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Soot oxidation over NO_x storage catalysts: Activity and deactivation

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Abstract

Soot oxidation activity and deactivation of NO_x storage and reduction (NSR) catalysts containing Pt, K, and Ba supported on Al_2O_3, are studied under a variety of reaction conditions. K-containing catalysts decrease soot oxidation temperature with O_2 alone and the presence of Pt further enhance the activity due to synergetic effect. The active species responsible for synergism on Pt/K–Al_2O_3 are unstable and cannot be regenerated. Soot oxidation temperature decreases by about 150 °C with NO + O_2 exhaust feed gas and under lean conditions NSR system acts as catalysed soot filter (CSF). The reactions that are mainly responsible for decreasing soot oxidation temperature are: (i) soot oxidation with NO_2 followed by NO recycles to NO_2, and (ii) soot oxidation with O_2 assisted by NO_2.

Only a part of the stored NO_x that is decomposed at high temperatures under lean conditions is found to be useful for soot oxidation. NO_x storage capacity of NSR catalysts decreases upon ageing under soot oxidising conditions. This will lead to a decreased soot oxidation activity on stored nitrate decomposition. Pt/K–Al_2O_3 catalyst is more active, but least stable compared with Pt/Ba–Al_2O_3.

Keywords: Soot oxidation; Filter regeneration; NSR catalysts

1. Introduction

Diesel engines are the most preferred for heavy-duty applications and light-duty trucks due to its superior fuel economy (decreased CO_2 emissions) and high torque. However, diesel engine exhaust gases contribute significantly to urban and global air pollution. Emissions of hydrocarbon (HC) and CO from diesel exhaust gases are low and can be easily converted by using diesel oxidation catalyst (DOC). Further improvements in modern diesel engine designs and combustion process will lead to decreased NO_x ($NO + NO_2$, mainly present as NO) and particulate (soot or carbon particulates) emissions. Improvements in diesel fuel properties and combustion processes alone will not meet the Legislation of Euro V (2008) and US'7 and US'10 (2007, 2010) for both NO_x and soot. Therefore, the abatement technologies for both soot and NO_x are a topic of intense research.

During most of the diesel engine operations the exhaust gas temperature is below 300 °C and that temperature is too low for initiating continuous un-catalysed soot oxidation, which occurs around 600 °C [1]. Soot particulates in the exhaust gas are, therefore, collected on a filter and is periodically oxidised to CO_2 at high temperatures to regenerate the filter. Active and passive filter regeneration strategies are being used in practice to burn soot. During the active filter regeneration, the high temperatures required for un-catalysed soot oxidation, are generally achieved by burning diesel fuel, and such a process is relatively simple, but inefficient, uncontrolled, and uneconomic.

Catalysed soot oxidation (passive regeneration) is expected to decrease the soot oxidation temperature in a controlled fashion and, thereby, increasing efficiency and fuel economy. Laboratory experiments show that catalysed soot oxidation (when catalyst–soot mixtures are milled, called tight contact) with O_2 is possible at low temperatures compared with un-catalysed oxidation. The lattice oxygen or 'active oxygen' of the oxygen storage components, redox catalyst such as CeO_2, generally used in the after-treatment systems, are capable of oxidising soot around 450 °C [2]. However, in real situation the contact between catalyst and soot particles, solid–solid contact, is poor (loose contact) and, therefore, the traps still need frequent high temperatures excursion for active soot filter regeneration. The catalyst–soot contact problem can be overcome by fuel borne additives, which on combustion in the engine leads to uniform dispersion of catalyst embedded in

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soot particulates leading to intimate contact and the embedded catalyst can decrease soot oxidation temperature by about 200 °C, compared with un-catalysed soot oxidation [3]. NO_2 is more powerful oxidant than O_2 and if enough NO_2 is present in the exhaust gas, soot can be oxidised around 350 °C [4]. In a catalysed soot filter (CSF) and continuously regenerating trap (CRT), NO in the exhaust gas is converted to NO_2 and NO_2 can oxidise the deposited soot in the filter. The above-mentioned after-treatment technologies (fuel borne additives and CRT) are already commercially available for decreasing particulate emissions from various sources.

Past few years a major part of the after-treatment research is focussed on NO_x conversion to N_2 over NO_x storage and reduction (NSR) catalysts or lean NO_x catalysts (LNC). Toyota Corporation has developed diesel particulate-NO_x reduction (DPNR) system, based on NSR catalysts, which can reduce NO_x to N_2 and simultaneously oxidise soot to CO_2 [5]. The NSR catalysts are generally composed of precious and base metal supported catalysts such as Pt–Rh/Ba–Al_2O_3 and Pt–Rh/K–Al_2O_3 [5]. During longer lean period NO in the exhaust gas is oxidised to NO_2 over Pt and NO_2 is stored as nitrates over Ba and K. Under rich conditions the stored nitrates are released as NO_x, which is further reduced to N_2 by CO and HC over Pt/Rh. Various surface compounds such as nitrates and active oxygen generated during storage and reduction steps are proposed as active soot oxidation species and, thereby, decreasing the oxidation temperature. NO_2 produced over noble metals of NSR catalysts can be trapped as nitrates and can also react with soot generating NO again. Under lean conditions NSR system can be expected to function as CSF. It is also proposed that under rich conditions active oxygen generated on the catalyst can oxidise the trapped soot.

Currently, two very different strategies to convert NO_x to N_2 and soot to CO_2 are developed for the diesel engine application. NO_x can be selective catalytically reduced (SCR) to N_2 using NH_3 (urea) or HC as a reductant. Catalysts based on oxides, precious and transition metal supported oxides and zeolite based catalysts are studied for SCR of NO_x [6]. The above-mentioned SCR systems have, however, only a minor activity for soot oxidation. If both NO_x and soot levels have to be decreased to acceptable levels of forthcoming legislations, SCR and soot oxidation catalytic systems have to be integrated. This could impose logistical and maintenance problems along with fuel penalty. If soot oxidation system has to be integrated with SCR system, than the NO_x reduction catalyst is preferred downstream of soot oxidation catalyst. The high temperatures downstream of such a system, at some stage of soot oxidation, can have a detrimental effect on SCR catalyst. If SCR system is placed upstream of soot oxidation, it will render the soot oxidation catalyst inefficient and increasing fuel penalty. DPNR or NSR catalysts in this respect will have obvious advantages as it can reduce emission of both the pollutants and acts as ‘4-way’ catalyst.

