ELSEVIER

Catalysis Today 60 (2000) 43–49

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The role of NO in the regeneration of catalytic ceramic filters for soot removal from exhaust gases

P. Ciambelli [a,*], V. Palma [a], P. Russo [a], S. Vaccaro [b]

[a] *Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy*
[b] *Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy*

Abstract

The effect of NO and H_2O on the activity of a Cu/V/K/Cl/Ti based catalytic filter in the combustion of soot generated in the flame of a gas-oil burner has been investigated. Temperature programmed oxidation (TPO) of soot collected on a ceramic filter supporting the Cu/V/K/Cl/Ti catalyst was performed with a flow micro-reactor in the absence and in the presence of NO and H_2O in the reactant gas. The presence of NO and H_2O resulted in a substantial increase of the rate of carbon combustion, and also affected the selectivity (CO_2/CO ratio). The enhanced activity is mainly due to carbon oxidation by NO_2 formed by NO oxidation on the same catalyst. TPO test performed after sulphation of the catalytic filter evidenced a marked loss of activity. However, in the presence of NO and H_2O the activity of soot oxidation was mostly preserved. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Soot abatement; Catalytic oxidation; No effect; TPO

1. Introduction

An effective way for soot removal from diesel exhausts consists in the use of ceramic traps suitable for collection and subsequent combustion of trapped carbon particulate at diesel exhaust temperatures. Since diesel soot spontaneously burns at 800–900 K and such temperatures are far from typical values of diesel engine exhaust, it is necessary to develop a suitable oxidation catalyst. Such a catalyst should reduce the soot combustion temperature either allowing less frequent trap regeneration at lower temperature and avoiding filter melting or breaking caused by combustion of large quantities of particulate [1,2]. Therefore, various catalysts with specific activity towards the total oxidation of the soot carbonaceous matrix have been so far developed [3–7]. An alumina supported Cu–V–K–Cl based catalyst (137AA), very active in laboratory tests, was formulated by Ciambelli et al. [8]. Specifically, in the presence of this catalyst, soot burn out was already achieved in the range of temperatures 573–673 K [9]. However, in the practical application of diesel exhaust treatment, various aspects such as contact efficiency between soot and catalyst [10–12] and influence of secondary exhaust gas components such as NO_x, SO_2 and H_2O on catalyst performances and/or deactivation must be taken into account [13–19]. This work aims at investigating this latter aspect by performing regeneration tests of uncatalytic, catalytic, and sulphated catalytic filters, previously loaded with soot at the exhaust of a gas-oil burner. Filter's regeneration was carried out in the presence of O_2, O_2 and NO, and O_2, H_2O and NO.

---

[*] Corresponding author. Tel.: +39-089-964151;
fax: +39-089-964057.
E-mail address: ciambell@dica.unisa.it (P. Ciambelli)

0920-5861/00/$ – see front matter
PII: S0920-5861(00)00315-1

2. Experimental

2.1. Powder catalyst

Powder catalyst (named 137TF) was prepared by impregnating TiO_2 (DT51D, Rhone Poulenc) with aqueous solution of NH_4VO_3, $CuCl_2 \cdot 2H_2O$ and KCl (Baker Chemicals). The sample was then dried at 393 K and calcined at 973 K overnight. Such a procedure was previously employed to prepare the alumina supported catalyst 137AA [8].

2.2. Catalytic and uncatalytic filter

A 29 mm OD, 13 mm ID alumino-silicate tube (Goodfellow) with 50% porosity and 200 μm mean pore size was divided into 30 mm length sections. Catalytic and uncatalytic filters were made by dipping the tube sections in slurries of 137TF/ethylene glycol and of TiO_2/ethylene glycol, respectively. Filters were then dried at 393 K and calcined at 773 K for 2 h. Dipping in the TiO_2 support powder/ethylene glycol slurry was carried out prior to 137TF deposition so that the amount of catalyst deposited on the catalytic filter was about 2 g. Some catalytic filters were severely sulphated before soot deposition and regeneration steps. The sulphation treatment, carried out at 693 K in a gas stream containing 1000 ppm SO_2, 10% H_2O and 3% O_2 in N_2, took about 40 h.

