ELSEVIER

Catalysis Today 53 (1999) 623–630

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The influence of NO_x on the oxidation of metal activated diesel soot

S.J. Jelles, R.R. Krul, M. Makkee *, J.A. Moulijn

Delft University of Technology, Section Industrial Catalysis, Julianalaan 136, 2628 BL, Delft, The Netherlands

Abstract

The influence of NO on the oxidation of metal (cerium, copper, and iron)-activated soot was studied. Without NO in the gas phase, the activation energy of soot is ≈170 kJ/mol, independent of the type of metal applied in the soot. The rate-limiting step in the oxidation with oxygen is probably the decomposition of surface oxygen complexes. In presence of NO, the oxidation rate of soot mixed with a supported platinum catalyst is increased significantly, especially for cerium-activated soot. The activation energy of the oxidation reaction is decreased by the presence of NO in the gas phase. The increase in reaction rate as a result of NO and a platinum catalyst is explained by a cycle of two catalytic reactions, where platinum oxidises NO to NO_2, which subsequently oxidises soot using cerium as a catalyst, forming NO which can participate in the reaction more than once. This oxidation mechanism can be put into practice by combining a platinum-activated particulate trap with a combination of platinum and cerium fuel additives. This combination might be a breakthrough in the search for an applicable catalytic soot removal system. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Diesel; Soot; Oxidation; Catalyst; Fuel additives; Metal-activated soot; NO_x

1. Introduction

Removal of carbon particulate matter (‘soot’) from diesel exhaust gas is a challenging and relevant topic in automotive catalysis and engineering. The emission standards are tightened world-wide, whereas the intensive engine development and optimisation programmes will probably not result in the required reduction of emissions [1], resulting in a need for after-treatment techniques.

The most promising technique of soot removal is after treatment, namely: particulate capture and subsequent catalytic oxidation. From the catalytic-filter system design and energy consumption considerations, an important parameter is the oxidation rate of soot as a function of the exhaust-gas composition and, of course, the temperature of the filter device.

Two systems have been the subject of substantial developments: the first uses a fuel additive in combination with an uncatalysed filter. Examples of additives include fuel soluble compounds of Mn, Fe, Cu, Ce and Pt — metals that are active catalysts for the oxidation of carbon particulates [1–3].

In this system, the metal after combustion in the engine serves as a nucleus for the soot deposition. In this way, a well-defined dispersed metal is entrapped in the soot particulate and thereby guarantees a close (‘tight’) contact between the catalyst (metal) and the soot. The second system uses one or more filters pre-catalysed with metals, such as platinum, which are effective in oxidising carbon particulate. Platinum catalysed filters have been reported which regenerate at temperatures of 625 K and above, but suffer from sulphate formation [4]. A recent development utilises a platinum-based

---

* Corresponding author. Tel.: +31-15-278-1391; fax: +31-15-278-4452

E-mail address: m.makkee@stm.tudelft.nl (M. Makkee)

PII: S0920-5861(99)00150-9

precatalyst system to oxidise NO to NO_2 that subsequently oxidises carbon particulate on a filter. The system is reported to be effective in continuous filter regeneration at temperatures in the region of 575 K using low sulphur fuel (50 ppm (wt)) [5].

Both the systems described above use only one concept; either metal-fuel additive catalysed oxidation or NO_x-assisted oxidation. A newly developed system that combines platinum and cerium fuel additives with a platinum-containing wall-flow monolithic filter is reported, which integrates these two above-mentioned oxidation mechanisms [6,7]. In this work, the influence of NO_x in the gas phase on the oxidation of cerium-, copper-, and iron-activated soot will also be discussed.

