

## 〈Invited Review Article〉

# Overview of the Effect of Catalyst Formulation and Exhaust Gas Compositions on Soot Oxidation in DPF

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This work reviews the effects of catalyst formulation and exhaust gas composition on soot oxidation in CDPF (Catalytic Diesel Particulate Filter). DOC's (Diesel Oxidation Catalysts) have been loaded with Pt catalyst (Pt/Al<sub>2</sub>O<sub>3</sub>) for reduction of HC and CO. Recent CDPF's are coated with the Pt catalyst as well as additives like Mo, V, Ce, Co, Fe, La, Au, or Zr for the promotion of soot oxidation. Alkali (K, Na, Cs, Li) doping of metal catalyst tends to increase the activity of the catalysts in soot combustion. Effects of coexistence components are very important in the catalytic reaction of the soot. The soot oxidation rate of a few catalysts are improved by water vapor and NO<sub>x</sub> in the ambient. There are only a few reports available on the mechanism of the PM (particulate matter) oxidation on the catalysts. The mechanism of PM oxidation in the catalytic systems that meet new emission regulations of diesel engines has yet to be investigated. Future research will focus on catalysts that can not only oxidize PM at low temperature, but also reduce NO<sub>x</sub>, continuously self-cleaning diesel particulate filters, and selective catalysts for NO<sub>x</sub> reduction.

**Key Words :** Diesel Engine, Soot Oxidation, Particulate Matter (PM), Catalyst, Diesel Particulate Filter (DPF)

## 1. Introduction

The diesel engine is popular because of its thermal efficiency, reliability, durability and relatively low fuel price. However, its adverse effects from NO<sub>x</sub> and soot emission on the health of the environment are also of concern. Emissions of particulate matter (PM), soot and NO<sub>x</sub> from diesel engines are the target of increasingly stringent environmental regulations. In recent decades

the formation processes of diesel PM and in-cylinder oxidation have been studied extensively. The results of the studies have been applied to dramatically improve the quantity and quality of the emissions of diesel engines. (Yezerets et al., 2003).

Advanced combustion, electronic controls, series turbocharging, advanced injection strategies, intake valve control and an oxidation catalyst enabled the diesel engine to meet the 2002 US regulations. Due to the enactment of the 0.01 g/hp-hr PM standard that year, diesel particulate filter (DPF), either catalyzed or with a pre-filter catalyst, are expected to be installed in 100% of the engines that will be produced from the year 2007, although regeneration strategies and durability demonstrations are still underway (Leet et

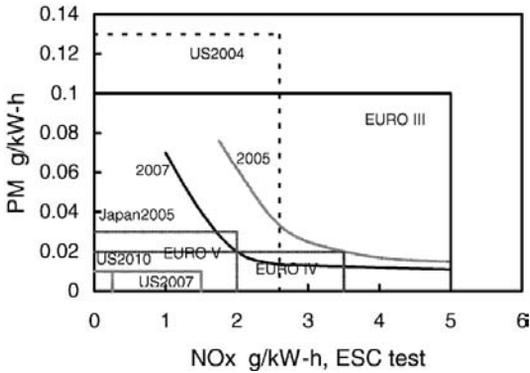
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**Fig. 1** Engine-out emission regulations for heavy-duty (Leet et al., 2004)

al., 2004).

Figure 1 shows the engine emissions for heavy-duty vehicles in 2005 and those for later this decade (Leet et al., 2004). Although European engines with advanced fuel injection equipment and cooled-EGR (exhaust gas recirculation) can meet the 2005 Euro IV regulations, SCR (selective catalytic reduction) will be used instead of EGR. By 2007, further advances in fuel injection, boost, EGR and especially engine management will enhance engine emissions to the required levels. In the US, the use of DPFs and advanced engine strategies are expected to enable engines to meet the 2007 US regulations.

Table 1 summarizes the advanced emission control measures that will be needed to meet the key regulations of this decade. The technologies shown in Table 1 may be implemented earlier than expected due to various incentives (Johnson, 2004). These technologies include DPF, the diesel particulate filter, for particulate control; SCR, the selective catalytic reduction; and LNT, the lean NOx traps for NOx reduction technology. There are several different types of after-treatment systems being considered for the diesel engine such as DPF (Oh et al., 2002; Vincent et al., 2002), DPNR (diesel particulate and NOx reduction) (Chatterjee et al., 2001) and CRT (continuously regeneration trap) (Hanamura et al., 2003; Kim et al., 2005).

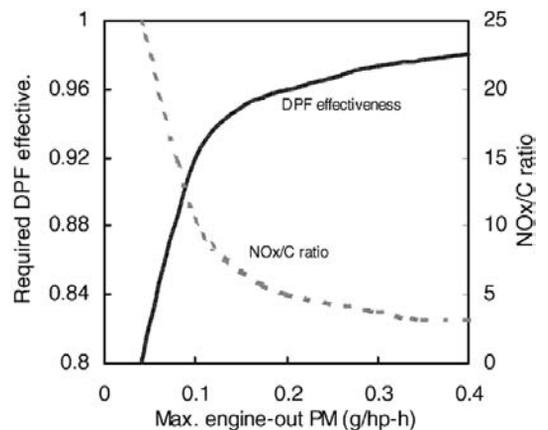
CRT technology is based on the reaction of the diesel soot oxidation by use of NO<sub>2</sub>. This is a breakthrough in the effort to abate diesel emis-

**Table 1** General overview of diesel regulations and expected emission control technologies (Johnson, 2004)

Year	Heavy-duty regulation and technology	Light-duty regulation and technology
2005	Japan 2005 : DPF Euro IV : SCR ; DPF or DOC	Japan : DPF Euro IV : DPF For >1.7ton
2006		US Tier 2 : DPF+LNT
2007	US 2007 (1 <sup>st</sup> Phase) : DPF ; DPF+SCR	
2008	Euro V : SCR DPF or DOC	
2010	US2007 (full) : DPF+LNT DPF+SCR	Euro V : SCR DPF+LNT

sions. In CRT technology, NO<sub>2</sub> is generated from the oxidation of NO over a platinum catalyst. The coexistence of the component gases of NOx, H<sub>2</sub>O, CO and CO<sub>2</sub> is very important to achieve the optimal oxidation of diesel soot in the CRT unit. DPNR technology is the integration of LNT (lean NOx trap) technology used in lean-burning engines and DPF technology.

