



The influence of NO_x on soot oxidation rate: molten salt versus platinum

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Abstract

A systematic study was carried out to assess the influence of simulated diesel exhaust on the activity of molten salt, $\text{Cs}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5$, supported on ceramic foam and Pt/ γ -alumina catalysts in the oxidation of diesel soot. Gas compositions containing O_2 , NO_x , CO, C_3H_6 , and SO_2 were used. The activity of molten salt catalyst, an active catalyst for the oxidation of soot with O_2 , is slightly affected by the gas component due to NO_2 already present in NO_x . In contrast, the presence of NO_x , significantly increases the soot oxidation rate with platinum catalyst. These changes were due to the catalytic oxidation of NO to NO_2 with platinum, followed by soot oxidation with NO_2 . Three configurations are compared, viz. a fixed bed containing a physical mixture of Pt catalyst and soot, Pt catalyst upstream of a fixed bed containing soot, and Pt catalyst upstream of soot loaded on ceramic foam supported molten salt. The reaction cycle of oxidation of NO, followed by soot oxidation with the NO_2 produced, was observed only in a physical mixture of platinum catalyst and soot. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molten salt; Platinum; Soot oxidation; NO_x ; Reaction cycle

1. Introduction

Increasing concerns on health effect and pressure to fulfil the emission regulation of noticeable diesel emission, soot, urges the development of tailored after-treatment systems. This stimulates the development of both diesel particulate filter (DPF) and the invention of catalyst materials for the oxidation of trapped diesel soot. Among others, the catalysts being developed are “volatile material” like Cu–K–V–Cl based [1] and “mobile material” like molten salt system [2–4]. Under simulated laboratory conditions, molten salt catalyst appeared to be promising and

showed a comparable activity with commercially available catalytic fuel additives. Eutectic mixtures of Cs_2SO_4 , V_2O_5 , MoO_3 , and Cs_2O are active in soot oxidation in the presence of 10% O_2 .

Previous researchers concluded that open pore ceramic foams are good candidates as support for the molten salt as well as a soot trap [5]. The low porous properties of ceramic foam offer the possibility to stabilize the catalyst in a way that the catalyst material remains accessible for the deposition of soot under practical conditions [6].

The concentration of the raw exhaust gases of diesel engines, hydrocarbon (HC), CO, and NO_x , although relatively low compared to those of gasoline, might affect the performance of soot oxidation catalyst. For example, if the catalyst has an activity in the oxidation of NO to NO_2 the presence of NO can be an advantage

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in soot abatement. The commercial application of continuously regenerating trap (CRT) [7,8], is mainly relying on the conversion of NO, from diesel exhaust, to NO₂ in a “flow-through” honeycomb monolithic substrate. NO₂ then subsequently oxidizes soot on a wall-flow monolith filter.

SO₂, up to now an unregulated diesel exhaust component, is a common poison for almost all catalyst applications due to sulfate compound formation. Some soot oxidation catalyst performances were investigated with respect to SO₂. It was reported that sulfur dioxide acts as poison for Cu–K–V–Cl [1] and CeO₂ [9] catalysts. This SO₂ could also deactivate molten salt catalysts.

Those effects might occur if molten salts are introduced in the real application. Reported data on the effect on soot oxidation of either individual or combination of gases present in diesel exhaust systems is very limited, especially with molten salt catalysts. Therefore, the activity of molten salt catalysts in soot oxidation is tested in the presence of those gases using a gas composition close to the real diesel exhaust. Platinum, a well-known catalyst for NO oxidation to NO₂, was used as reference. Soot oxidation rates with NO₂ were investigated in different catalysts soot configurations of catalyst-soot to get information on the effect of different reactor structure that might be useful for the development of diesel particulate catalytic filter.