2. Experimental

2.1. Soot samples

The soot samples containing metal originated from metal additives in the fuel of a diesel engine. The soot samples were taken from the exhaust gas of a two-cylinder Lister–Petter LPW2 direct injected, water-cooled, and naturally aspired diesel engine equipped with a generator. The electrical power generated (75% of maximum rated power) was dissipated through an electrical resistor. The metal fuel additives used and its concentration in the fuel are listed in Table 1. The soot was collected by passing the full exhaust gas stream through a fiberglass filter contained in a filter holder until the back pressure reached 0.5 bar. The back pressure was then maintained at 0.5 bar using a slipstream valve. During this operation, the engine exhaust temperature increased by about 40 K. The total sampling time was 6 min. When soot samples were taken with a new fuel composition, the engine was run-in on the new fuel for at least 24 h to prevent substantial memory effects and the engine exhaust pipe and the filter holder were cleaned. The collected soot was scraped of the filter and sieved. The soot collection procedure and the equipment are discussed in more detail in [6]. All metals, except cerium, were atomically dispersed in the soot. The metal particles were barely observable with a high-resolution transmission electron microscope (HRTEM; 0.2-nm spot resolution), whereas with energy dispersive X-ray analysis (EDX) — clearly a background signal of the added metal — was observed. For platinum, ≈15% was detected in the soot particulate by chemical analysis, the rest of the platinum was deposited in the engine combustion chamber, engine valves, exhaust manifold, exhaust pipe, etc. For the other metal additives, ≈50% was recovered in the soot. The addition of fuel additives for the applied dosage rate has hardly any influence in the soot production rate of the engine.

Table 1
Additives used during the experimental program

Metal	Additive	Metal in fuel (ppm)
Cerium	Rhône–Poulenc DPX9	50
Copper	Lubrizol OS-96401	22
Iron	Aldrich Ferrocene	20

2.2. Flow-reactor experiments

Laboratory flow-reactor soot oxidation experiments were performed with the equipment shown in Fig. 1. A constant gas flow of 200 ml/min, containing 10 vol% of oxygen in argon was used for each soot sample. Before each experiment, 20 mg of soot was mixed with 6 mg of a supported platinum catalyst (1 wt% platinum metal on amorphous silica-alumina (ASA)) using a spatula, diluted with 400 mg of silicon carbide and placed in a quartz reactor.

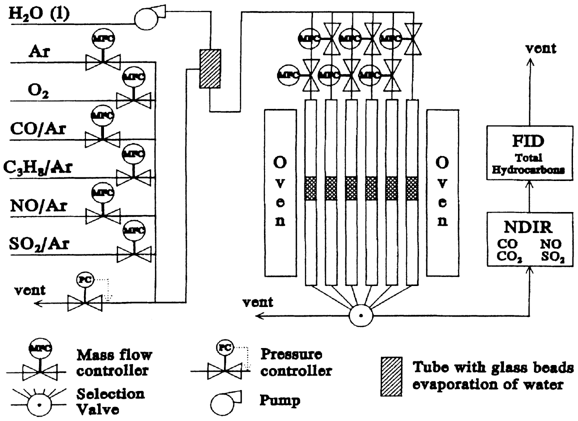

Fig. 1. Layout of the flow-reactor equipment used for the oxidation experiments.

In one series of experiments, the concentration of NO in the gas phase was varied from 0 to 1500 vol ppm at a temperature of 650 K and an oxygen concentration of 10 vol% in argon. In another series of experiments, the temperature was varied with 10 vol% of oxygen in the gas phase. Finally, in a third series of experiments, the temperature was varied in the presence of 10 vol% of oxygen and 250 ppm of NO in the gas phase. During each experiment, the inlet NO concentration and the temperature were kept constant. The CO, CO_2, and NO concentrations in the outlet were measured with a Hartmann and Braun URAS 10 non-dispersive infrared analyser (NDIR). Based on the flow and the CO and CO_2 concentrations at the outlet of the reactor, the soot oxidation rate was calculated, which was integrated to find the total amount of carbon oxidised. The carbon mass balance was always in the range of 90% to 110%. The oxidation rate calculated was normalised for the calculated total amount of soot oxidised and will be expressed in $\mu g/(g_{initial}\ s)$. In the experimental programme, only NO concentration was monitored. Since it was assumed that the NO over platinum catalyst can be only converted to NO_2 and the concentration of NO at the inlet of the reactor was almost identical to the NO concentration at the outlet of the reactor (the formed NO_2 will be reduced to NO over the metal activated soot). Therefore, the conversion of NO_x (NO and NO_2) over either the platinum and the metal activated soot or the soot itself into N_2 and N_2O was not taken in account.