2.3. Soot deposition

Soot particulate was generated by a gas-oil burner for home heating (Fig. 1), equipped with a nozzle giving a gas-oil mass flow rate of 1.9 kg/h. Commercially available gas-oil (H/C molar ratio=1.75 and sulphur content=0.05 wt.%) was employed. Air flow rate to the burner was 28.5 N m^3/h to obtain an air/fuel mass ratio (α) equal to 20. Before each regeneration test, soot deposition over uncatalytic or catalytic filter was carried out at the burner exhaust. For this purpose, the soot-free filter was placed in a quartz tube (400 mm length, 35 mm ID) heated by an electrical furnace driven by a temperature programmer controller (Ascon PY87). A fraction (2500 N cm^3/min) of the burner exhaust stream, isokinetically sampled, was forced to pass radially through the filter to perform soot loading. The temperature of the sampling line was maintained at 423 K to avoid water and hydrocarbon condensation. During each deposition run, about 10 mg of soot were collected on the filter. Therefore, in the combustion tests the catalyst/soot initial mass ratio was about 200.

2.4. Regeneration testing in micro-reactor

After soot deposition described above, temperature programmed oxidation (TPO) testing was performed with an apparatus described in detail elsewhere [10]. The filter was placed in a quartz tubular flow

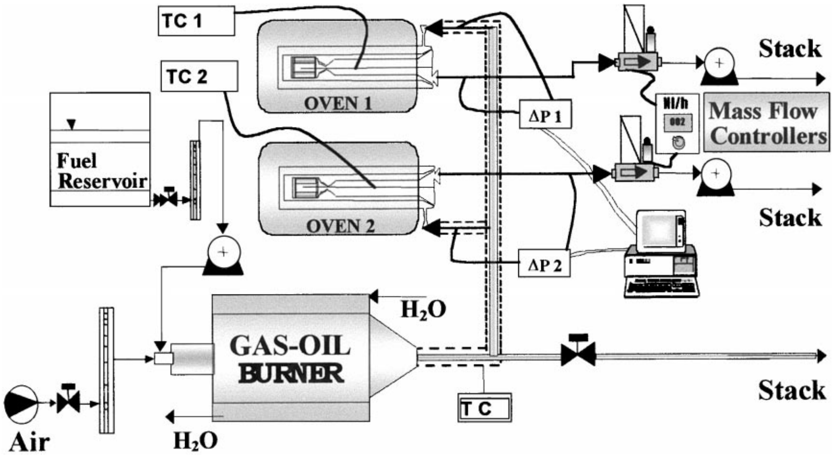

Fig. 1. Experimental apparatus for soot generation and deposition on catalytic and uncatalytic filters.

micro-reactor (400 mm length, 35 mm ID) electrically heated to controlled temperature (Ascon PY87). The reactor inlet gas flow rate was 500 N cm^3/min of cylinder gas containing 10 vol.% O_2 in N_2. The effect of the presence of secondary components in the feeding gas was studied by performing TPO tests in which 1000 ppm NO, or 1000 ppm NO and 10 vol.% H_2O were added to the reactor inlet gas stream. The temperature was raised at 10 K/min up to 873 K in the presence of catalyst, and up to 973 K in the absence of catalyst while the operating pressure was 101 kPa. The tests were carried out with fresh or previously sulphated catalytic filters. NDIR continuous analysers (Hartmann & Braun Uras 10E) measured CO and CO_2 concentrations at the reactor outlet. Such concentration data were jointly integrated to calculate the overall conversion of carbon (X) and the overall carbon reactivity (dX/dt). X was calculated as $(m_0-m)/m_0$, m and m_0 being the current and the initial mass of carbon, respectively. Concentration data were also separately processed to evaluate the partial conversions to carbon monoxide (X_{CO}) and carbon dioxide(X_{CO_2}), and therefore the partial carbon reactivities (dX_{CO}/dt) and(dX_{CO_2}/dt). Carbon mass balance was verified within a 5% tolerance range for all tests. Two NDIR analysers and a paramagnetic analyser performed continuous monitoring of NO, ($NO+NO_2$) and O_2 concentrations, respectively. All signals from the analysers were acquired and processed by a personal computer.

In the experiments with powder catalyst, soot collected at the burner exhaust was mixed with catalyst by thorough pounding in a mortar, thus resulting in a very tight carbon–catalyst contact. Samples containing 5 mg of soot mixed with 50 mg of catalyst were placed in the micro-reactor of the combustion apparatus operated as described in the experiments with filters.