2. Experimental

The molten salt catalyst system used was Cs₂SO₄·V₂O₅ (0.55 mol Cs₂SO₄; 0.45 mol V₂O₅; melting point of 625 K) supported on ceramic foam. The ceramic foam used was Porvair α-Al₂O₃ with 20 pores/cm, 87% porosity, and 398 g/l density. Cylindrical ceramic foam with 7 mm diameter and 25 mm length was loaded by molten salt using method described elsewhere [3,4]. Molten salt catalysts were prepared by melting at its eutectic ratio [2]. Catalyst loading on ceramic foam was 80 g/l_{foam}. Before and after the experiment the chemical composition of the eutic mixture was determined by XRF and showed the composition remained unchanged. Only when the molten salts are heated to extreme high temperatures (above 1075 K for a period over at least 1 week) vapor-

ization of sulfate and partial of cesium was observed. Since platinum catalyst is well known to be a good catalyst for NO–NO₂ oxidation, 1 wt.% Pt/γ-alumina catalyst was prepared for comparison. The catalyst was prepared by impregnating 63–100 μm γ-alumina (Akzo Nobel 003-1.5e) with [Pt(NH₃)₄]Cl₂ solution, dried for 2 h at 355 K, and calcined at 725 K for 2 h.

Temperature programmed oxidation (TPO) and isothermal experiments were carried out in microflow equipment. The reactors were made of quartz and had an inner diameter of 7 mm. The equipment consists of six parallel reactor tubes and a gas mix section which can provide Ar, O₂, CO, NO, C₃H₆, and SO₂ gas mixtures. The gas-mass flow to each reactor was 200 ml/min. A Hartman & Braun Uras 10E non-dispersive infra-red analyzer (NDIR) is used to analyze the gas effluent of different reactors. The microflow equipment was described in more detail elsewhere [10].

Every catalyst was tested in parallel in the presence and absence of soot in the same experiment. For supported molten salt catalysts, soot was deposited by immersing the foam in *n*-heptane dispersed soot (1.5 g/50 ml) for 2 min to deposit approximately 20 mg soot. This immersion method is fast, easy to perform and given an excellent reproduction of the real diesel soot trapping on these ceramic foam [6]. For Pt/γ-alumina catalysts, 40 mg catalyst was physically mixed, in “loose contact”, with 20 mg synthetic soot (Printex-U; Degussa), then diluted with 400 mg SiC. Platinum catalysts were also directly placed upstream of a soot bed diluted with 400 mg SiC, and upstream of soot loaded on ceramic foam supported molten salt.

The samples were then heated to 775 K at 0.6 K/min with a 200 ml/min simulated diesel exhaust gas. Subsequently, they were heated to 900 K where they were kept for 30 min to achieve complete oxidation in order to establish the mass balance. The mass balance for soot oxidation was calculated by integrating the amounts of CO and CO₂ released during reaction from the reactor in which the catalyst was mixed with soot, then subtracted by the amounts of CO and CO₂ released from the reactor loaded only with catalyst (no soot loaded). The gas components, concentration, and the compositions used are listed in Table 1. Argon was used as a balance gas.

Table 1
Gas components, concentration, and composition used in experiments^a

Gas component	O ₂ (%)	NO _x (ppm)	C ₃ H ₆ (ppm)	CO (ppm)	SO ₂ (ppm)
Compositions					
a	10	–	–	–	–
b	10	600	–	–	–
c	10	660	800	500	50

^a Argon is used as balance gas.

3. Results

3.1. Soot oxidation rate with the catalysts

Fig. 1 represents soot oxidation rate, normalized for the initial soot mass, as a function of temperature with different gas compositions catalyzed by ceramic foam supported Cs₂SO₄·V₂O₅. It is obvious that, with only O₂, the molten salt catalyst shifts the onset temperature of non-catalytic soot oxidation from about 675 to about 600 K. When NO_x (contain about 540 ppm NO and 120 ppm NO₂) is introduced into the system, soot

oxidation already starts at 550 K. This is not the case when NO was added to the system. The gas mixture containing only O₂ + NO, ‘without NO₂’, shows an almost identical soot oxidation profile as the one with only O₂. In the presence of CO + C₃H₆ + SO₂ the beneficial effect of NO₂ disappears.