3. Results

3.1. Influence of NO concentration on the soot oxidation rate

In the flow-reactor experiments discussed here, the oxygen concentration is 10 vol% in argon and the temperature 650 K. In Fig. 2, the oxidation rate of cerium-activated soot, mixed with a supported platinum catalyst, is plotted as a function of the conversion for NO concentrations of 0, 250, 500, and 1500 ppm. In Figs. 3 and 4, the same types of data are plotted for copper- and iron-activated soot, respectively. The effect of NO on the oxidation rate is significantly more pronounced for cerium-activated soot than for iron- or copper-activated soot. The effect of NO on the combustion rate is more clearly illustrated in Fig. 5. In this figure, the acceleration of the oxidation as a result of NO addition, calculated with *(rate with NO)/(rate without NO)* is plotted as a function of the inlet NO concentration. For cerium, the oxidation rate in the presence of 1500 ppm NO is around 20 times higher than the rate measured in the absence of NO. For iron and copper this ratio is ≈7. When the supported platinum catalyst is omitted, the effect of NO in the gas phase is less significant: for cerium- activated soot in the absence of a platinum catalyst, the oxidation rate

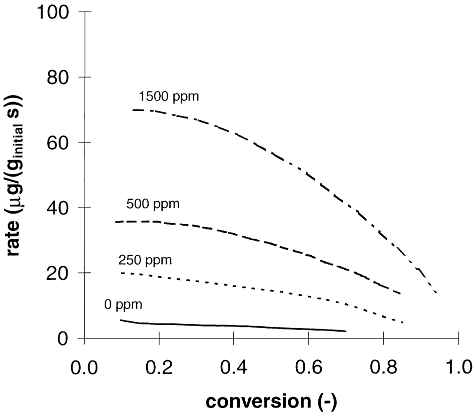

Fig. 2. Oxidation rate of cerium-activated soot mixed with supported platinum catalyst at different NO concentrations at a temperature of 650 K and an oxygen concentration of 10%.

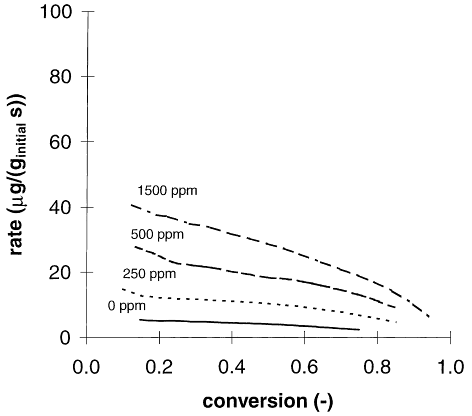

Fig. 3. Oxidation rate of copper-activated soot mixed with supported platinum catalyst at different NO concentrations at a temperature of 650 K and an oxygen concentration of 10%.

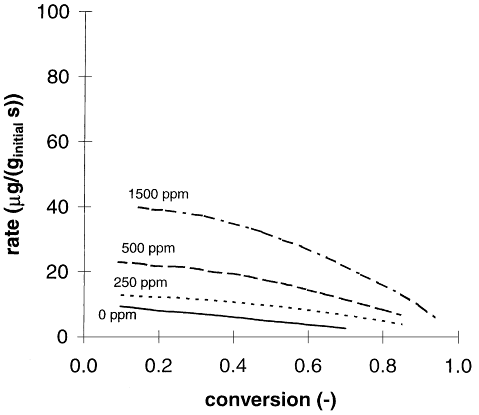

Fig. 4. Oxidation rate of iron-activated soot mixed with supported platinum catalyst at different NO concentrations at a temperature of 650 K and an oxygen concentration of 10%.