3. Results

Fig. 2 depicts the comparison of the reactivity temperature profiles in O_2–N_2 flow of soot deposited over uncatalytic and catalytic filter, and of soot–powder catalyst mixture. It appears that the catalytic filter markedly promotes soot combustion by lowering the ignition temperature, the reactivity peak temperature and the burnout temperature as compared to the uncatalytic combustion. However, the activity of the catalytic filter is lower than that of the powder catalyst, the peak temperature of dX/dt relevant to uncatalysed soot oxidation being decreased by about 180 K with the catalytic filter and 240 K with the powder catalyst.

In principle these differences could be due to a lower intrinsic catalytic activity or to a less effective carbon–catalyst contact or to both. However, the

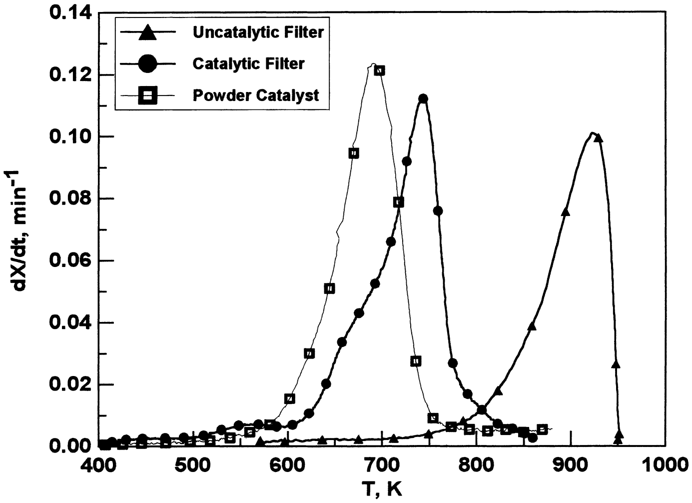

Fig. 2. Reactivity temperature profiles of catalytic and uncatalytic soot combustion (feeding gas, 10 vol.% O_2 in N_2; gas flow rate=500 N cm^3/min; heating rate=10 K/min).

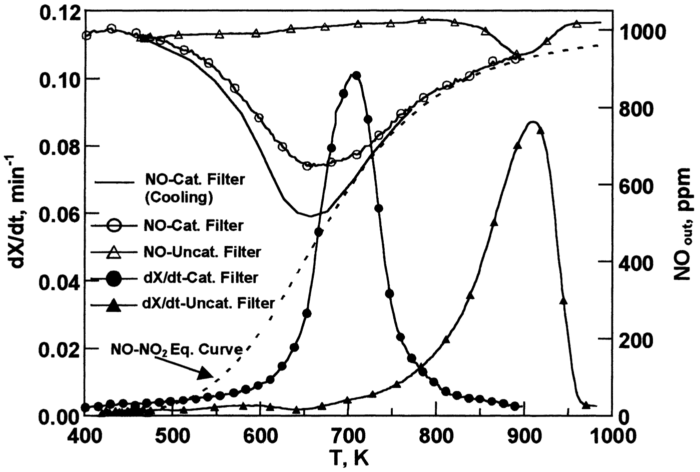

Fig. 3. Reactivity temperature profiles of catalytic and uncatalytic soot combustion in the presence of NO and relevant NO_{out} concentrations (feeding gas, 10 vol.% O_2, 1000 ppmv NO, balance N_2; gas flow rate=500 N cm^3/min; heating rate 10 K/min).

comparison of the shapes of d*X*/d*t* profiles in Fig. 2 suggests that the soot–catalyst contact effectiveness may play a major role, since the profile relevant to the catalytic filter shows, besides the major peak, a shoulder at about 700 K, where the powder catalyst's profile shows its reactivity peak. This behaviour may reflect the different contact effectiveness of soot over the filter.

Fig. 3 depicts the results of a TPO test of soot deposited on catalytic and uncatalytic filter when the feed gas contained 1000 ppm of NO in addition to O_2 and N_2. It is observed that the presence of NO further enhances the soot catalytic combustion rate in the whole range of temperatures where carbon consumption occurs, as, with the catalytic filter, the peak temperature of d*X*/d*t* curve is reduced from 745 (Fig. 2) to 700 K (Fig. 3). In contrast, the uncatalysed soot combustion does not seem to be influenced by the presence of NO in the feeding gas, the d*X*/d*t* curve in Fig. 3 being practically the same as in Fig. 2.