The experiments performed with Pt/γ-alumina catalyst are shown in Fig. 2. A remarkably different result is observed from the physical mixture of Pt and soot. The onset temperature of soot oxidation with only oxygen in the feed, is about 675 K, while in the presence of NO_x, it decreases to about 550 K. Unlike with the

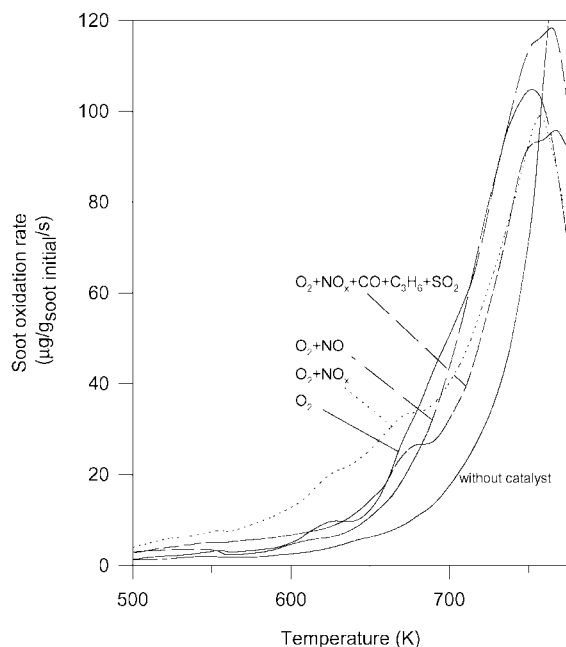


Fig. 1. Effect of gas compositions on soot oxidation rate with Cs₂SO₄·V₂O₅ catalyst supported on ceramic foam; temperature programmed oxidation, heating rate of 0.6 K/min.

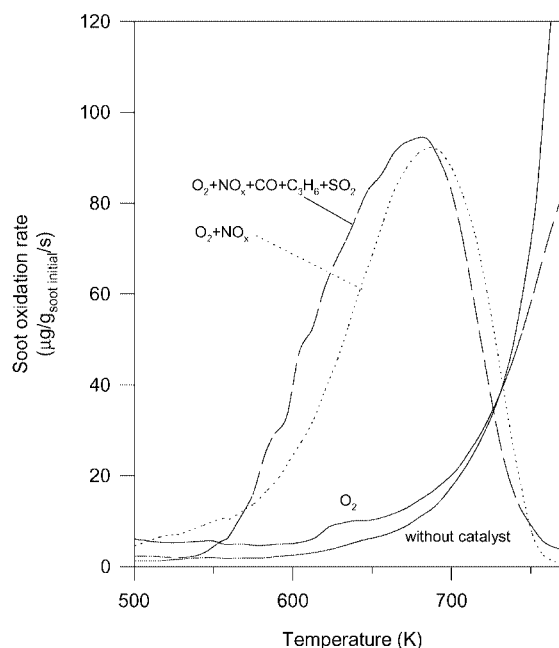


Fig. 2. Effect of gas compositions on soot oxidation rate with Pt/γ-alumina catalyst; temperature programmed oxidation, heating rate of 0.6 K/min.

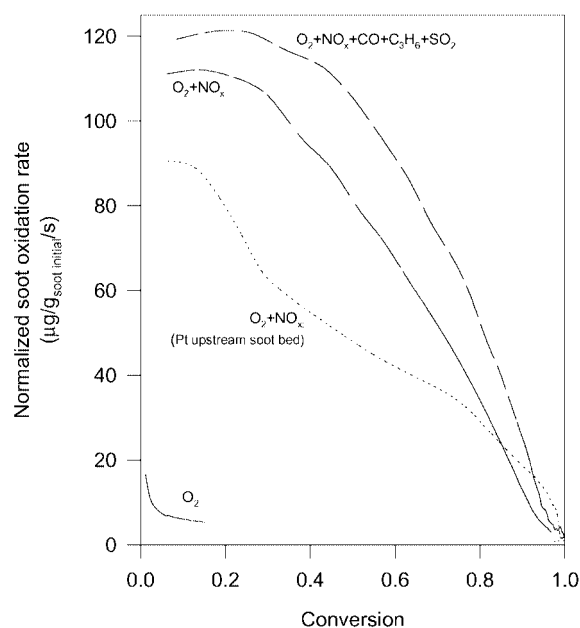


Fig. 3. Effect of gas compositions on isothermal soot oxidation rate at 675 K with Pt/ γ -alumina catalyst.