Only a few studies over ‘4-way’ catalytic materials that can store NO_x, such as Co, CeO_2, Ba and K-containing catalysts, for soot oxidation are reported [5,7]. In this paper various parameters that can have influences on soot oxidation over Pt/Al_2O_3 and Pt/K–Al_2O_3 and Pt/Ba–Al_2O_3 NO_x storage and reduction catalysts and on their stability towards soot oxidation, are presented.

2. Experimental

2.1. Materials

Printex-U from Degussa S.A. is used as a model soot. NSR catalysts are obtained from Engelhard Corporation, USA. The physico-chemical properties of the NSR catalysts are listed in Table 1. Unless otherwise indicated, the catalysts are used as supplied without pre-treatment.

2.2. NO_x-TPD by MS-DRIFT

The total NO_x storage capacity of catalysts is determined by NO_x-TPD with a spectratech DRIFT (diffuse reflectance IR) high temperature cell connected to a mass spectrometer (MS-DRIFT). The catalysts are pre-treated at 450 °C for 1 h in He, and followed by NO_x adsorption at 200 °C with a feed gas containing NO + 10 vol.% O_2 in He (20 ml/min) for about 1 h. After the adsorption the catalysts are flushed in He till a stable base line is obtained at 200 °C and NO_x-TPD is carried out with a heating rate of 10 °C/min up to 600 °C.

2.3. Soot oxidation in TGA

Soot oxidation in air over NSR catalysts is studied in thermo-gravimetric analyser (TGA/SDTA851^e, Mettler Toledo). Tight contact (ground in a mortar for about 5 min) catalyst–soot mixtures (4:1 wt./wt.) are heated in 100 ml/min air flow from RT up to 800 °C with 10 °C/min heating rate.

2.4. Soot oxidation in fixed-bed reactor

A loose contact mixture of 80 mg of catalyst and 20 mg of soot (mixed with a spatula) diluted with 400 mg of SiC is

Table 1
Physico-chemical properties of NO_x storage catalysts

Catalyst	Pt (wt.%)	K_2O or BaO (wt.%)	K or Ba (μmol g_{cat}^{-1})	Pt C.S[a] (nm)	BET ($m^2\,g^{-1}$)	NO_x uptake (μmol g_{cat}^{-1})
K–Al_2O_3	–	4	849	–	141	–
Pt/Al_2O_3	2.5	–	–	5.6	145	425
Pt/K–Al_2O_3	2.5	4	849	8.2	141	660
Pt/Ba–Al_2O_3	2.5	13.4	874	6.0	121	680

[a] Estimated from XRD.

packed between two quartz wool plugs in a tubular quartz reactor. Soot oxidation is studied with 10 vol.% O_2 or 600 ppm NO_x + 10 vol.% O_2 in Ar. The total flow rate of 200 ml/min is maintained through the reactor with a resulting space velocity of around 43 000 l/l/h (based on catalyst + the diluant SiC). NDIR analyser is used to monitor the reactant and product gases CO_2, CO, and NO. NO_2 is calculated from the difference of NO inlet and outlet concentrations. Over Pt-containing catalysts soot is oxidised selectively to CO_2, and will not be discussed further.

The influence of stored NO_x on soot oxidation activity is studied in a fixed-bed reactor and MS-DRIFT set-ups. NO_x is stored over the catalyst at 200 °C by treating loose contact catalyst–soot mixtures with NO + 10 vol.% O_2 for about an hour. After NO_x storage, the feed gas is switched to 10 vol.% O_2 and the temperature is raised to 600 °C at a rate of 0.6 or 10 °C/min.

Ageing of NO_x storage catalysts (up to five cycles) is carried out by repeated soot oxidation of loose contact catalyst–soot mixtures, from RT to 600 °C, in a fixed-bed reactor with 600 ppm NO_x + 10 vol.% O_2.

3. Results

3.1. Soot oxidation with O_2

Fig. 1 shows soot oxidation to CO_x (CO + CO_2) with 10 vol.% O_2 in a fixed-bed reactor over NSR catalyst–soot loose contact mixtures. In general soot oxidation started above 350 °C. Un-catalysed soot oxidation starts above 400 °C and is complete around 575 °C. Pt/Al_2O_3 and Pt/Ba–Al_2O_3 catalysts have very limited influence in decreasing soot oxidation temperature. K–Al_2O_3 catalyst shows relatively more soot oxidation activity and peak of maximum shifts by about 50 °C. Over Pt/K–Al_2O_3 catalyst the soot oxidation is shifted by about 80 °C to lower temperature and the profile is different compared with un-catalysed soot oxidation. It is important to note that 33% of soot is converted to CO_2 below 450 °C even with loose contact Pt/K–Al_2O_3–soot mixture and using O_2 in Ar alone possibly due to synergetic effect. The origin of such synergetic effect between Pt and K in decreasing soot oxidation temperature is further studied in TGA under tight contact conditions (Fig. 2). Pt/Al_2O_3 hardly shows catalytic soot oxidation activity even in tight contact with soot, compared with un-catalysed soot oxidation. K–Al_2O_3 decreases soot oxidation temperature by about 150 °C and intimate presence of Pt and K seems to further improve low temperature soot oxidation rate as observed in the case of loose contact mixtures.

