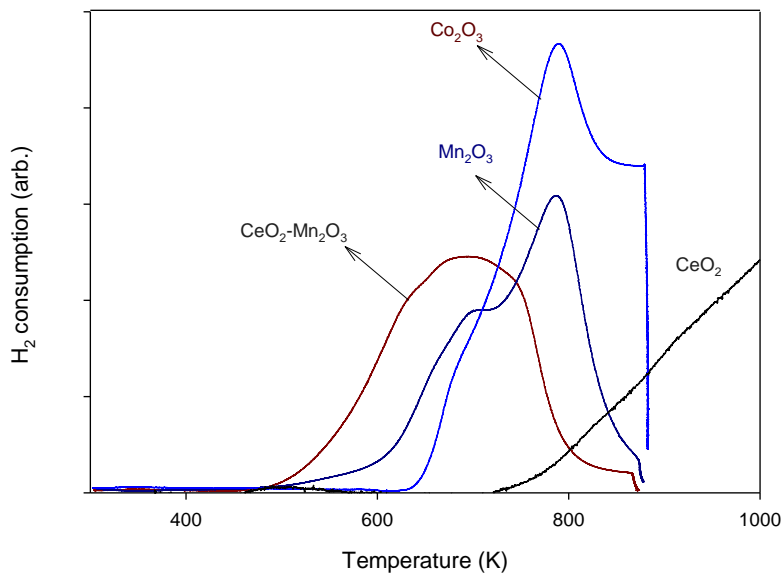


Figure 3.3 Temperature Programmed reduction of the prepared catalyst with Xx ml/min flowing H<sub>2</sub>, temperature programmed of aa K/min

### 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.

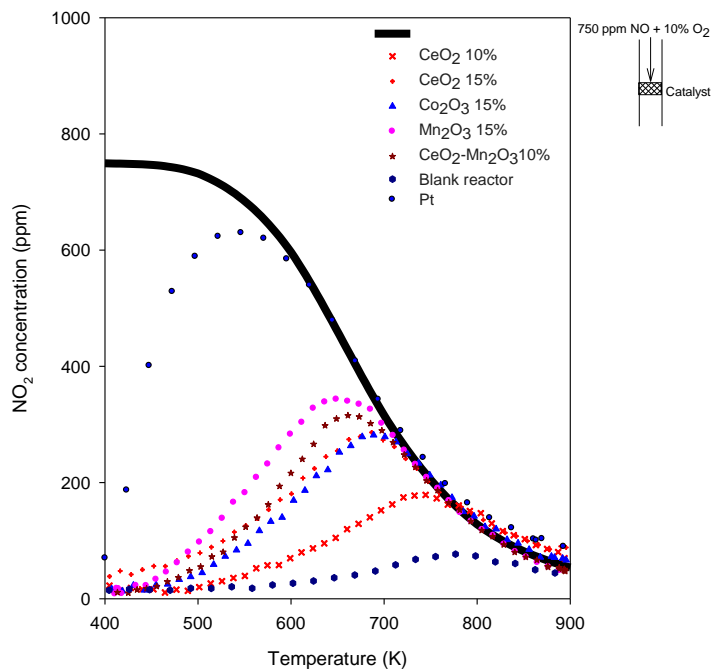


Figure 3.4 Catalyst activity in NO oxidation to NO<sub>2</sub> by Platinum catalyst and prepared non-noble metal catalysts with 700 ppm NO and 10% O<sub>2</sub>, heating reate of 1.5 K/min.

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.

When non-noble metal catalysts were placed downstream of Pt catalyst, the formation of NO<sub>2</sub> is presented in 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>