molten salt catalyst, the addition of $\text{CO} + \text{C}_3\text{H}_6 + \text{SO}_2$ slightly increases the soot oxidation rate. The effect of gas composition for the platinum catalyst system is clearly demonstrated in Fig. 3, in which the isothermal soot oxidation rate is presented. The components CO , C_3H_6 , and SO_2 do not inhibit but even increase the rate. It is also worthwhile to underline that a physical mixture outperforms a configuration with Pt catalyst upstream.

The influence of the reactor configuration for both types of catalysts is clear from the TPO results in Fig. 4. Comparing the *physical mixture* of platinum with soot and platinum *upstream* of the soot bed, at the region below 615 K, the profiles are approximately the same. Above 615 K the oxidation rate of the upstream configurations is significantly lower. When soot was loaded on ceramic foam supported molten salt and compared to only soot loaded on SiC bed both in combination with an upstream Pt catalysts, the oxidation rate below 660 K is higher for the soot loaded on SiC bed than that for the soot loaded on ceramic foam supported molten salt, while in the region above 660 K the opposite result was observed.

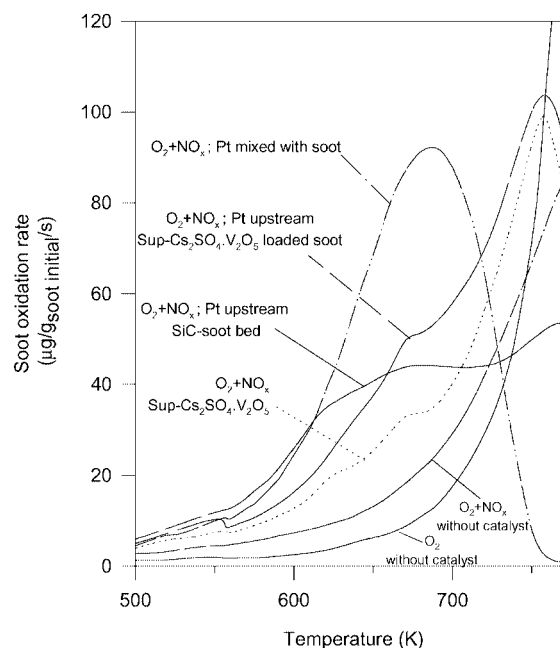


Fig. 4. Soot oxidation rate as a function of temperature with $\text{O}_2 + \text{NO}_x$ for different catalysts soot configurations; temperature programmed oxidation, heating rate of 0.6 K/min.

In the system where $\text{O}_2 + \text{NO}_x$ are introduced, soot oxidation takes place both with O_2 and with NO_2 . It is difficult to quantify the amount of NO_2 produced from the catalyst-soot bed in the configurations investigated. Therefore, we assume that the maximal amount of NO_2 produced in all configurations is the same as that produced from NO oxidation with platinum catalyst upstream, as shown in Fig. 5a. These amounts are assigned as base case of NO_2 produced in the system.

The value of base case NO_2 at several temperatures as well as the concentration of $\text{CO} + \text{CO}_2$ produced in different Pt-soot configurations is presented in Table 2. The concentration of $\text{CO} + \text{CO}_2$ due to carbon oxidation with NO_2 , assigned as NO_2 contribution, is evaluated by subtracting the concentration of $\text{CO} + \text{CO}_2$ released from $\text{O}_2 + \text{NO}_x$ reaction system with the concentration of $\text{CO} + \text{CO}_2$ from O_2 reaction system. Data of the temperature higher than 700 K is excluded because at those high temperatures the reaction has reached high conversion at which the amount of unburned soot is already very small, leading to relatively large errors.