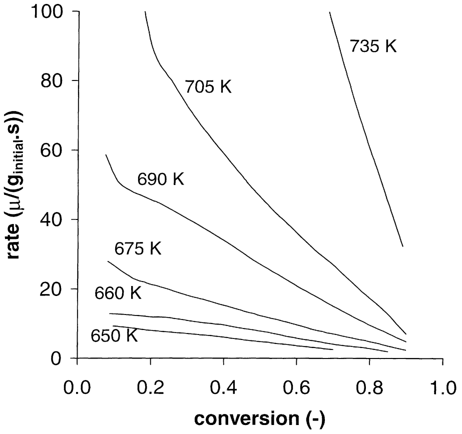

Fig. 6. Oxidation rate of iron-activated soot in 10% oxygen at different temperaures.

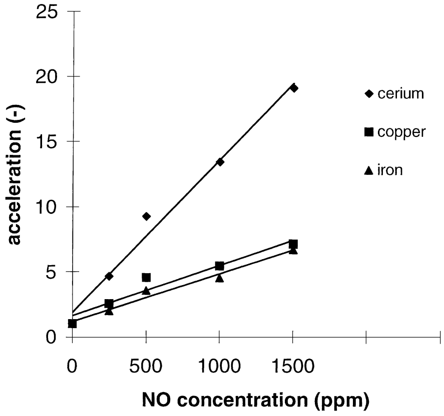

Fig. 5. Acceleration of the oxidation rate as a result of NO, defined as (rate with NO/rate without NO), as a function of the NO concentration. Temperature is 650 K and the oxygen concentration of 10%.

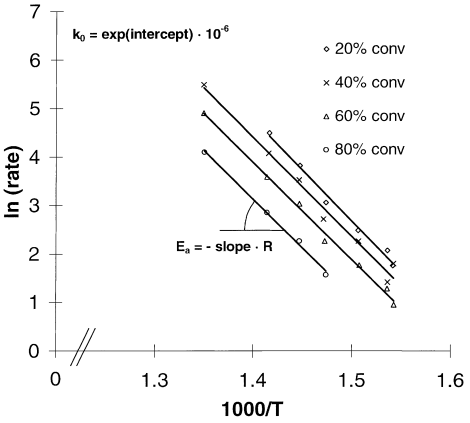

Fig. 7. Arrhenius plot of the oxidation of iron-activated soot in 10% oxygen. From this plot the activation energy, E_a, is calculated from the slope and the frequency factor from the intercept.

in the presence of 1000 ppm NO is less than one-third of the oxidation rate of the same cerium soot under identical conditions, but mixed with a platinum catalyst. Furthermore, the platinum catalyst is only active when it is homogeneously mixed with the soot. When the platinum catalyst is placed upstream of the soot, the same results are obtained as though no platinum catalyst was present (not shown). Without NO in the gas phase the oxidation rates of the investigated soot types are unchanged in the presence of a platinum catalyst, whether this catalyst is homogeneously mixed with the soot or placed upstream of the soot.

3.2. Influence of temperature on the soot oxidation rate

In Fig. 6, the oxidation rate is plotted as a function of conversion for iron activated soot in 10% oxygen in argon for several temperatures. Similar plots were made for soot without metal and for both copper- and cerium-activated soot (not shown). From the oxidation rates between a soot conversion in the range 0.2–0.8, the activation energy was calculated using an Arrhenius plot as shown in Fig. 7. From the slope of the line, the activation energy, E_a, was calculated, and from the

Table 2
Activation energy for oxidation of plain soot and cerium- and iron-activated soot in 10% oxygen, and 10% oxygen and 250 ppm NO

	10% O_2		10% O_2 and 250 ppm NO	
	E_a (kJ/mol)	k_0 at $\xi = 0.5 \times 10^7$ (s^{-1})	E_a (kJ/mol)	k_0 at $\xi = 0.5 \times 10^4$ (s^{-1})
Plain soot	168 ± 1	1.3 ± 1	n.d.[a]	n.d.[a]
Cerium-activated soot	167 ± 4	9.0 ± 0.6	93 ± 10	439 ± 31
Iron-activated soot	170 ± 4	17 ± 0.7	120 ± 4	2.2 ± 0.2