Figure 2 shows the relationship between the conversion efficiency and NOx/C ratio required of the DPF performance so that the emission



**Fig. 2** Required DPF effectiveness as a function of engine-out PM to achieve 0.008 g/hp-hr PM (Leet et al., 2004)

target is not exceeded at the tail pipe. This figure illustrates how quickly the NO<sub>x</sub>-C ratio decreases as the engine-out PM emissions increases for a fixed 1.0 g/hp-hr NO<sub>x</sub> level.

To satisfy the new standards, including the 2007 US regulation for automobile diesel applications, PM emissions must be further reduced. Beginning in 2005, permissible diesel tailpipe emissions for highway trucks will be cut approximately 80% in Europe and Japan, and in 2007 they will be cut to approximately 80% of the current level in the US. These levels of reduction require step-changes in emission control technology (Leet et al., 2004).

Devices such as the DPF and DPNR have been investigated extensively as a means of meeting the more stringent standards. In most driving conditions, regeneration of DPF by oxidation of PM and the reduction of NO<sub>x</sub> in the presence of excess oxygen are challenging. Knowledge about the fundamental processes involved in these after-treatment devices is insufficient.

This work reviews the oxidation characteristics of diesel soot, and the effect of noble metal catalysts and/or additives as well as various diesel engine exhaust conditions on the characteristics of catalytic and non-catalytic oxidation reactions of the diesel PM.

## 2. Research Trends of PM Oxidation

### 2.1 Soot oxidation

Soot combustion in DPF is a slow process, whose duration exceeds the particulate residence time in the exhaust system. The CDPF system adds various catalysts to promote soot oxidation. In this section, we discuss the characteristics of soot oxidation without catalysts. For laboratory experimental purposes, diffusion flame soot produced by high temperature pyrolysis (Printex-U for Degussa Co.) well approximates diesel soot (Van Setten et al., 2002; Stannore et al., 2001; Mul et al., 1998; Setiabudi et al., 2002). Yezerets et al. (2003) collected soot samples by running an engine through respective low-load cycles. The result was equivalent to a first order reaction for

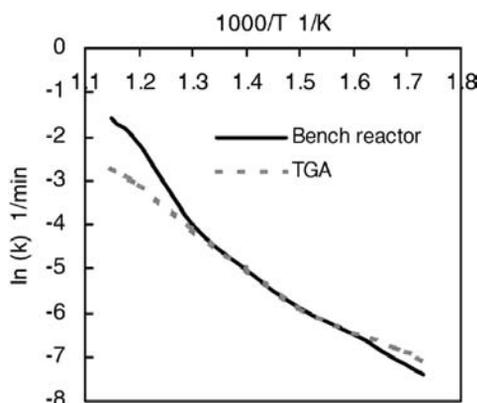
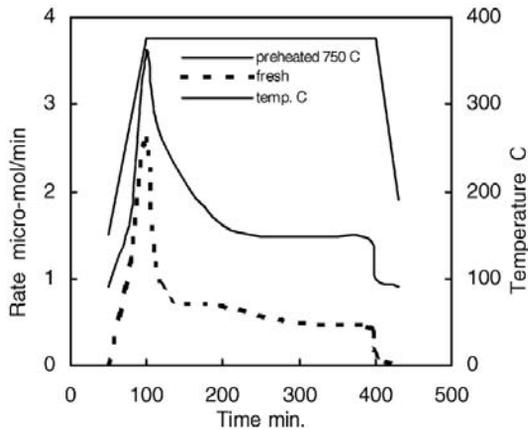


Fig. 3 TPO experiment results of diesel soot obtained low-load engine running cycle (Yezerets et al., 2003)

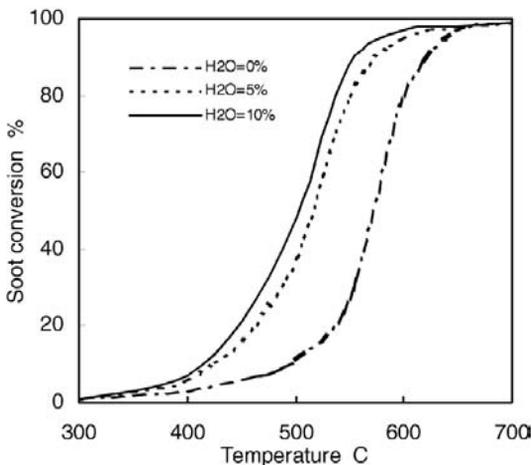
carbon, as reflected in the units of the rate constant (mol carbon oxidized/min)/(mol carbon still present) = min<sup>-1</sup> (Fig. 3) They mentioned that the characteristic shape is retained even if a different assumption about the carbon order is made from 0.67 to 1.0. (Stannore et al., 2001; Mul et al., 1998)

In order to better understand the relationship between the integral conversion of particulate matter and the changes in its reactivity, an additional set of isothermal experiments was performed on soot samples in a low-load steady-state. A relatively low temperature (375°C) was chosen to achieve a low oxidation rate and thus better resolve the activity changes with time. Fig. 4 contains the TPD results for the fresh and TPD-preheated soot samples (Yezerets et al., 2003). For several hours after reaching the target temperature, the rate of oxidation steadily decreased. Little difference was observed between the results obtained from the fresh and TPD-preheated samples, with the exception of the SOF desorption/oxidation peak observed around 250°C when heating the fresh sample to the target temperature. Thus both fresh and TPD-preheated samples demonstrated initial high reactivity.

Van Setten et al. (2002) showed that increasing the H<sub>2</sub>O concentration up to 10% Vol. significantly enhanced the oxidation rate of the diesel soot sample (Printex U of Degussa Co.) (Fig. 5). However, a further increase from 10 to 15% Vol.



**Fig. 4** TPD results of the isothermal experiments with soot in a low-load steady-state mode, (a) preheated by TPD to 750°C, (b) fresh sample, (c) temperature trace (Yezerets et al., 2003)



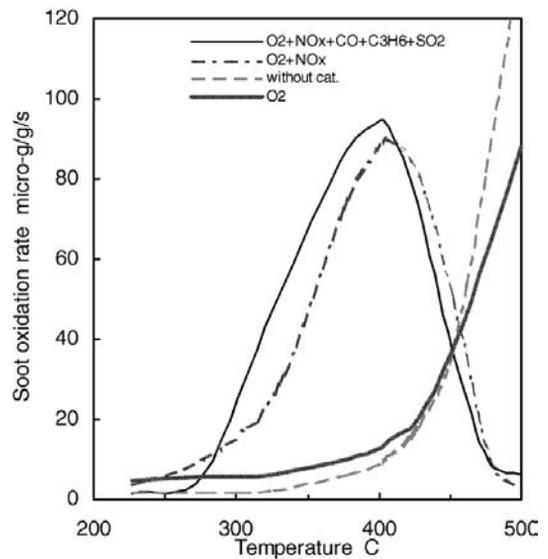
**Fig. 5** Effect of H<sub>2</sub>O concentration on the oxidation of diesel soot and carbon black samples (Van Setten et al., 2002)

H<sub>2</sub>O did not result in any additional improvement.