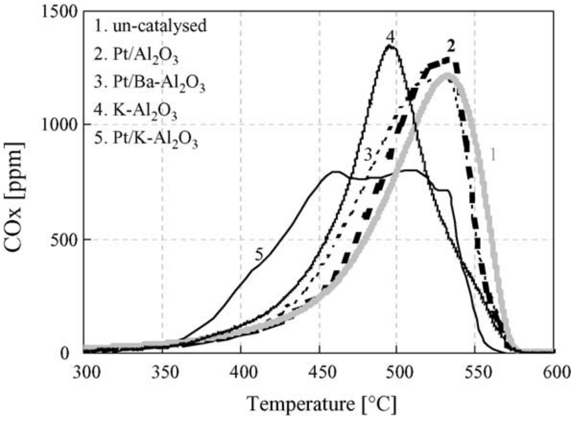


Fig. 1. Un-catalysed and catalysed soot oxidation. Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 10 vol.% O_2; heating rate, 0.6 °C/min.

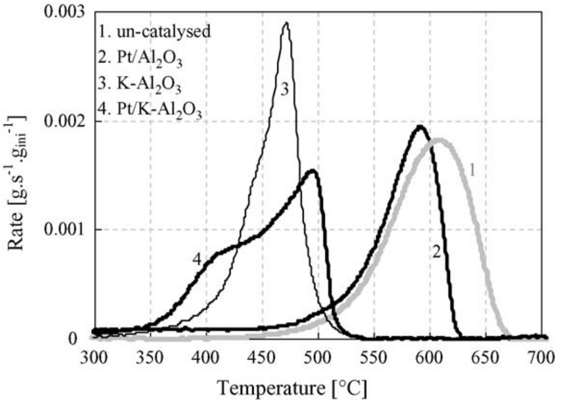


Fig. 2. Un-catalysed and catalysed soot oxidation. Catalyst–soot, 4:1 wt./wt.; contact, tight; reactor, TGA; feed gas, 100 ml/min air; heating rate, 10 °C/min.

The soot oxidation activities of fresh and spent Pt/K–Al_2O_3 (used once for a soot oxidation under loose contact conditions with O_2) are shown in Fig. 3. The soot oxidation profile of spent Pt/K–Al_2O_3 is almost similar to un-catalysed reaction. This observation indicates that the species responsible for synergetic effect of Pt/K–Al_2O_3 are not stable and are irreversibly lost. From Figs. 1–3, especially the tight contact experiments of K-containing catalysts, it can be concluded that the active species responsible for decreasing soot oxidation temperature are originating from K and only once. Pt is probably enhancing the mobility of such species leading to good contact and the observed synergetic effect.

3.2. Soot oxidation with NO + O_2

Soot oxidation with 600 ppm NO + 10 vol.% O_2 in loose contact with NSR catalysts is shown in Fig. 4. Under the

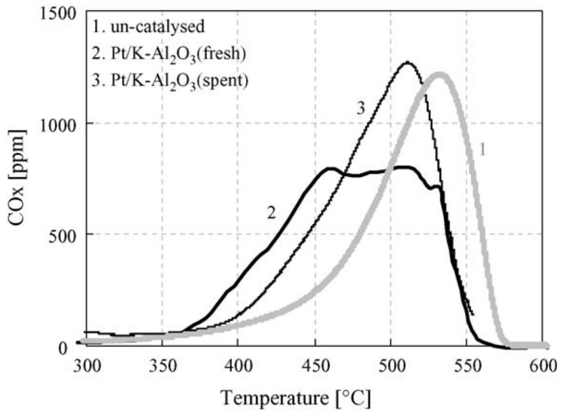


Fig. 3. Soot oxidation over fresh and used Pt/K–Al_2O_3 catalyst. Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 10 vol.% O_2; heating rate, 0.6 °C/min; spent, used once for soot oxidation.

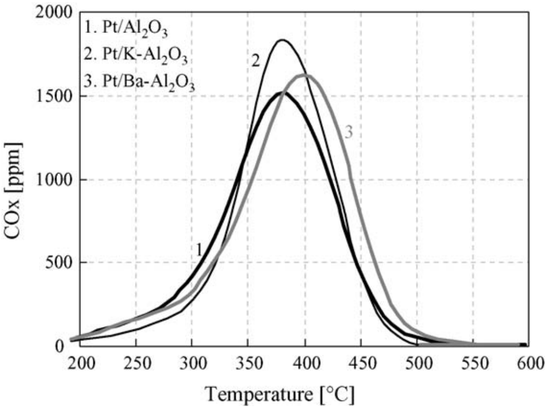


Fig. 4. Soot oxidation over NO$_x$ storage catalysts. Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 600 ppm NO + 10 vol.% O$_2$; heating rate, 1 °C/min.

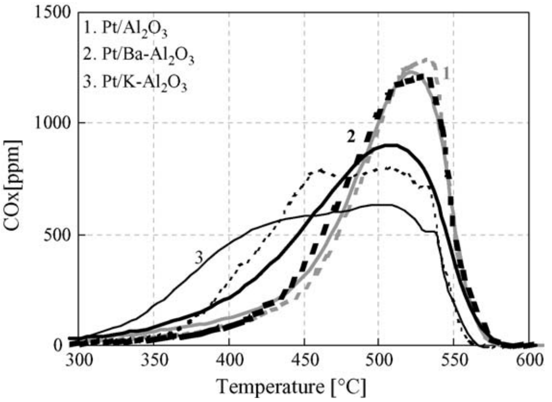


Fig. 5. Soot oxidation over fresh (dashed curve) and NO$_x$ treated (solid curve). Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 10 vol.% O$_2$; heating rate, 0.6 °C/min; NO$_x$ treatment at 200 °C with 1000 ppm NO + 10 vol.% O$_2$.

reaction conditions used all the catalysts are very active and decreased soot oxidation temperature by about 150 °C, compared with un-catalysed reaction (Fig. 1). The main oxidation function in these catalysts is expected to be arising from Pt component. K and Ba component seems to slightly decrease the soot oxidation activity of Pt/Al$_2$O$_3$. Though the differences are small, the soot oxidation activity decreases with in the order Pt/Al$_2$O$_3$ > Pt/K–Al$_2$O$_3$ > Pt/Ba–Al$_2$O$_3$. In 350–450 °C range, where most of the soot is oxidised, significant NO$_2$ slip is observed (not shown).