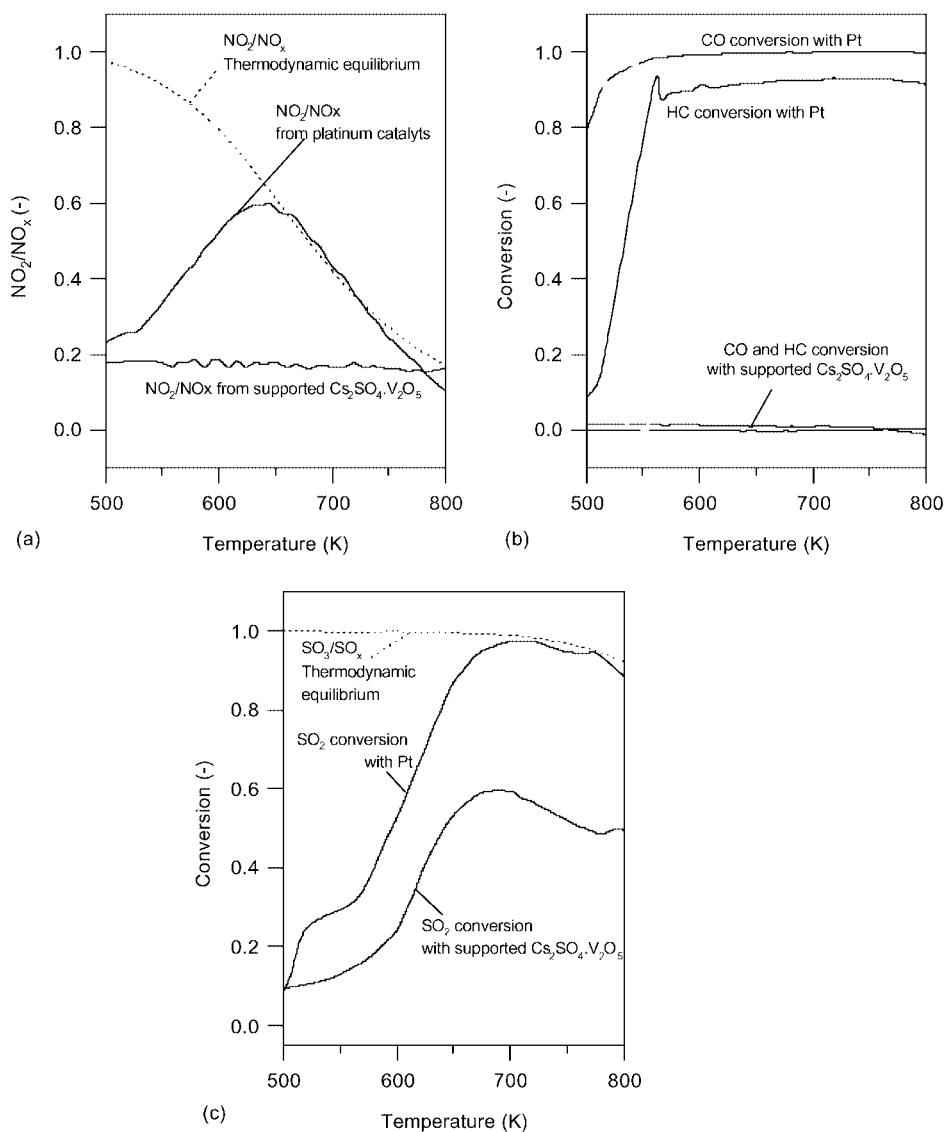


Fig. 5. Catalysts activities in the conversion of NO, C_3H_6 , CO, and SO_2 .

Interesting is the ratio between NO_2 produced and NO_2 contribution to $\text{CO} + \text{CO}_2$ released. In the physical mixture configuration, except at 600 K, the concentration of $\text{CO} + \text{CO}_2$ released from the reaction with NO_2 is always higher than the base case concentration of NO_2 produced, in particular at high temperature. For platinum upstream the soot bed, except perhaps at 675 K, the concentrations of $\text{CO} + \text{CO}_2$ at all temperatures is less than the concentration of NO_2 produced.