Lee et al. (2005) found that the activation energy of the soot oxidation was 177 kJ/mol for a reaction order of 0.8 and was 200 kJ/mol for a reaction order of 1.

## 2.2 Carbon oxidation on the catalysts and with coexistence gases

The CDPF has some kinds of catalysts to



**Fig. 6** Effect of gas compositions on soot oxidation rate with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst supported on ceramic foam by TPO (Setiabudi et al., 2002)

promote the oxidation of the soot. The catalysts, Pt and Pd have been employed in the diesel oxidation catalysts and in some CDPF systems (Choi et al., 2005; Chatterjee, et al., 2001). A noble metal has good oxidation activity, but its availability is limited for automotive after-treatment devices. Rare earth elements such as alkali have to be considered as additives of main catalysts to promote soot oxidation.

The effect of additives (washcoat) in the main Pt catalyst on the combustion of the soot is discussed. Setiabudi et al. (2002) showed the experimental results of soot oxidation on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 6). The Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was physically mixed with CB (Printex U from Degussa Co.). The temperature at which the onset of soot oxidation occurred with a feed of only O<sub>2</sub> was about 675 K, while in the presence of NO<sub>x</sub> it decreased to approximately 550 K. Unlike the situation with the Cs<sub>2</sub>SO<sub>4</sub>.V<sub>2</sub>O<sub>5</sub> catalyst, the NO<sub>2</sub>/NO<sub>x</sub> ratio is constant over the entire temperature window. The Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was very active in NO<sub>x</sub>, CO and C<sub>3</sub>H<sub>6</sub> oxidation. Pt, a soot oxidation catalyst that is less active than molten salt when O<sub>2</sub> is applied, became more active in the

presence of NOx. Pt converted NO to NO<sub>2</sub> and the NO<sub>2</sub> formed increased the rate of soot oxidation. Conversely, the activity of the molten salt catalyst in the conversion of NO to NO<sub>2</sub> was limited. Therefore, the effect of NO on the oxidation of PM has to be researched with various catalysts.

Oi-Uchisawa et al.(2001) showed NO oxidation activity at low temperatures (Fig. 7). T<sub>10</sub>, T<sub>50</sub> and T<sub>90</sub> indicate the temperature at which a 10%, 50% and 90% oxidation ratio of the CB was reached during the TPR procedure. The order of the carbon oxidation activity is Pt/TiO<sub>2</sub>/SiC > Pt/ZrO<sub>2</sub>/SiC > Pt/Al<sub>2</sub>O<sub>3</sub>/SiC. These oxides are

good supports for Pt particles and prevent their sintering. They concluded that the Pt/TiO<sub>2</sub>/SiC catalyst exhibited the highest activity and durability against high temperatures and exposure to SO<sub>3</sub>.

Oi-Uchisawa et al.(2003) showed the effect of the support material and SO<sub>2</sub> pretreatment for carbon oxidation over Pt/MOx catalysts (Fig. 8). The reaction gases were composed of 550 ppm NO, 1.5 ppm SO<sub>2</sub>, 8% H<sub>2</sub>O and 7.5% O<sub>2</sub> with N<sub>2</sub> making up the balance. For the Pt/SiO<sub>2</sub> catalyst, the activity was not influenced by the presence of SO<sub>2</sub>. In contrast, the activity was markedly improved by the SO<sub>2</sub> pretreatment of the Pt/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts because the TiO<sub>2</sub> substrate adsorbed more sulfate than the SiO<sub>2</sub> substrate. Sulfate (SO<sub>4</sub><sup>2-</sup>), that comes from the SO<sub>2</sub> pretreatment process, accumulated on the catalyst and influenced the behavior of the carbon oxidation. Pt catalyst applied to the TiO<sub>2</sub>-SiO<sub>2</sub> substrate showed higher catalytic activity than when applied to the individual oxides.

Oi-Uchisawa et al.(2003) represented the effect of the TiO<sub>2</sub>/(TiO<sub>2</sub>+SiO<sub>2</sub>) molar ratio on the carbon oxidation activity when passed over Pt/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts (Fig. 9). The specific surface area decreased with increasing TiO<sub>2</sub> content, whereas Pt dispersion varied less. The catalytic activity for carbon oxidation was improved by

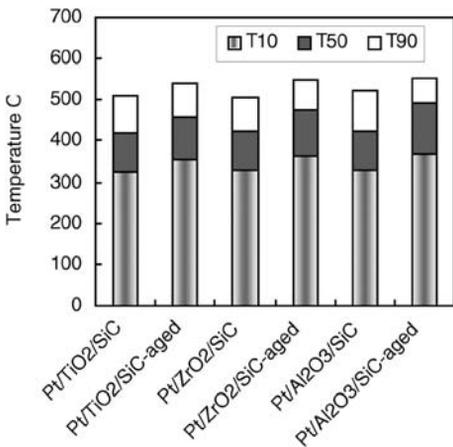


Fig. 7 TPR results for various Pt/Mox/SiC systems after thermal treatment (Oi-Uchisawa et al., 2001)

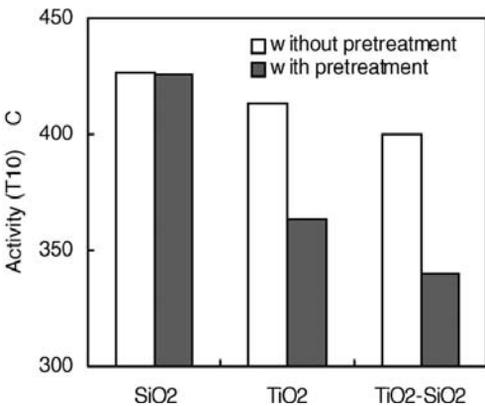


Fig. 8 Effect of the support material and SO<sub>2</sub> pretreatment for carbon oxidation over Pt/Mox (Oi-Uchisawa et al., 2003)