The maximum concentration of NO$_2$, that can be produced at 375 °C, is calculated from Arrhenius equation (Eq. (1)), and the possible amount of NO$_2$ used in soot oxidation is estimated (Table 2). The amount of CO$_2$ produced at 375 °C is almost two times higher than the amount of NO$_2$ that is used in soot oxidation (Table 2). At this temperature soot oxidation with O$_2$ (Fig. 1) or NO alone is not significant. So it is concluded that over NSR catalysts in the presence of NO$_2$, soot is directly oxidised by O$_2$ [8].

3.3. Soot oxidation with stored NO$_x$ under lean conditions

NO$_x$ is stored over NSR catalysts-soot mixtures by treating with NO + O$_2$ at 200 °C, where soot oxidation is negligible. During this treatment NO is oxidised over Pt to NO$_2$ and NO$_x$ in the gas phase is stored as nitrites/nitrates [9]. Majority of the adsorbed species is expected to be nitrates due to oxidising atmosphere and prolonged exposure times. After the NO$_x$ storage step, NO in the feed gas is switched off and the catalyst-soot mixture is flushed with 10 vol.% O$_2$ in Ar to remove any gas phase and weakly adsorbed NO$_x$, before increasing the soot oxidation reaction temperature. Fig. 5 shows the influence of stored nitrates on soot oxidation activity with O$_2$ over loose contact NSR catalyst–soot mixtures. For comparison the soot oxidation over an un-treated NSR catalysts is also presented in Fig. 5. Soot is oxidised at significantly lower temperatures over NO$_x$ treated Pt/K–Al$_2$O$_3$ and Pt/Ba–Al$_2$O$_3$ catalysts compared with the fresh catalysts, respectively. NO$_x$ stored Pt/Al$_2$O$_3$ has no influence on soot oxidation. It is expected that the nitrates on Pt/Al$_2$O$_3$ will be decomposed at temperature where it is not effective for soot oxidation. On the other hand K and Ba store substantial amount of NO$_x$ decomposes at high temperature as will be shown in the next section. The decomposed NO$_x$ is desorbed as or converted to NO$_2$ under lean conditions, which increases the soot oxidation rate and thus the observed decrease in soot oxidation temperature over NO$_x$ stored NSR catalysts (Fig. 5).

3.4. NO$_x$-TPD and soot oxidation in MS-DRIFT

Due to the slow ramping rate in a fixed-bed reactor, the stored NO$_x$ released under soot oxidation conditions could not be measured. In order to calculate the number of possible recycles of NO to NO$_2$ over NO$_x$ stored NSR catalysts (NO$_2$ is primarily responsible for improved soot oxidation), NO$_x$-TPD and soot oxidation in MS-DRIFT set-up is studied at higher heating rates where CO$_2$ and NO$_x$ can be monitored. Fig. 6 shows the NO$_x$-TPD over NSR catalysts in MS-DRIFT set-up. Pt/Al$_2$O$_3$ is able to store significant amount of NO$_x$ (425 μmol g$_{cat}^{-1}$), which is mainly decomposed below 400 °C.

Table 2
Data from soot oxidation with NO + O$_2$ and NO oxidation to NO$_2$ at 375 °C

Catalyst	NO$_2$ from Eq. (1) (ml s^{-1})	NO$_2$ slip[a] (ml s^{-1})	NO$_2$ used[b] (ml s^{-1})	CO$_x$ observed[c] (ml s^{-1})	CO$_x$/NO$_2$ used
Pt/K–Al$_2$O$_3$	0.0048	0.0012	0.0036	0.006	1.7

[a] NO$_2$ slip observed during soot oxidation.
[b] Possible amount of NO$_2$ used for soot oxidation = NO$_2$ from Eq. (1): NO$_2$ slip.
[c] From Fig. 4.

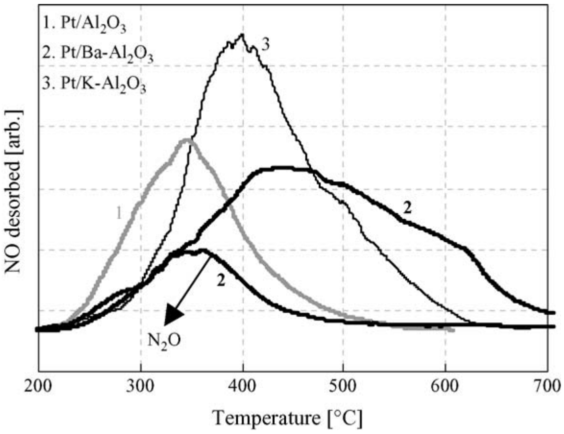


Fig. 6. NO$_x$-TPD in MS-DRIFT set-up over NSR catalysts.

On the other hand Pt/K–Al$_2$O$_3$ and Pt/Ba–Al$_2$O$_3$ catalysts store much higher amounts of NO$_x$ that decompose at relatively higher temperatures (Fig. 6 and Table 1). It should be noted that around 350 °C significant amount of stored NO$_x$ over Pt/Ba–Al$_2$O$_3$ also decomposed to N$_2$O.

Fig. 7a and b shows soot oxidation with O$_2$ in MS-DRIFT set-up over un-treated Pt/Ba–Al$_2$O$_3$ and NO$_x$ treated Pt/Ba–Al$_2$O$_3$ and Pt/K–Al$_2$O$_3$ catalysts. Fig. 7a shows the NO MS-signal and Fig. 7b shows CO$_2$-MS signal during temperature ramp in 10 vol.% O$_2$. In the presence of soot stored nitrates decompose at slightly lower temperature compared with nitrate decomposition in the absence of soot. In the absence of stored nitrates soot oxidation starts above 500 °C and stored nitrates significantly decrease soot oxidation temperature over Pt/Ba–Al$_2$O$_3$ and Pt/K–Al$_2$O$_3$. From Fig. 7a it is observed that below 400 °C around 50% of nitrates are decomposed and no significant soot oxidation is observed (Fig. 7b). The NO$_x$, released above 400 °C, is able to efficiently oxidise soot, compared with fresh Pt/Ba–Al$_2$O$_3$ catalyst. Above 400 °C NO$_x$ released over Pt/K–Al$_2$O$_3$ is lower than that of Pt/Ba–Al$_2$O$_3$, however, the soot oxidation activity of Pt/K–Al$_2$O$_3$ is significantly higher.