[a] Not determined.

intercept the frequency factor. k_0, was calculated at 50% conversion. From Fig. 7, the apparent activation energy for the soot oxidation for iron activated soot is calculated as 170 ± 4 kJ/mol and the frequency factor as $17 \times 10^7\ s^{-1}$. The same calculations were made for the other soot types. For the copper-activated soot, E_a and k_0 could not be calculated with an acceptable error and these values are, therefore, omitted. In Table 2 the activation energies and the frequency factors at 50% conversion for the other soot types are listed. In contrast with the frequency factor, the activation energy is not dependent of the soot conversion. Further, it is clear that the activation energy is around 170 kJ/mol for all soot types. The observed difference in the oxidation rate is a result of a difference in the frequency factor.

For cerium- and iron-activated soot, the activation energy and the frequency factor at 50% conversion of the oxidation in the presence of 250 ppm NO and a supported platinum catalyst is also given in Table 2. For iron- and cerium-activated soot, the activation energies are 120 ± 4 and 93 ± 10 kJ/mol, respectively, which is substantially lower than in the absence of NO in combination with a supported platinum catalyst. The frequency factor of the reaction in presence of NO and a platinum catalyst is substantially lower than that of the reaction without NO, but as a result of the low activation energy, the reaction in presence of NO occurs faster at a lower temperature. The activation energy of cerium-activated soot slightly increases with increasing conversion.

4. Discussion

The activation energy and the frequency factor of the oxidation were calculated for the investigated soot types using the Arrhenius equation:

$$r = k_0 e^{-E_a/RT} \tag{1}$$

In the absence of NO in the gas phase, the apparent activation energies of all the investigated soot types are equal, 170 kJ/mol. This indicates that the rate-determining step in the soot oxidation with oxygen is not affected by the presence of a metal and that the reaction by which soot is oxidised with oxygen will follow the same mechanism for each type of soot, whether it is metal activated or not. The presence of a metal in the soot increases the frequency factor which indicates that the presence of a metal results in more sites in the soot where the oxygen–soot reaction can take place, leading to a higher oxidation rate. Although the exact mechanism of the metal catalysed reaction is not yet clear, it can be concluded that it is probably similar to the non-catalytic. A possible mechanism for this reaction is dissociative chemisorption of oxygen, leading to oxygen radicals that subsequently form (unstable) surface oxygen complexes that subsequently will decompose forming CO and CO_2. The dissociation of oxygen and the formation of the surface oxygen complexes can be catalysed by the metal present in soot. The decomposition of the surface oxygen complexes is probably the rate-determining step, because the activation energy of oxidation in oxygen is not changed by the presence of any of the studied metals. When the concentration of oxygen complexes on the soot surface is high, the rate of decomposition will also be high, which is in agreement with literature [8].

In the presence of 250 ppm NO and a supported platinum catalyst, the activation energy is lower for both, the iron-activated soot, 120 kJ/mol, and cerium-activated soot, 93 kJ/mol. Cooper and Thoss reported an activation energy for pure soot of 17 kJ/mol in the presence of NO, measured with 400 ppm NO and 12% O_2 in the gas phase without a platinum catalyst [9]. This observed apparent

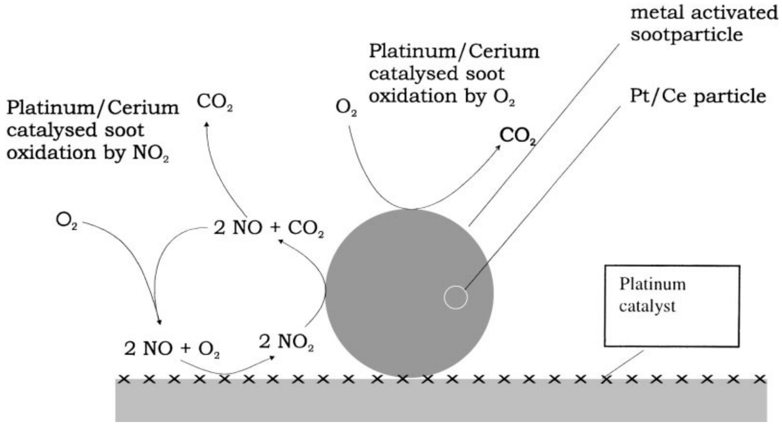

Fig. 8. Postulated oxidation mechanism that can explain the observed high oxidation rate of cerium-activated soot mixed with a platinum catalyst in the presence of NO and oxygen.