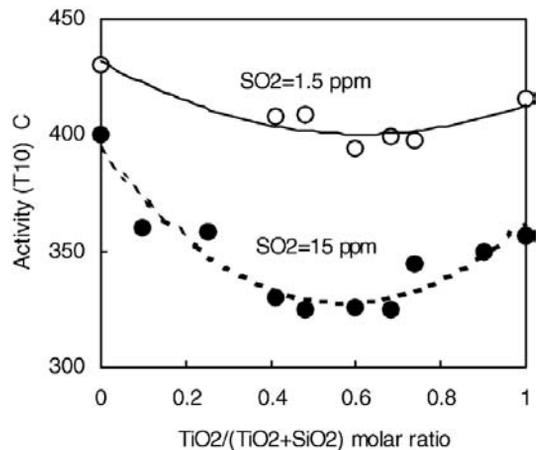
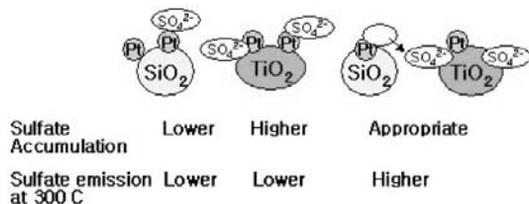


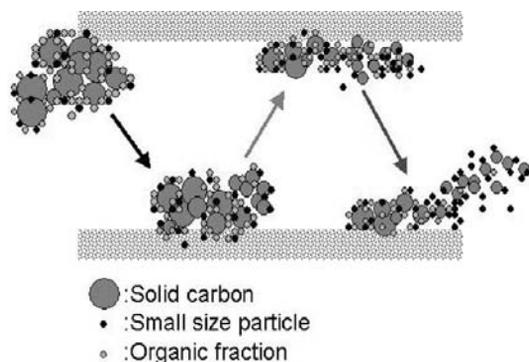
Fig. 9 Effect of TiO<sub>2</sub>/(TiO<sub>2</sub>+SiO<sub>2</sub>) molar ratio on the activity for carbon oxidation over Pt/TiO<sub>2</sub>-SiO<sub>2</sub> (Oi-Uchisawa et al., 2003)

mixing the two components. The best  $\text{TiO}_2/(\text{TiO}_2+\text{SiO}_2)$  mixing ratio was between 0.4 and 0.7. They showed that a positive synergistic effect exists for the improvement of carbon oxidation when combining  $\text{TiO}_2$  and  $\text{SiO}_2$ .

Oi-Uchisawa et al. (2003) showed the mechanism for the improvement of carbon oxidation using  $\text{TiO}_2\text{-SiO}_2$  as the support substrate (Fig. 10). Carbon oxidation using  $\text{NO}_2$  catalyzed by  $\text{H}_2\text{SO}_4$  starts at around  $300^\circ\text{C}$ , which is  $100^\circ\text{C}$  lower than oxidation with only  $\text{NO}_2$  present. For  $\text{Pt/SiO}_2$ , most the accumulated sulfate was released before  $300^\circ\text{C}$ .  $\text{SO}_4^{2-}$ , which is converted from the  $\text{SO}_2$  present in the reactant gas, can be utilized in the carbon oxidation process. For  $\text{Pt/TiO}_2$ , the capacity for sulfate accumulation is much higher than that of  $\text{Pt/SiO}_2$ . An optimum sulfate holding capacity of the support materials was achieved when  $\text{TiO}_2$  was mixed equally with  $\text{SiO}_2$ , which enabled the reversible accumulation and release of sulfate at around  $300^\circ\text{C}$ . It is not clear how  $\text{SO}_4^{2-}$  can contribute to the process



**Fig. 10** Concept for improvement of carbon oxidation using mixed oxide as a support (Oi-Uchisawa et al., 2001)

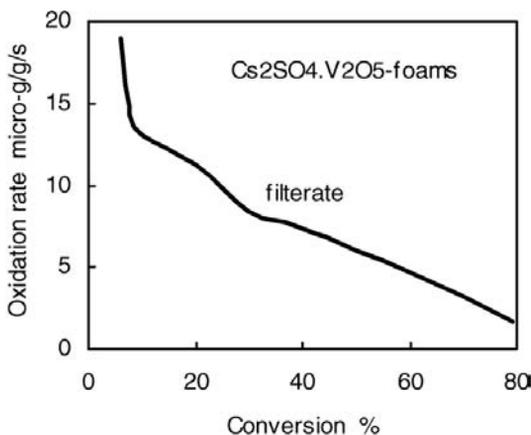


**Fig. 11** Model of the PM oxidation on the catalyst (Choi et al., 2005)

of carbon oxidation.

We described the model of the PM oxidation on the Pt catalyst (diesel oxidation catalyst) as shown in Fig. 11 (Choi et al., 2004; 2005). Larger scale PM, that has high specific surface carbonaceous particles, physically adsorbed vapor phase hydrocarbons onto the surface and was adsorbed on the high specific catalyst surface. In the next step, larger scale PM react on the catalyst with organic fractions, and they partially oxidized at high temperature conditions, or cracked to mid-or small-scale particles.

Alkali and rare earth elements in the main noble metals may be very effective in the promotion of soot oxidation. Van Setten et al. (1999) showed the soot activity with a  $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$ -foam catalyst (Fig. 12). The soot was oxidized at a high, but rapidly declining rate, up to 6% of the oxidation rate. This rate is high due to the conversion of hydrocarbons absorbed on Printex U. Above 6%, the carbon core is combusted and the oxidation rate decreased slowly with the ongoing combustion reaction because of the decreasing amount of soot. The ceramic foam catalyst can act as both a support and soot filter. However, to determine the real potential of the catalytic foams, the stability of the molten salt catalyst in combination with the support substrate and their performance in diesel exhaust gas should be investigated further.