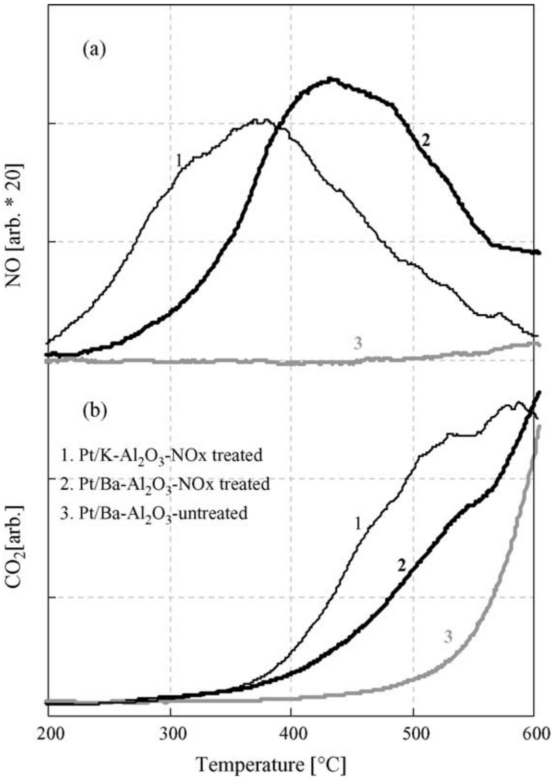


Fig. 7. Soot oxidation over fresh and NO$_x$-treated NSR catalysts in MS-DRIFT. (a) NO desorbed, (b) soot oxidised to CO$_2$. Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, MS-DRIFT; feed gas, 10 vol.% O$_2$; heating rate, 10 °C/min; NO$_x$ treatment at 200 °C in 1000 ppm NO + 10 vol.% O$_2$.

3.5. Stability of NSR catalysts under soot oxidation conditions

Soot oxidation over loose contact NSR catalyst-soot mixtures is carried out with NO + O$_2$ from RT to 600 °C. At the end of the reaction the catalyst is cooled to room temperature and soot is added to the spent catalyst and the above reaction sequence is repeated. Five such soot oxidation cycles are carried out and soot oxidation during these cycles are shown in Fig. 8a–c. All the NSR catalysts studied showed stable activity during the five cycles and the influence of catalyst ageing is not evident under these conditions.

At the end of fifth cycle the catalyst is cooled to room temperature and mixed with soot. NO$_x$ storge over catalyst–soot mixture is carried out at 200 °C with NO + O$_2$, followed by soot oxidation in O$_2$ as described earlier (see Section 3.3). Fig. 9 shows the soot oxidation profiles due to stored NO$_x$ on the fresh and aged NSR catalysts. The soot oxidation temperature range of fresh and aged Pt/Al$_2$O$_3$ are almost identical to un-catalysed soot oxidation (Fig. 1). The soot oxidation ability of aged Pt/K–Al$_2$O$_3$ and Pt/Ba–Al$_2$O$_3$ catalysts significantly decreased compared with fresh catalysts and approached that of Pt/Al$_2$O$_3$ soot oxidation. From a separate NSR catalyst ageing study it is found that the amount of NO$_x$ stored on aged Pt/K–Al$_2$O$_3$ catalyst decreased and the stored NO$_x$ seems to decompose at relatively lower temperature where soot oxidation is not efficient by NO$_2$. This explains the observed aged catalyst behaviour.

4. Discussion

The DPNR system developed by Toyota claims to reduce both NO$_x$ and soot from exhaust gases [5,10]. The nitrate and ‘active oxygen’ present on the catalyst surface are proposed as possible species responsible for improved soot oxidation activity under lean and rich conditions. To efficiently utilise these species present on a NO$_x$ storage catalyst, soot should be in intimate contact with catalysts [11]. Though the filters developed are able to improve such a large number of contact points needed between soot and catalyst, their effects in practice are still limited in realising meaningful improvement in soot oxidation using oxygen alone. In the present investigation soot oxidation activity of NSR catalysts, which are the main components in DPNR system, under different exhaust gas and catalyst-soot contact conditions are studied.

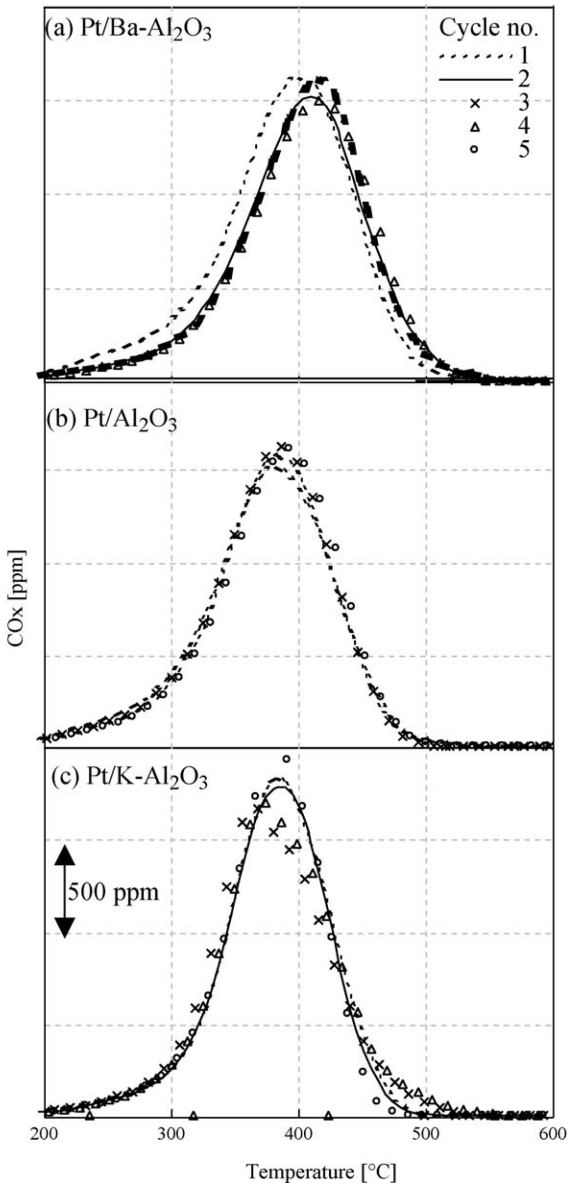


Fig. 8. NSR catalyst ageing under soot oxidation conditions. Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 600 ppm + 10 vol.% O_2; heating rate, 1 °C/min; spent catalyst is repeatedly used for five times.