3.2. Conversion of gas components

The activities of the catalysts in the conversion of gas components were also evaluated. Fig. 5a compares the concentration ratio of NO_2 to NO_x dictated by thermodynamic equilibrium, and the observed values for both catalyst systems. For the Pt catalyst the ratio increases with temperature up to approximately 650 K where the thermodynamic value is reached. For the

Table 2

Comparison between CO + CO₂ concentrations at several temperatures released from the physical mixture of platinum soot and platinum upstream of soot bed and NO₂ produced in the system (base case NO₂) with O₂ and O₂ + NO_x as feed gas

Temperature (K)	Base case of (NO ₂) (ppm)	(CO + CO ₂) released (ppm)				
		O ₂ contribution; physical mixture of Pt-soot with O ₂	O ₂ + NO ₂		NO ₂ contribution	
			Physical mixture of Pt-soot	Pt upstream soot bed	Physical mixture of Pt-soot	Pt upstream soot bed
600	340	55	250	265	195	210
625	365	95	465	380	370	285
650	355	115	735	430	620	315
675	325	145	950	465	805	320
700	275	235	940	455	705	220

Cs₂SO₄·V₂O₅ system the NO₂/NO_x ratio is constant over the whole temperature window.

As expected the platinum catalyst was very active in CO and C₃H₆ oxidation. Conversely the molten salt is very poor in converting CO and C₃H₆. This result is shown in Fig. 5b. In case of SO₂ oxidation, Fig. 5c, the molten salt catalyst activity was significant, about half of that of the platinum catalyst.

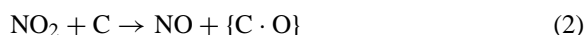
4. Discussion

From Figs. 1 and 2, it is clear that platinum is a less active soot oxidation catalyst under the applied conditions (loose contact and the ratio between catalyst and soot) than molten salt in the presence of only O₂. The platinum catalyst is, however, more active in the presence of simulated diesel exhaust. This indicates that a gas component has a major impact in soot oxidation in platinum system rather than in molten salt catalysts. In Fig. 5a it can be seen that a molten salt is very poor in oxidizing NO to NO₂, while NO oxidation with platinum takes place in a significant amount. Different activity in oxidizing NO to NO₂ clearly leads to the difference in the activity of soot oxidation. NO₂, a better oxidant than O₂, can oxidize soot at relatively low temperature. This observation is in agreement with the reported data by Cooper and Thoss [7] and Jelles et al. [10].

In the presence of O₂ and NO₂, soot oxidation takes place both with O₂ and NO₂. The reaction of carbon with NO₂ can be described as:



Soot oxidation with NO₂ is a (non-)catalytic reaction. This reaction has lower activation energy than one for the reaction of carbon with O₂, i.e. –44 kJ/mol for the reaction with NO₂ compared to –160 kJ/mol for the reaction with O₂ [11]. The reaction is proposed to proceed through an oxidized yet non-volatile carbon species {C · O}. In some literature the {C · O} species is named as surface oxygen complexes (SOC). This species will release CO and CO₂ when heated [12]:



Therefore, we can assume that one molecule CO or CO₂ is produced from the oxidation of C with one NO₂ molecule.

At our experimental conditions, 100–120 ppm CO + CO₂ produced in feed gas, is equivalent to around 8–10 μg/g_{soot} initial soot oxidation rate. As we noted before, the amount of NO₂ in the feed gas is about 120 ppm. This explains the result of experiments with molten salt catalyst. The presence of 120 ppm NO₂ in NO_x + O₂ caused a higher soot oxidation rate at the onset temperature in TPO experiment as shown in Fig. 1.

When NO + O₂ was used as feed gas, without NO₂, increased soot oxidation rate was not observed in the case molten salt catalyst. This is in agreement with previous observations that explain that the activity of NO in carbon oxidation, in the absence of NO₂ is low compared to that of O₂ [13]. NO is also a less active oxygen-containing compound than oxygen in carbon gasification [14]. Even an inhibition of soot oxidation with NO at 298 K has been reported [15].

In real diesel exhaust gas, the majority of NO_x is emitted as NO. The amount of NO₂ from diesel engine is about 5–10% of the total NO_x. However,

increased emission of NO₂ can be expected from idling spark-ignited engine as well as diesel engine under low load conditions [16]. As shown in this experiment, for an inactive NO oxidation catalysts, like molten salt, the oxidation of soot with NO_x could only take place by NO₂ that was already present in the system. Therefore, the low amount of NO₂ in the real diesel exhaust will not significantly improve the performance of molten salt.