activation energy is probably disguised by diffusion limitations. The observation that the influence of NO is only significant in the presence of a supported platinum catalyst indicates that NO_2 plays an important role in the oxidation mechanism. This observation is supported by the fact that the oxidation rate of soot with NO, in the absence of oxygen, at the investigated temperature range is negligible and the enhancement of the soot oxidation rate is only observed with NO in the presence of both, O_2 and a platinum catalyst mixed in the (metal-activated) soot. The soot oxidation rate shows a large acceleration effect, if the metal-activated soot is composed of cerium. The change in activation energy indicates a change in oxidation mechanism. This observation was also made by Cooper and Thoss [9]. The role of NO in the oxidation mechanism can be summarised in the following reactions:

$$\mathrm{NO} + \frac{1}{2}\mathrm{O_2} \Leftrightarrow \mathrm{NO_2} \quad \text{catalysed by platinum} \qquad (1)$$

$$2\mathrm{NO_2} + \mathrm{C} \rightarrow 2\mathrm{NO} + \mathrm{CO_2} \quad \text{catalysed by cerium} \qquad (2)$$

Reaction (1) is known to be catalysed by platinum. Reaction (2) is reported to be non-catalytic for non-activated soot [10]. From the results reported in this work it can be concluded that reaction (2) is clearly catalysed by cerium present in the soot. This conclusion is based on the observation that when used in combination with a supported platinum catalyst and 1500 ppm of NO in the gas phase at 650 K, the oxidation rate of cerium-activated soot is at least twice as high as that of copper- or iron-activated soot, as shown in Figs. 2–4. The oxidation of soot with NO_2 occurs possibly via a route similar to the one with oxygen, as described above, but the activation energy of this reaction is dependent of the type of metal present in the soot, indicating that the rate-determining step is affected. The observation that the oxidation rate is not increased significantly when the platinum catalyst is placed upstream of the soot indicates that the reaction chain (1–2) has to be accomplished several times, resulting in multiple oxidation cycles of NO over the platinum catalyst as observed by Mul et al. [11]. It might be surprising that a platinum catalyst placed upstream of the soot has no influence on the oxidation rate with NO in the gas phase. However, it should be realised that, in fact, an NO/NO_2 mixture is used because conversion of NO to NO_2 takes place in the equipment. Therefore, the platinum catalyst can only have a minor effect on the NO_2 concentration.

A postulated mechanism that can explain the high oxidation activity of cerium-activated soot mixed with a platinum catalyst in the presence of NO and oxygen in the gas phase is shown in Fig. 8. The oxidation of soot with oxygen is catalysed by the metal particles in the soot. Apart from (non-) catalytic oxidation with oxygen, a second reaction *cycle*, catalysed by cerium *and* platinum, results in a high oxidation rate. In this cycle, NO is oxidised over platinum to NO_2 (reaction 1), which subsequently reacts with the soot, forming NO and CO_2 (reaction (2)). The resulting NO can subsequently participate again in reaction (1).