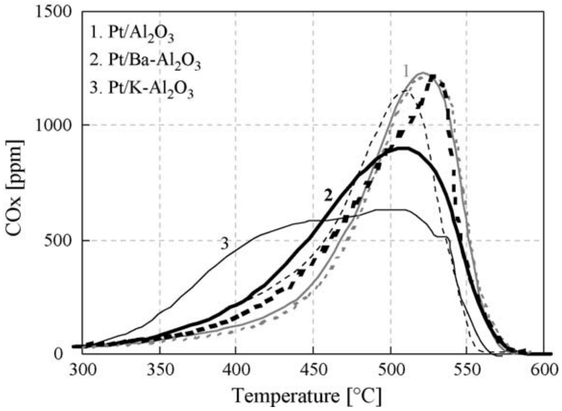


Fig. 9. Soot oxidation over NO_x treated catalysts. Fresh (solid lines) and used (broken lines). Catalyst–soot, 4:1 wt./wt.; contact, loose; reactor, fixed-bed; feed gas, 200 ml/min 10 vol.% O_2; heating rate, 0.6 °C/min; NO_x storage at 200 °C with 1000 ppm NO + 10 vol.% O_2.

As expected, soot oxidation is not significant with 10 vol.% O_2 when Pt/Al_2O_3 and Pt/Ba–Al_2O_3 are in loose contact with soot. Interestingly, K–Al_2O_3 and Pt/K–Al_2O_3 show significant decrease in soot oxidation temperature even under loose contact conditions (Fig. 1). Courcot et al. [12] have observed such a decrease over loose contact K–Cu/TiO_2–soot mixtures. Some of the chemicals used for K–Cu/TiO_2 catalyst preparation contain nitrate precursor. Querini et al. [13] have observed that when any of the precursors used in catalyst preparation is a nitrate, trace amounts of KNO_3 will end up in the final catalyst. Though the presence of trace amount of nitrate species cannot be completely ruled out during the NSR catalyst preparation, it is important to mention that K is introduced into the catalyst by non-nitrate precursor and the catalysts are calcined above 550 °C. The observed decrease in soot oxidation activity over K-containing catalysts can be attributed to the volatile nature of possible oxides, peroxides of K or trace nitrates still present on the catalyst. The mobility of such compounds is expected to be high, leading to the observed decrease in soot oxidation temperature [12,14,18]. Platinum is probably enhancing the migration of such active species responsible for soot oxidation at much lower temperature compared with K–Al_2O_3 catalyst alone. Whichever the active species under loose contact conditions might be, it is irreversibly lost even after using the catalyst once in soot oxidation.

K–Al_2O_3 and Pt/K–Al_2O_3 have shown excellent soot oxidation activity when in tight contact with soot in 10 vol.% O_2 (Fig. 2). Various K-compounds are known to oxidise carbon and soot efficiently and several reaction mechanisms are invoked in literature [15]. It has been previously demonstrated that over a redox system like CeO_2 in tight contact with soot, soot oxidation takes place by lattice oxygen transfer to the soot surface, which is quickly replenished by the gas-phase oxygen [2]. The redox system like ‘KOx’ present on K–Al_2O_3 or Pt/K–Al_2O_3 catalysts follows similar oxidation path [15]. Pt/Al_2O_3 on the other hand did not show significant improvement in soot oxidation activity even when in tight contact with soot. This in agreement with Jelles et al. [16], who studied Pt catalyst embedded in soot (derived from fuel borne catalyst). In the presence of soot and high temperatures Pt will be present in metallic state and is unable to supply the lattice oxygen for soot oxidation. The adsorbed oxygen over metallic Pt, which is responsible for NO oxidation to NO_2, is unable to oxidise soot [17]. From the loose and tight contact soot oxidation experiments with O_2 it can be stated that the K or the species present on K are responsible for the decrease in soot oxidation temperature. The tight contact catalyst-soot mixture is not realistic and if used in real systems, Pt/K–Al_2O_3 catalyst will have a very limited influence on soot oxidation with O_2 alone. However, compared with Pt/Al_2O_3 and Pt/Ba–Al_2O_3, Pt/K–Al_2O_3 may have slight advantage in terms of activity.

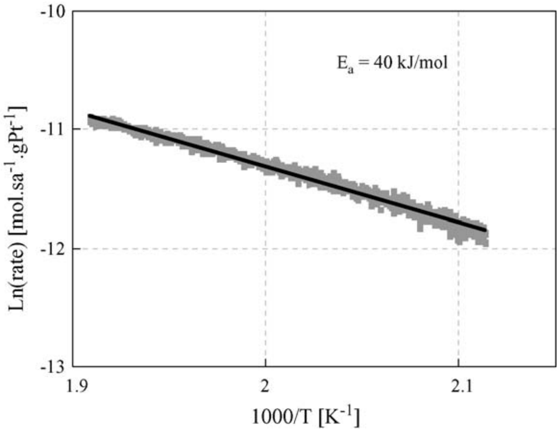


Fig. 10. Arrhenius plot of NO oxidation to NO_2 over Pt/K–Al_2O_3. Reactor, fixed-bed; feed gas, 200 ml/min 600 ppm NO + 10 vol.% O_2; data collected while cooling catalyst after soot oxidation experiment.