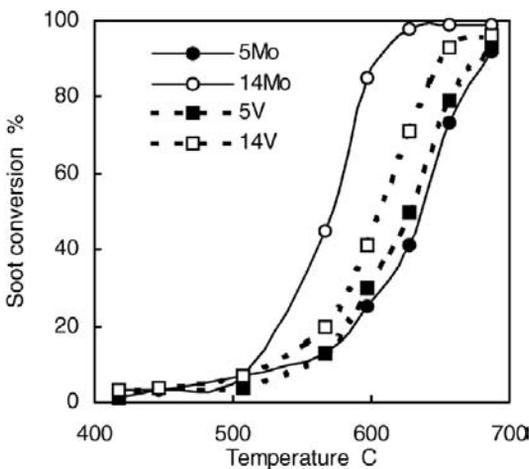
**Fig. 12** Soot oxidation rate as a function of soot conversion at  $650^\circ\text{C}$  of  $\text{Cs}_2\text{SO}_4\cdot\text{V}_2\text{O}_5$ -foams (Van Setten et al., 1999)

Lecocadio et al.(2004) displayed the soot conversion rate versus temperature obtained from TPO results for the non-catalyzed reaction and for reactions in the presence of 5Mo/Al<sub>2</sub>O<sub>3</sub>, 14Mo/Al<sub>2</sub>O<sub>3</sub>, 5V/Al<sub>2</sub>O<sub>3</sub> and 14V/Al<sub>2</sub>O<sub>3</sub> catalysts (Fig. 13). They used the PM sample of Printex U. When examining the conversion rate for the 14Mo catalyst, the curve shifted to lower temperatures and exhibited a different shape, with a higher slope, reaching 100% conversion very quickly. It implies the catalysts containing a higher loading of Mo and V exhibit the best performance. Better performance of the Mo catalyst was obtained with the greater ability for decomposition of those carbonated species on Mo superficial dispersed species.

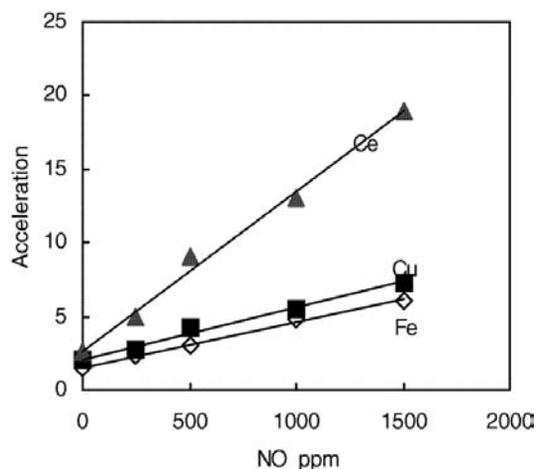
Craenenbroeck et al.(2002) studied diesel soot oxidation over Au-VOx/TiO<sub>2</sub> and Au-VOx/ZrO<sub>2</sub> catalytic systems with different vanadium (V) loadings. They concluded that catalysts with higher V loadings show a higher activity but there were no synergistic effects between Au and V. Flouty et al.(2003) studied the influence of Mo on Ce activity, CO<sub>2</sub> selectivity and resistance to sulfur poisoning in the oxidation of soot (N330 from Degussa Co.). Jelles et al.(1999) studied the total combustion of carbon black (CB) with Mo-Ce catalysts using TG-DTA analysis techniques.

The CB combustion was improved by the presence of Mo-Ce catalysts, which enabled soot oxidation to occur at lower temperatures (below 400°C). The catalytic activity decreased progressively with increased Mo loadings. The structure and the dispersion of Mo oxide on the Ce surface played an important role in the catalytic behavior of the system during the oxidation reaction of CB in the presence of SO<sub>2</sub>. Flouty et al. (2003) concluded that SO<sub>2</sub> acts as a real poison for the catalysts lowering their activity with respect to the combustion of CB, but that the presence of Mo enhanced Ce resistance to sulfur poisoning. With alkali doping of CuFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>, and K doping of LaFeO<sub>3</sub>, the highest level of soot combustion activity was in the order of K>Na>Cs>Li (An et al., 2005).

The effect of coexistence components on the catalytic reaction of soot is a very important parameter. The effect of NO on the oxidation rate of carbon is illustrated in Fig. 14 (Jelles et al., 1999). The acceleration in oxidation rate was calculated according to the equation : (oxidation rate with NO)/(oxidation rate without NO). For Ce, the oxidation rate in the presence of 1500 ppm NO is around 20 times higher than the rate measured in the absence of NO. When the supported Pt catalyst is omitted, the effect of NO in the gas



**Fig. 13** Soot conversion versus temperature from TPO results for the noncatalyzed soot combustion reaction and soot mixed with the catalysts (Lecocadio et al., 2004)

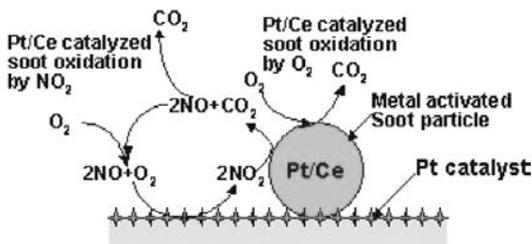


**Fig. 14** Acceleration of the oxidation rate as a result of NO addition with various NO concentrations (at 650 K and O<sub>2</sub>=10%) (Jelles et al., 1999)

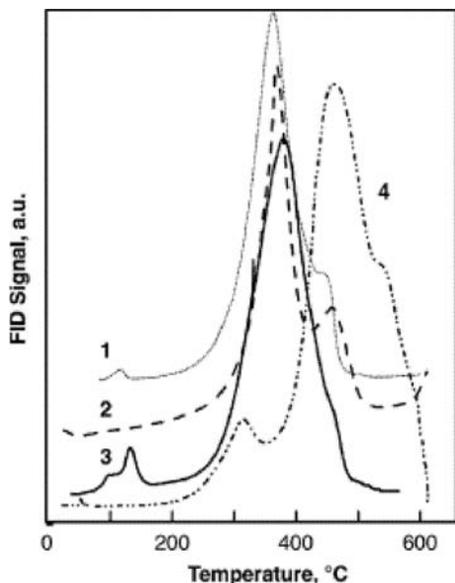
phase is less significant. The Pt catalyst is only active when it is homogeneously mixed with the soot.

The oxidation of soot with oxygen is catalyzed by the metal particles in the soot (Fig. 15) (Jelles et al., 1999). Apart from catalytic oxidation with oxygen, a second reaction cycle, catalyzed by Ce and Pt, results in a higher oxidation rate. In this cycle, NO is oxidized over Pt to NO<sub>2</sub> ( $\text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2$ ), which subsequently reacts with the soot, forming NO and CO<sub>2</sub> ( $2\text{NO}_2 + \text{C} \rightarrow 2\text{NO} + \text{CO}_2$ ).