Table 3
Minimum operation temperature

Additive	Concentration (ppm wt)	Filter	Minimum temperature (K)
None		EX80	810–830
None		platinum activated EX80	690–700
Cerium	100	EX80	705
Platinum–Cerium	0.5–5	platinum activated EX80	600
Platinum–Copper	0.5–5	platinum activated EX80	620
Platinum–Iron	0.5–22	platinum activated EX80	630

The postulated mechanism is supported by the results from filter experiments with a side stream of a small diesel engine in our laboratory as reported in Ref. [5]. The minimum temperatures, at which a Corning EX80 filter can regenerate continuously, were measured using several traps and additives (Table 3). This temperature is indicative of the activity of a fuel additive/filter system. The minimum temperature of a plain filter in combination with a cerium additive is comparable with that of a platinum-activated filter without an additive, ≈700 K. When these two systems are integrated using a platinum activated filter and a platinum/cerium fuel additive, the minimum temperature is lowered to 600 K. Whereas copper and iron are known to be more active as an individual additive, their combination with a platinum additive and a platinum-activated filter does not result in an even lower minimum temperature. This supports the conclusion that platinum and cerium show synergy in the oxidation of soot in a practical application. In this process, platinum will act as an NO-oxidation catalyst, whereas the cerium incorporated in the soot acts as a surface-oxygen complex generator. High levels of surface-oxygen complexes onto the soot will lead to an enhanced decomposition of these complexes, resulting in a higher soot oxidation rate. It should be noted that this minimum temperature strongly depends on the type of diesel engine and its load; in other words, on the soot production as a function of NO in the exhaust gas stream. The platinum/cerium combination might be a breakthrough in the search for an applicable catalytic soot removal system.

5. Conclusion

The apparent activation energy of the oxidation of soot with oxygen is 170 kJ/mol and is not affected by the presence of metal in the soot. The rate of oxidation is increased by the presence of metal in the soot. The rate determining step in the soot oxidation with oxygen is probably the decomposition of surface oxygen complexes on the soot. The activation energy of the oxidation of metal-activated soot is influenced significantly by the presence of NO in the gas phase in combination with a supported platinum catalyst. Cerium, in combination with platinum, can maintain an oxidation cycle that results in high soot oxidation rates and in which NO_2 plays an important role. Copper and iron maintain this combined oxidation cycle of NO into NO_2 over platinum, and subsequent oxidation of the metal-activated soot with NO_2 less efficiently than cerium. This cycle of NO to NO_2 will be passed several times over the filter system per pass of the exhaust gas. This oxidation mechanism can be put into practice by combining a platinum activated particulate trap with a platinum/cerium fuel additive.

References

[1] J.P.A. Neeft, M Makkee, J.A. Moulijn, Diesel particulate emission control, Fuel Process. Technol., 47 (1996) 1.

[2] G. Lepperhoff, H. Lüders, P. Barthe, J. Lemaire, Quasi continuous particle trap regeneration by cerium additives, SAE paper 950369, 1995.

[3] J.C. Summers, S. van Houtte, D. Psaras, Simultaneous control of particulate and NO_x emissions from diesel engines, Appl. Catal. B: Environmental, 10 (1996) 139.

[4] B.E. Enga, M.F. Buchman, Catalytic filters control diesel particulate, SAE paper 820184, 1982.

[5] B.J. Cooper, H.J. Jung, J.E. Thoss, Treatment of diesel exhaust gas, US Patent 4,902,487, 1990.

[6] S.J. Jelles, M. Makkee, J.A. Moulijn, G.J.K. Acres, J.D. Peter-Hoblyn, Diesel particulate control. Application of an activated particulate trap in combination with fuel additives at an ultra low dose rate, SAE paper 990113, 1999.

[7] J.D. Peter-Hoblyn, J.M. Valentine, B.N. Sprague, W.R. Epperly, Methods for reducing harmful emissions from a diesel engine, Patent WO 97/04045, 1997.

[8] F. Kapteijn, J.A. Moulijn, Kinetics of catalysed and uncatalysed coal gasification, carbon and coal gasification, NATO ASI Series, Series E: Appl. Sci., No. 105, 1986, pp. 291–360.

[9] B.J. Cooper, J.E. Thoss, Role of NO in diesel particulate emission control, SAE paper 890404, 1984.

[10] E. Xue, Studies using Pt-based catalysts of reactions involved in catalytic control of diesel engine particulate emission. PhD thesis, University of Twente, the Netherlands, 1993 (in English).

[11] G. Mul, W. Zhu, F. Kapteijn, J.A. Moulijn, Appl. Catal. B. 17 (1998) 205.