Suzuki and Matsumoto [5] have observed improved soot oxidation when the catalyst contains NO_x storage material. In their experiment soot is collected under real diesel exhaust gas conditions at 200 °C and is oxidised with 500 ppm NO + 10 vol.% O_2 at high temperatures. In the present investigation it is found that soot oxidation activity with 600 ppm NO + 10 vol.% O_2 is similar in the presence (Pt/K–Al_2O_3 and Pt/Ba–Al_2O_3) and absence (Pt/Al_2O_3) of NO_x storage material (Fig. 4). In all cases most of the soot is oxidised below 450 °C. Over NSR catalysts studied NO in the feed gas is converted to NO_2, which is a more powerful oxidant than O_2 and initiates soot oxidation at lower temperatures compared with un-catalysed oxidation. With increasing temperature the rate of NO_2 formation and its reaction with soot increase, resulting in substantial decrease in soot oxidation temperature. During the longer lean NO_x storage cycles in DPNR like system, similar soot oxidation will occur, and DPNR system acts as CSF.

The possible amount of NO_2 that can be formed under the reaction conditions is calculated from Arrhenius relation (Eq. (1)). Fig. 10 shows the Arrhenius plot of NO oxidation to NO_2 in the temperature range 200–250 °C over Pt/K–Al_2O_3 in the absence of soot. The apparent activation energy (E_a) of NO oxidation to NO_2 is 40 kJ/mol. The rate of NO_2 that is produced at 375 °C (Table 2), in the absence of soot over Pt/K–Al_2O_3, is estimated from Eq. (1):

$$\ln(\text{rate}) = A\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

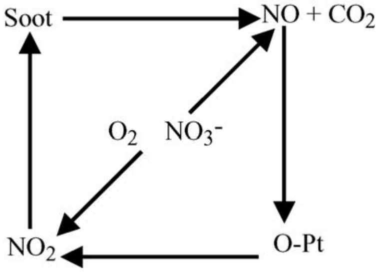
where A is frequency factor and E_a is apparent activation energy.

NO_2 involved in soot oxidation is obtained by subtracting the observed NO_2 slip from possible amount of NO_2 that is formed. From Table 2 it is seen that, at 375 °C the rate of NO_2 consumed (0.0036 ml s^{-1}) is much smaller than the rate of CO_x produced (0.006 ml s^{-1}). This suggests that soot oxidation is not only taking place by NO_2 but also by O_2. From the ratio of CO_2 produced to NO_2 consumed, around 40% contribution to observed CO_2 is from soot oxidation by O_2 assisted by NO_2. Using O_2 (Fig. 1) alone soot oxidation is not significant at 375 °C. Therefore, the two main reactions that can be proposed in general for soot oxidation with NO + O_2 over Pt-containing NSR catalysts are: (i) soot oxidation with NO_2 followed by NO recycles to NO_2, and (ii) soot oxidation with O_2 assisted by NO_2. These observations are in agreement with that of Setiabudi et al. [8] over un-catalysed soot oxidation with NO_2 and $NO_2 + O_2$. It is proposed that NO_2 initiates the formation of surface oxygen complexes (SOC) at relatively low temperatures. High temperatures are needed for such SOC formation with O_2. Once SOC formation is initiated by NO_2, O_2 present in excess can further react to form less stable complexes and also participate in their decomposition. The kinetics of NO oxidation to NO_2 in the presence of soot and its reaction with soot should be studied in more detail, in order to obtain accurate contribution of O_2 and NO_2 towards soot oxidation in the presence of a catalyst. Without accurately knowing the NO_2 concentration under soot oxidation conditions, it is hard to estimate the exact number of NO recycles to NO_2. Therefore, efficiency of NO_2 defined by Eq. (2) is used to evaluate the catalyst potential:

$$\text{Efficiency of } NO_2 = \frac{CO_x \text{ observed with}(NO + O_2) - CO_x \text{ observed with} O_2}{\text{Equilibrium } NO_2 \text{ concentration}} \tag{2}$$

The efficiency of NO_2 over NSR catalysts is around 4 at 375 °C. The small number indicates that both recycle of NO to NO_2 and NO_2 reaction with soot is not very efficient at these temperatures.

The main function of NSR catalysts is to trap NO_x from the gas phase [9]. In the first step NO in the exhaust gas is oxidized over Pt to NO_2. The NO_2 generated can either react with soot or trapped as nitrates. If NO_2 encounters the soot particle first, it will react to form SOCs and the released NO is further recycled over Pt to NO_2. However, if it encounters the storage components like Ba or K first it will get trapped as surface nitrate and decreases the gas-phase NO_2 concentration. In NSR like system it is expected that NO_2 can be trapped more efficiently compared with the soot oxidation. This is because NO_2 is formed over Pt sites in close proximity to the storage component compared with soot particle (in poor contact). In catalysed soot filter (CSF) due to lack extensive NO_x trapping capacity all the NO_2 generated over Pt will only react with soot. Furthermore storage component will decrease the activity of Pt for NO conversion to NO_2 [9]. Therefore, NSR like systems are expected to act like a less effective CSF. In the present investigation the differences are, however, not observed between Pt/Al_2O_3 (CSF like system) and Pt/Ba–Al_2O_3 and Pt/K–Al_2O_3 (NSR like systems) (Fig. 4). This is due to continuous supply of NO + O_2 in the gas phase and slow temperature ramping.



Scheme 1. Soot oxidation with different species due to stored NO_x decomposition over NSR catalysts.

The total NO_x storage capacity and its influence on soot oxidation with O_2 is described in Figs. 5–7. The total NO_x storage capacity is similar over Pt/K–Al_2O_3 and Pt/Ba–Al_2O_3 and significantly higher than that of Pt/Al_2O_3. The soot oxidation activity of Pt/K–Al_2O_3 and Pt/Ba–Al_2O_3 improves after NO_x pre-treatment compared with Pt/Al_2O_3 or untreated Pt/Ba–Al_2O_3 (Figs. 5 and 7b). Pt/Al_2O_3 can store significant amounts of nitrates, but it decomposes at lower temperatures where soot oxidation is less efficient. Over Pt/K–Al_2O_3 and Pt/Ba–Al_2O_3 the stored nitrate decomposition occur at relatively higher temperatures and the reactions in the presence of soot are described in Scheme 1. NO_x released below 400 °C is not efficiently utilised (Fig. 7a and b) in soot oxidation as described previously. Above 400 °C, NO is efficiently converted over Pt to NO_2 that also efficiently reacts with soot forming SOCs and NO. During this process soot is also oxidised by O_2 assisted by NO_2. The NO formed in the process can be recycled over Pt to NO_2 and can be reutilised for soot oxidation (Scheme 1). Such recycles of NO to NO_2 and soot oxidation with NO_2, and O_2 assisted by NO_2 over NSR catalysts explains the observed soot oxidation in Figs. 5 and 7 and in references [5,10].