As can be seen in Fig. 16 (Pisarello et al., 2002), K/La<sub>2</sub>O<sub>3</sub> and K/CeO<sub>2</sub> catalysts display



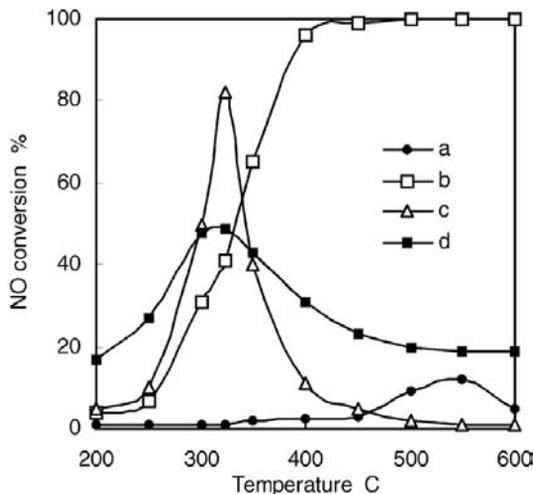
**Fig. 15** Soot oxidation mechanism of Ce-activated soot mixed with a Pt catalyst in the presence of NO and O<sub>2</sub> (Jelles et al., 1999)



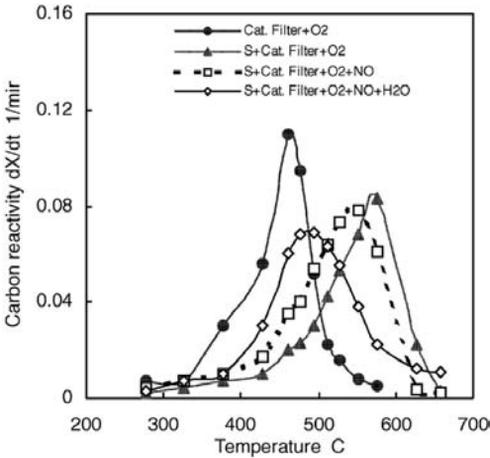
**Fig. 16** TPO profiles of soot-catalyst mixture: (1) K(4.5)/CeO<sub>2</sub>, (2) K(4.5)/La<sub>2</sub>O<sub>3</sub>, (3) Ba(22), K(7)/CeO<sub>2</sub>, (4) Ba(22)/CeO<sub>2</sub> (Pisarello et al., 2002)

good activity for soot combustion with a maximum observed in the TPO profile between 350 and 400°C. K and La<sub>2</sub>O<sub>3</sub> interact with CO<sub>2</sub> at temperatures as high as 500°C (Pisarello et al., 2002). La<sub>2</sub>O<sub>3</sub> contributes to this with a reaction path leading to the formation of carbonate-type intermediates, which decomposes at the reaction temperature, in a similar way to the effect shown by the K catalyst. CeO<sub>2</sub> supplies the oxygen necessary for the redox mechanism to take place.

Hong et al.(2000) indicated the effect of the simultaneous removal of particulate matter and NO<sub>x</sub> over lanthanoid perovskite-type catalysts in Fig. 17. They showed the temperature dependence of NO conversion over La<sub>0.6</sub>Ce<sub>0.2</sub>Cs<sub>0.2</sub>CoO<sub>3</sub> at various reaction conditions. (a) In the absence of O<sub>2</sub>, NO is decomposed at higher temperature. (b) NO is gradually reduced with increasing temperature and completely decomposed above 400°C. (c) NO conversion shows a maximum value at 300°C and drops sharply owing to desorption of the charged carbon particulate at higher temperature. (d) NO conversion shows a maximum value at approximately 300°C. However, NO is still decomposed above 400°C.



**Fig. 17** NO conversion during TPR over La<sub>0.6</sub>Ce<sub>0.2</sub>Cs<sub>0.2</sub>CoO<sub>3</sub> at various reaction conditions: NO=1000 ppm, O<sub>2</sub>=4%: (a) NO+carbon+O<sub>2</sub>, (b) NO+carbon+catalyst, (c) NO+carbon+catalyst+O<sub>2</sub>, (d) NO+catalyst+O<sub>2</sub> (Hong et al., 2000)

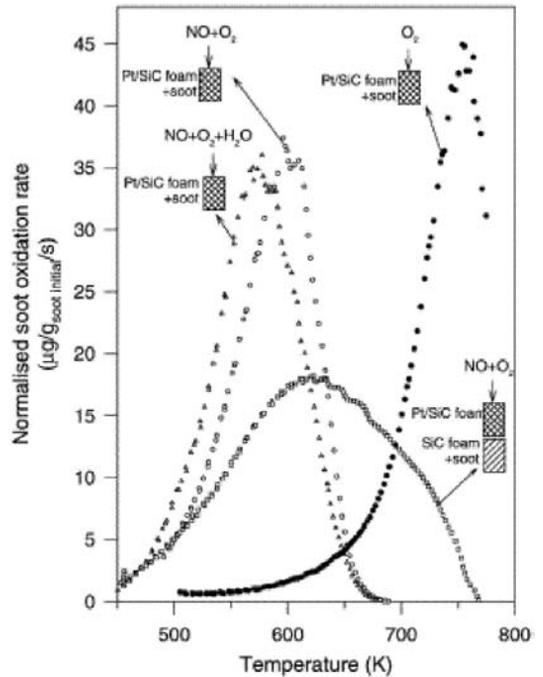


**Fig. 18** Reactivity temperature profiles of soot combustion on fresh and sulfated catalytic filters in the presence of NO and NO+H<sub>2</sub>O (Ciambelli et al., 2000)

In the LaCo<sub>3</sub>-type perovskite oxide, the partial substitution of Cs into the A-site enhanced the oxidation rate of carbon particulates and NO conversion. The ignition temperature of the carbon particulate on La<sub>1-x</sub>Cs<sub>x</sub>CoO<sub>3</sub> catalysts decreases with increasing x value.

Ciambelli et al. (2000) showed the effect of catalyst sulfate content on soot (from gas-oil burner) combustion activity in Fig. 18. X was calculated as  $(m_0 - m) / m_0$  equation, where m and m<sub>0</sub> represent the current and initial mass of carbon, respectively. The dX/dt is the overall carbon reactivity. After being sulfated, the catalyst activity decreased giving rise to a 130 K shift of the peak temperature of the dX/dt curve. When 1000 ppm NO was added to the gas mixture, the catalyst activity increased. If the reactant gas mixture also contained 10% water, the reactivity profile shifted further to lower temperatures. In the presence of a Cu/V/K/Cl/Ti catalyst, the enhancing effect of NO on the catalyst performance was observed for sulfated catalytic filters. The activity loss caused by the sulfate treatment was partially recovered when NO was present and reduced by the combined effect of NO and H<sub>2</sub>O.