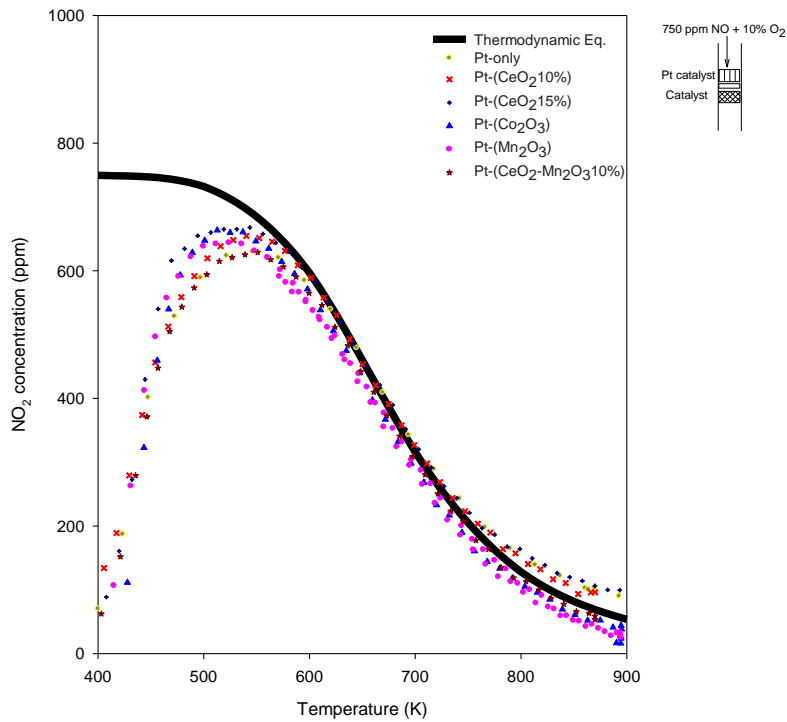


Figure 3.5 Formation of  $\text{NO}_2$  with Pt catalysts and non-noble catalysts downstream Pt catalyst configuration

### C. $\text{NO}_2$ assisted soot oxidation by non-noble metal catalyst

When prepared catalysts were mixed with soot and  $\text{NO} + \text{O}_2$  gases mixture was flown, soot oxidation with both  $\text{O}_2$  and  $\text{NO}_2$  can take place. The reaction products ( $\text{CO}$  and  $\text{CO}_2$ ) as a function of temperature are shown in Figure 3.6. Since the experiments were done at constant heating rate, the production of  $\text{CO} + \text{CO}_2$  describes the oxidation rate of the systems. It can be evaluated that non-noble metal catalyst decreases the oxidation temperature as low as 100 K.  $\text{Mn}_2\text{O}_3$  catalysts perform the best.



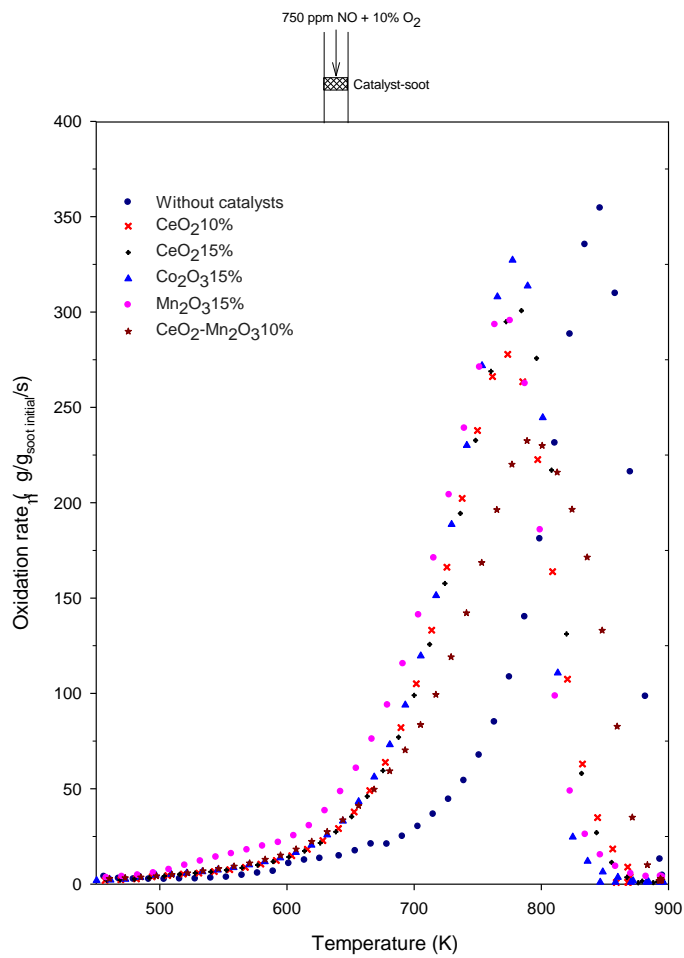


Figure 3.6 Catalysts activity in soot oxidation, temperature programmed oxidation in flowing 700 ppm NO and 10% O<sub>2</sub>. The catalysts and soot are physically mixed