More interesting are the results of the experiments with platinum catalyst, especially when the physical mixture of platinum and soot is applied. Besides shifting the onset temperature of soot oxidation from about 675 to about 550 K, a multiple use of NO₂ in the system seemed to take place. The lower onset temperature is clearly due to the production of NO₂ at the temperature at which soot oxidation by NO₂ also starts to occur.

In Table 2, for a physical mixture of platinum and soot at 600 K, the amounts of CO+CO₂ produced from the reaction of NO₂ with soot are less than the amount of NO₂ produced (base case of NO₂) by platinum catalyst. This indicates that only part of NO₂ effectively oxidizes soot. At higher temperature region, at which the amounts of CO + CO₂ produced from NO₂ contribution are higher than the amount base case NO₂, the recycle reaction might take place. NO produced from the reaction of NO₂ with soot, reaction (1), was re-oxidized to NO₂ and then repeatedly oxidized soot.

The same reasoning is applicable to the increase of 100 μg/g_{soot initial} initial rate in isothermal experiment with platinum catalyst, Fig. 3. At 675 K the amount of NO₂ presence in the system is about 325 ppm. The increase of 100 μg/g_{soot initial} rate is equivalent with about 1000 ppm CO + CO₂. This implies that in average NO was at least recycled for about three times. On the basis of thermodynamic evaluation the number of recycles could be smaller than 3, but it is still larger than 1. On the basis of our kinetic data this value should be at least 3. This number could also be higher since the formed NO₂ can also leave the reaction zone before reacting with the soot (by-passing of the soot or a sticking coefficient of less than 1).

When platinum catalyst was placed upstream of the soot bed, the recycle reaction mode has not been observed. The oxidation profile of the system below 615 K was approximately the same with the physical mixture, see Fig. 4. Above 615 K, the oxidation rate

of upstream configuration was lower than that of the physical mixture. At this temperature region the equilibrium of NO/NO₂ is almost established. Therefore, the increase in temperature was not followed by the increase of NO₂ in the system, as a result increased of temperature does not significantly influence the oxidation rate. The contribution of NO₂ to CO + CO₂ production in this configuration is always lower than the concentration of base case NO₂ with an exception at 675 K. This suggests that only part of NO₂ oxidized soot and that the NO produced from the reaction was not recycled to NO₂. This means that the NO-NO₂-soot reaction did not take place.

It might be surprising that below 625 K the configuration consisting of Pt upstream of and either soot deposited on ceramic foam supported molten salt or the soot-SiC bed do not give identical results because at that low temperature the molten salt is inactive. Probably, the reason is non-ideal reactor behavior of the ceramic foam due to by-passing effects,

It is interesting that the molten salt catalyst is less active in simulated diesel exhaust gas than in the corresponding O₂/NO_x atmosphere. Probably, the reason is the presence of SO₂. In the presence of SO₂, there are at least two possible reactions with NO₂. The first is carbon oxidation, reaction (1), and the second is SO₂ oxidation, reaction (3):



This gas-phase reactions couple is well-known to be the basis of the so-called lead chamber process. Reaction (3) might be in competition with soot oxidation by NO₂, reaction (1). Therefore, reaction (3) could suppress soot oxidation rate with NO₂ in the presence of supported Cs₂SO₄·V₂O₅ catalyzed system. The decrease is not expected due to the presence of CO and C₃H₆, because those gases did not undergo any reaction during the process in the presence of molten salt catalyst.

In contrast with the foregoing, the presence of SO₂ + CO + HC slightly increases soot oxidation rate for the platinum catalyst. Such effect was also observed by Uchisawa et al. [17] with Pt/SiO₂ catalyst in the presence of water. They proposed that SO₃ produced from SO₂ over Pt catalyst has a role as catalyst that accelerates carbon oxidation by NO₂ in the presence of water. The presence of a trace of water, in our reaction conditions, might occur as a result

of hydrocarbon oxidation. This interpretation agrees with the observation that molten salt catalysts, that do not exhibit this increase in catalytic activity, do not catalyze the oxidation of hydrocarbons. It should be noted that also the heat released from CO and HC combustion might cause a local heating of the catalyst surface that could increase the soot oxidation rate.