Setiabudi et al. (2003) compares the oxidation profiles of soot in the presence of NO+O<sub>2</sub> and in the presence of NO+O<sub>2</sub>+H<sub>2</sub>O in Fig. 19. At

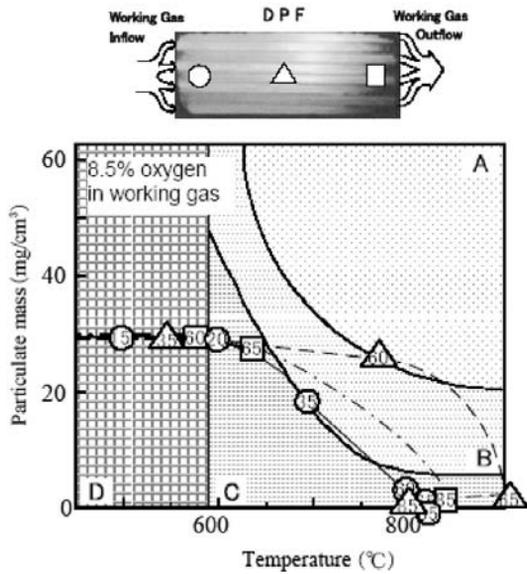


**Fig. 19** Effect of coexistence gases on soot oxidation rate by TPR (Setiabudi et al., 2002)

low temperature, the oxidation profiles are similar between soot oxidations of NO+O<sub>2</sub> and NO+O<sub>2</sub>+H<sub>2</sub>O. At higher temperature the separated system shows a moderate increase in soot oxidation rate with increases in temperature. For practical applications, the presence of 3% water in the NO+O<sub>2</sub> gas stream was shown to be beneficial. Due to the presence of water, the soot oxidation rate significantly increased, especially at low temperatures. Future research will focus on catalysts that can not only oxidize PM at low temperature, but also reduce NO<sub>x</sub>, continuously self-cleaning diesel particulate filters, and selective catalysts for NO<sub>x</sub> reduction.

**2.3 Example of PM oxidation in DPF**

Studies on DPF have been published since the early 1990s. However, studies on oxidation and catalytic oxidation of the diesel PM have been limited. Hanamura et al. (2003) represented the mechanisms of ignition and propagation in the reaction zone for regeneration (Fig. 20). It shows that no particulate mass was consumed until the temperature rose to approximately 600°C. The



**Fig. 20** Concept of ignition and propagation mechanism using reaction diagram (Hanamura et al., 2003)

PM was not ignited, but rather was consumed slowly until the reaction conditions entered the area labeled as C. The pressure drop around the entrance region slightly decreased, and therefore a larger volume of working gas flowed through the wall. In this case, the trapped PM was heated from the outflow-channel through the wall. Once ignited, since there was no PM present on the wall, most of the working gas flowed through the regenerated region. A reaction zone with a high brightness was produced between the regenerated region and the region that still contained the PM and propagates in both the upstream and the downstream directions.

### 3. Summary

The review has provided the catalyst composition and coexistence gas compositions on soot oxidation. These approaches can be summarized as follows:

- (1) The carbon oxidation reaction order is approximately 0.8 to 1.0.
- (2) In effects of coexistence gases, H<sub>2</sub>O concentrations of approximately 10% Vol. or coexis-

tence of NO enhance the oxidation of the diesel soot sample.

(3) In effects of catalysts such as Pt/Al<sub>2</sub>O<sub>3</sub> was very active in soot oxidation. Pt catalysts applied to TiO<sub>2</sub>-SiO<sub>2</sub> showed higher catalytic activity than when the catalyst was applied to the individual oxides. The best activity was achieved with a TiO<sub>2</sub>/(TiO<sub>2</sub>+SiO<sub>2</sub>) molar ratio range from 0.4 to 0.7. The Pt/TiO<sub>2</sub>/SiC catalyst exhibited the highest activity and durability against high temperatures and exposure to SO<sub>3</sub>.

(4) For metal catalysts effects, Mo, V, Ce, Co, Fe, Ba, K, La, Au-VO<sub>x</sub>/TiO<sub>2</sub> and Au-VO<sub>x</sub>/ZrO<sub>2</sub> were effective in the oxidation of soot, but these metal catalysts did not show superior activity to precious metal catalysts. K/La<sub>2</sub>O<sub>3</sub> and K/CeO<sub>2</sub> catalysts displayed good activity for soot combustion between 350 and 400°C.

(5) With alkali doping of CuFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>, and K doping of LaFeO<sub>3</sub>, the highest level of soot combustion activity was in the order of K > Na > Cs > Li.

In the future, to determine the real potential of various catalyst substrates, the stability and performances of catalysts in combination with the support substrates (gamma-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, SiC, etc.) in diesel exhaust gas should be investigated further. The effects of coexistence components, such as NO, CO, CO<sub>2</sub>, HC and H<sub>2</sub>O, on PM oxidation should be researched as well. Pt oxidizes PM well, but its natural supply is limited, so we must consider it as an additive of main catalysts to promote soot oxidation. A few studies have investigated the detailed mechanisms of PM oxidation on the catalyst, but further studies are needed to find improved catalysts that can meet new emission regulations for diesel engines. Future research will focus on catalysts that can not only oxidize PM at low temperature, but also reduce NO<sub>x</sub>, continuously self-cleaning diesel particulate filters, and selective catalysts for NO<sub>x</sub> reduction.