Above 400 °C NO_x released over Pt/K–Al_2O_3 is lower than that of Pt/Ba–Al_2O_3 catalyst. The soot oxidation activity is, however, significantly higher over the former catalyst. Presence of Ba is known to negatively influence the NO oxidation activity of Pt catalysts thus decreases the efficiency of the cycles mentioned in Scheme 1 [9]. The NO_2 efficiency (Eq. (2), Scheme 1) of 25 at 475 °C over Pt/Ba–Al_2O_3 catalyst can be estimated. The high efficiency number (compared to 4 at 375 °C) is due to increased rate of NO_2 production and its reaction with soot. At these temperatures the contribution of soot oxidation with O_2 assisted by NO_2 is also be expected to be high.

When thermal nitrate decomposition occurs, during NO_x-TPD both NO_x (Fig. 6) and O_2 (not shown) are released together indicating the decomposition as a single event (Eq. (3)). The decomposition of nitrate, therefore, will not leave significant amount of residual oxygen on the catalyst surface. When the nitrates are reduced under rich conditions in the presence of CO, HC or H_2 similar phenomenon can be expected. For example, using CO or HC as a reductant to release the stored NO_x into gas phase, CO or HC has to reduce nitrate (Eqs. (4) and (5)). This reduction involves oxygen of nitrate, and reduction is generally accompanied by carbonate formation (Eq. (6)) that further diminishes the oxygen utilisation that can be active for soot oxidation under rich conditions. CO and HC further reduce the NO_x released to N_2 over Pt/Rh sites (Eq. (7)):

$$\mathrm{Cat(K/Ba)} - \mathrm{NO_3}^- \rightarrow \mathrm{Cat(K/Ba)} + \mathrm{NO_2} + 1/2\mathrm{O_2} \tag{3}$$

$$\mathrm{Cat(K/Ba)} - \mathrm{NO_3}^- + \mathrm{CO/HC} \rightarrow \mathrm{Cat(K/Ba)} + \mathrm{NO_2} + \mathrm{CO_2} \tag{4}$$

$$\mathrm{Cat(K/Ba)} - \mathrm{NO_3}^- + \mathrm{CO} \rightarrow \mathrm{Cat(K/Ba)}\text{–}\mathrm{O}^* + \mathrm{NO} + \mathrm{CO_2} \tag{5}$$

$$\mathrm{Cat(K/Ba)} - \mathrm{O}^{*-} + \mathrm{CO_2} \rightarrow \mathrm{Cat(K/Ba)} - \mathrm{CO_3}^{2-} \tag{6}$$

$$\mathrm{Pt/Rh} + 2\mathrm{NO} + 2\mathrm{CO} \rightarrow \mathrm{Pt/Rh} + \mathrm{N_2} + 2\mathrm{CO_2} \tag{7}$$

Gaseous reductant molecule can more easily access the surface residual oxygen than its transfer to soot surface (due to poor contact). However, soot oxidation under rich conditions can take place with the NO_2, and NO_2 can react only once as the recycles of NO to NO_2 and oxidation by O_2 assisted by NO_2 is not possible. All the above arguments suggest that soot oxidation, if any, will be negligible under rich conditions for NO_x storage catalysts.

NSR catalysts show deactivation during repeated soot oxidation cycles up to 600 °C (Fig. 8). Ageing experiments are also carried out in the presence of 3 vol.% H_2O over Pt/K–Al_2O_3 up to 600 °C under soot oxidation conditions (not shown) and no deactivation is found even under such conditions. However, the NO_x storage capacity of the catalysts has significantly decreased and stored NO_x is decomposed at relatively lower temperatures and in a smaller temperature window where the soot oxidation described by Scheme 1 is not very efficient. This will explain the decrease in soot oxidation activity over aged NO_x stored catalysts (Fig. 9).

The NSR catalytic system will have advantages when the exhaust gas temperatures are low, usually encountered in diesel engines, where soot oxidation is not efficient. During these conditions NO_x can be stored over the catalyst and during the high temperature excursion under lean condition this NO_x is released and can be efficiently utilised for soot oxidation. Under continuous lean-rich cycles such an effect will partly diminish. In DPNR like system where both NO_x and soot is oxidised, NSR storage components will reduce soot oxidation activity of the catalytic soot filter, compared with Pt only catalyst.

5. Conclusions

NSR catalysts are evaluated for soot oxidation under a variety of reaction conditions. It is found that Pt and K shows synergetic effect and soot oxidation temperature is decreased over Pt/K–Al_2O_3 even under loose contact using 10 vol.% O_2. The active species responsible for the synergism are, however, found to be unstable and are not easily regenerated. All the NSR catalysts studied showed about 150 °C decrease in soot oxidation temperature with NO + O_2 gas feed compared with un-catalysed soot oxidation. The reactions responsible for decreasing soot oxidation temperature are: (i) soot oxidation with NO_2 followed by NO recycles to NO_2, and (ii) soot oxidation with O_2 assisted by NO_2. NO_x storage and reduction system if used for both NO_x reduction and soot oxidation act as a less effective catalysed soot filter (CSF).

Only a part of the stored NO_x decomposed at high temperature under lean conditions is found to be useful during soot oxidation. NO_x storage capacity of NSR catalysts decreases on ageing under soot oxidising conditions. This will also decrease the soot oxidation arising due to stored NO_x. In general under a variety of reaction conditions Pt/K–Al_2O_3 catalyst is found to be more active but least stable compared with Pt/Ba–Al_2O_3.

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