Both catalysts are active in the oxidation of SO₂; the activity of molten salt is less pronounced than that of platinum catalyst. Their activity in SO₂ oxidation, could cause an additional number of particulate emission, or even catalyst deactivation. However, in tomorrow application when a low sulfur content in diesel fuel is applied those effects will largely be avoided.

5. Conclusion

Platinum, a less active soot oxidation catalyst than molten salt with O₂ is more active in the presence of NO_x in simulated diesel exhaust. Platinum converts NO to NO₂, and subsequently, NO₂ formed increases the rate of soot oxidation typically in the temperature window of 550–750 K. Conversely, the activity of molten salt catalyst in the conversion of NO to NO₂ is very limited. Therefore, with molten salt catalyst, only NO₂ already present in the system is beneficial. In the presence of NO a recycle mode of NO-NO₂-soot was observed in the physical mixture of platinum with soot, which is not the case for platinum placed upstream of the soot bed.

Soot oxidation activities of platinum and molten salt catalysts were not affected by the presence of CO and HC. Those gases undergo a complete oxidation reaction only in the presence of platinum catalyst. This is not the case with SO₂, which was oxidized to SO₃ by both catalysts. SO₂ slightly decreased soot oxidation

rate with NO₂ in molten salt system, but moderately increased soot oxidation in platinum system.

To utilize the beneficial effect of diesel exhaust gas, particularly NO, the soot oxidation reactor should have a structure in which the recycle reaction of NO-NO₂-soot takes place. The combination of depth filter loaded with platinum catalyst might be a choice.

References

- [1] C. Badini, G. Sarraco, V. Serra, V. Specchia, *Appl. Catal. B* 18 (1998) 137.
- [2] S.J. Jelles, B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 21 (1999) 35.
- [3] B.A.A.L. van Setten, P. Russo, S.J. Jelles, M. Makkee, P. Ciambelli, J.A. Moulijn, *React. Kinet. Catal. Lett.* 67 (1999) 3.
- [4] B.A.A.L. van Setten, S.J. Jelles, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 21 (1999) 51.
- [5] B.A.A.L. van Setten, J. Bremmer, S.J. Jelles, M. Makkee, J.A. Moulijn, *Catal. Today* 53 (1999) 613.
- [6] B.A.A. L van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 28 (2000) 253.
- [7] B.J. Cooper, J.E. Thoss, *SAE Paper* 890404 (1989).
- [8] P. Hawker, N. Meyers, G. Hühwohl, Th. Vogel, B. Bates, L. Magnusson, P. Bronnenberg, *SAE Paper* 971082 (1997).
- [9] A.F. Ahlström, C.U.I. Odenbrand, *Appl. Catal.* 60 (1990) 143.
- [10] S.J. Jelles, M. Makkee, J.A. Moulijn, G.J.K. Acres, J.D. Peter-Hoblyn, *SAE Paper* 990113 (1999).
- [11] S.J. Jelles, Diesel exhaust after treatment, development of catalytic systems for diesel particulate oxidation, PhD thesis, Delft university of Technology, 1999, p. 98.
- [12] K. Tabor, L. Gutzwiller, M.J. Rossi, *J. Phys. Chem.* 98 (1994) 6172.
- [13] H. Yamasita, A. Tomita, H. Yamada, T. Kyotani, L. Radovic, *Energy and Fuels* 7 (1993) 85.
- [14] J.A. Moulijn, F. Kapteijn, *Carbon* 33 (8) (1995) 1155.
- [15] B.G. Wicke, K.A. Grady, *Combustion and Flame* 69 (1987) 185.
- [16] M. Lenner, *Atmos. Environ.* 21 (1987) 37.
- [17] J.O. Uchisawa, A. Obuchi, A. Ogata, R. Enomoto, S. Kushiya, *Appl. Catal. B* 21 (1999) 9.