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## References

- An, H., Kilroy, C. and McGinn, P. J., 2004, “Combinatorial Synthesis and Characterization of Alkali Metal Doped Oxides for Diesel Soot Combustion,” *Catalysis Today*, Vol. 98, pp. 423~429.
- Chatterjee, S., Andrew, R. and Walker, P., 2001, “Emission Reduction in on-road Heavy-duty Diesel Applications with the Continuously Regenerating Technology (CRT) Diesel Particulate filter,” *SAE paper No. 2001-28-0049*.
- Choi, B. C., Jang, S. H. and Juhng, W. N., 2003, “ELPI Measurement of Particulate Matters from HSDI Diesel Engine with Diesel Oxidation Catalyst,” *SAE paper No. 2003-02-3159*.
- Choi, B. C., Yoon, Y. B., Kang, H. Y. and Lim, M. T., 2005, “Oxidation Characteristics of Particulate Matter on Diesel Warm-up Catalytic Converter,” *The 13<sup>th</sup> Int. Pacific Conf. on Automotive Engineering*, pp. 68~73.
- Ciambelli, P. P., Russo V. P. and Vaccaro, S., 2000, “The Role of NO in the Regeneration of Catalytic Ceramic Filters for Soot Removal from Exhaust Gases,” *Catalysis Today*, Vol. 60, pp. 43~49.
- Craenenbroeck, J. V., Andreeva, D., Tabakova, T., Werde, K. V., Mullens, J. and Verpoort, F., 2002, “Spectroscopic Analysis of Au-V-based Catalysts and Their Activity in the Catalytic Removal of Diesel Soot Particulates,” *J. of Catalysis*, Vol. 209, pp. 515~527.
- Flouty, R., Abi-Aad, E., Siffert, S. and Aboukas, A., 2003, “Role of Molybdenum Against Ceria Sulphur Poisoning in the Combustion of Soot Particles and the Oxidation of Propene,” *Applied Catalysis B*, Vol. 46, pp. 145~153.
- Hanamura, K., Suzuki, T., Tanaka, T. and Miyairi, Y., 2003, “Visulation of Combustion Phenomena in Regeneration of Diesel Particulate Filter,” *SAE paper No. 2003-01-0836*.
- Hong, S. S. and Lee, G. D., 2000, “Simultaneous Removal of NO and Carbon Particulates over Lanthanoid Perovskite-type Catalysts,” *Catalysis Today*, Vol. 63, pp. 397~404.
- Jelles, S. J., Krul, R. R., Makee, M. and Moulijn, J. A., 1999, “The Influence of NOx on the Oxidation of Metal Activated Diesel Soot,” *Catalysis Today*, Vol. 53, pp. 623~630.
- Johnson, T. V., 2004, “Diesel Emission Control Technology — 2003 in Review,” *SAE paper No. 2004-01-0070*.
- Kim, C. K., Cho, J., Kim, S. and Yeo G., 2005, “Continuous Soot Regeneration Technologies of a Catalyzed Particulate Filter for Diesel Passenger Car,” *The 13<sup>th</sup> Int. Pacific Conference on Automotive Engineering*, pp. 290~295.
- Lee, H. S. and Chun, K. M., 2005, “Experimental Investigation of Soot Oxidation Characteristics,” *The 13<sup>th</sup> Int. Pacific Conference on Automotive Engineering*, pp. 296~301.
- Leet, J. A., Simescu, S., Froelund, K., Dodge, L. G. and Roberts, C. E., 2004, “Emissions Solutions for 2007 and 2010 Heavy-duty Diesel Engines,” *SAE paper No. 2004-01-0124*.
- Lecocadio, I. C. L., Braun, S. and Schmal, M., 2004, “Diesel Soot Combustion on Mo/Al<sub>2</sub>O<sub>3</sub> and V/Al<sub>2</sub>O<sub>3</sub> Catalysts: Investigation of the Active Catalytic Species,” *J. of Catalysis*, Vol. 223, pp. 114~121.
- Miro, E. E., Ravelli, F., Ulla, M. A., Cornaglia, L. M. and Querini, C. A., 1999, “Catalytic Combustion of Diesel Soot on Co, K Supported Catalysts,” *Catalysis Today*, Vol. 53, pp. 631~638.
- Mul, G., Zhu, W., Kapteijn, F. and Moulijn, J. A., 1998, “The Effect of NOx and CO on the Rate of Transition Metal Oxidation Catalyzed Carbon Black Oxidation: An Exploratory Study,” *Applied Catalysis B*, Vol. 17, pp. 205~220.
- Nakatani, K., Hirota, S., Takeshima, S., Itoh, K., Tanaka, T. and Dohmae, K., 2002, “Simultaneous PM and NOx Reduction System for Diesel Engines,” *SAE paper No. 2002-01-0957*.
- Oh, S. K., Baik, D. S. and Han, Y. C., 2002, “Performance and Exhaust Gas Characteristics on Diesel Particulate Filter Trap,” *IJAT*, Vol. 3, pp. 111~110.
- Oi-Uchisawa, J., Obuchi, A., Enomoto, R., Xu, J., Nanba, T., Liu, S. and Kushiyama, S., 2001, “Oxidation of Carbon Black over Various Pt/

Mox/SiC Catalysts,” *Applied Catalysis B*, Vol. 32, pp. 257~268.

Oi-Uchisawa, J., Wang, S., Nanba, T., Ohi, A. and Obuchi, A., 2003, “Improvement of Pt Catalyst for Soot Oxidation Using Mixed Oxide as a Support,” *Applied Catalysis B*, Vol. 44, pp. 207~215.

Pisarello, M. L., Milt, V., Peralta, M. A., Querini, C. A. and Miro, E. E., 2002, “Simultaneous Removal of Soot and Nitrogen Oxides from Diesel Engine Exhausts,” *Catalysis Today*, Vol. 75, pp. 465~470.

Stannore, B. R., Brilhac, J. F. and Gilot, P., 2001, “Carbon Oxidation Rate,” *Carbon*, Vol. 39, pp. 2247.

Setiabudi, A., Van Setten, B. A. A., Makee, M. and Moulijn, J. A., 2002, “The Influence of NOx on Soot Oxidation Rate: Molten Salt Versus Platinum,” *Applied Catalysis B*, Vol. 35, pp. 159~166.

Setiabudi, A., Makkee, M. and Moulijn, J. A., 2003, “An Optimal NOx Assisted Abatement of

Diesel Soot in an Advanced Catalytic Filter Design,” *Applied Catalysis B*, Vol. 42, pp. 35~45.

Van Setten, B. A. A., Bremmer, J., Jelles, S. J., Makkee, M. and Moulijn, J. A., 1999, “Ceramic Foam as a Potential Molten Salt Oxidation Catalyst Support in the Removal of Soot From Diesel Exhaust Gas,” *Catalysis Today*, Vol. 53, pp. 613~621.

Van Setten, B. A. A., Currier, N. W., Eadler, H., Popuri, S. and Suresh, A., 2002, “Quantitative Flow-reactor Study of Diesel Soot Oxidation Process,” *SAE paper No. 2002-01-1684*.

Vincent, N. W., Richards, P. J. and Rogers, T. J., 2002, “Effective Particulates Reduction in Diesel Engines Through the Use of Fuel Catalysed Particulate Filters,” *IJAT*, Vol. 3, pp. 112~120.

Yezerets, A., Currier, N. M., Eadler, H. A., Suresh, A., Madden, P. F. and Branigin, M. A., 2003, “Investigation of the Oxidation Behavior of Diesel Particulate Matter,” *Catalysis Today*, Vol. 88, pp. 17~25.