Experiments were also carried out in which prepared catalysts were placed upstream of soot bed. Those experiments were intended to evaluate the potential of the catalyst as replacement for Pt catalyst in the CRT system. Therefore, experiment with Pt catalyst was also carried out for comparison. The results are shown in Figure 3.7

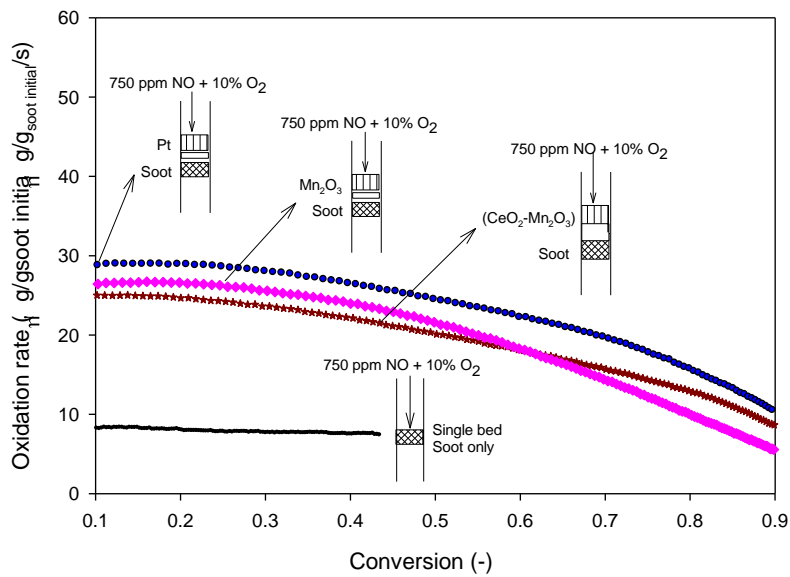


Figure 3.7 Catalysts activity in soot oxidation, isothermal experiment at 620 K in flowing 700 ppm NO and 10% O<sub>2</sub>. The catalysts and soot are placed in separate beds

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>. 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<sub>2</sub>O<sub>3</sub> based catalysts increase the oxidation rate significantly.

4.

## 5. Results

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

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 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.

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<sub>2</sub> 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<sub>2</sub> 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.

#### A. Direct Contact Diesel Soot Oxidation Catalysts

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

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

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.

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  $KCl \cdot KVO_3$  (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.

A good way of improving the quality of induced self-supporting regeneration of a particle filter is by to increasing the reactivity of the soot with a built-in metal catalyst. The 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].

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 ~~s~~ 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.

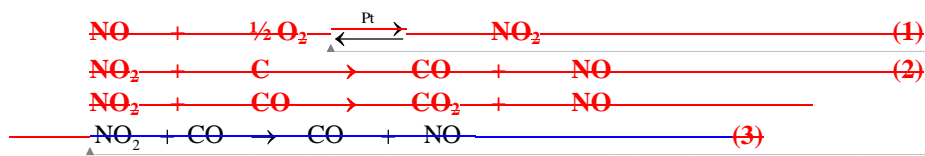
Figure 9 shows a reaction scheme of the proposed mechanism of the oxidation of soot by using platinum-cerium fuel additive. A Road trial of the mixed catalysts showed that not only the regeneration of the filter was altered but also the so was fuel combustion. The fuel efficiency increased by 5–7% and,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

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.

## B. Indirect Contact Catalysts for Diesel Soot Oxidation

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.

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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.

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  $\text{NO}_2$ .

### 2. Experiments

Base metal catalyst was prepared by

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

~~3. Results~~

~~4. Discussion~~