Moreover, in Fig. 3, the reactor outlet NO concentrations (NO_{out}), measured in the TPO test (i.e. in the presence of soot) with either uncatalytic or catalytic filters, are compared with NO_{out} measured during the reactor cooling after the TPO test (i.e. in the presence of catalyst only). In the presence of both soot and catalytic filter, at increasing temperature and carbon conversion, NO_{out} decreases rapidly from the inlet value (about 1000 ppm), reaches a minimum (650 ppm at about 670 K) and then increases approaching the NO–NO_2 equilibrium concentration curve, shown in the same figure for comparison. In the absence of soot, NO_{out} still follows a similar trend, but, at temperatures above 750 K, the NO_{out} values are close to those measured in the presence of soot, while below that temperature they are lower, indicating that the presence of carbon favours the formation of NO. In the case of uncatalytic filter, NO_{out} shows only a slight decrease ($<$100 ppm) with a minimum value at about 900 K in the range of temperatures where carbon conversion occurs. This is likely due to NO reduction by carbon since, as reported in the literature [20,21], at relatively high temperature NO can be reduced to N_2 by carbon in the presence of O_2.

The dramatic effect of catalyst sulphation on the activity in soot combustion is evidenced by the comparison shown in Fig. 4 between the d*X*/d*t*-temperature profiles relevant to TPO of fresh and sulphated catalytic filters in O_2–N_2 flow. Indeed, after sulphation the catalyst activity strongly decreases giving rise to a 130 K shift of the peak temperature of d*X*/d*t* curve. However, when 1000 ppm NO are added to the gas mixture, the catalyst activity increases and the reactivity temperature profile is displaced to 30 K lower temperature (Fig. 4). In addition, if the reactant gas mixture contains also 10 vol.% water, the reactivity

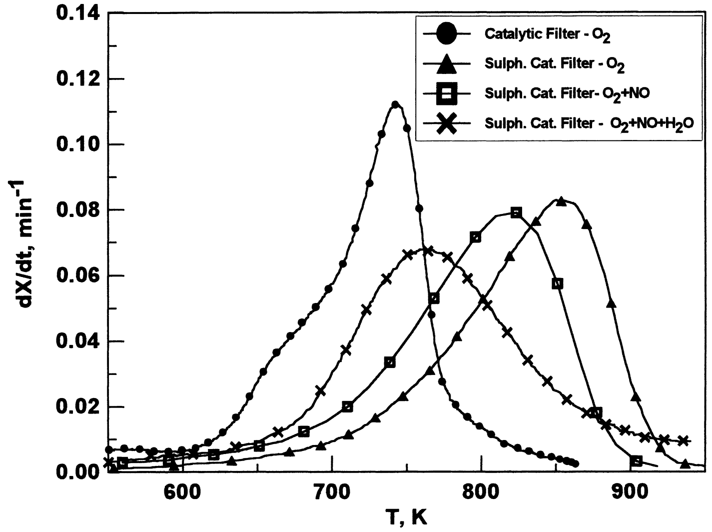

Fig. 4. Reactivity temperature profiles of soot combustion on fresh and sulphated catalytic filters in the presence of NO and NO+H_2O (feeding gas, 10 vol.% O_2, 0 or 1000 ppmv NO, 0 or 10 vol.% H_2O, balance N_2; gas flow rate=500 N cm^3/min; heating rate 10 K/min).

profile is further shifted towards lower temperatures and the peak temperature is only 25 K higher than that relevant to the regeneration of fresh catalytic filter in O_2–N_2.

A feature of soot catalytic combustion with O_2–N_2 is that the catalyst strongly promotes the production of carbon dioxide with respect to carbon monoxide [9]. This is confirmed by the results of the present work which also prove that the presence of NO influences the selectivity of carbon oxidation reaction. Fig. 5 shows that in the soot combustion, the addition of NO results in a lower CO_2/CO ratio in all the range of carbon conversion X for fresh catalytic filter, and in a higher ratio in the case of uncatalytic filter. It is worth noting that, irrespective of the presence of NO, the trend of the CO_2/CO ratio vs. X is different in the presence and in the absence of catalyst and with fresh and sulphated catalyst. Specifically, with fresh catalytic filter, the CO_2/CO ratio shows a maximum at about X=0.7 (Fig. 5), whereas, when the CO_2/CO ratio is reported as a function of temperature, it closely follows the relevant dX/dt-temperature profile and shows a CO_2/CO maximum at the same temperature where dX/dt maximum occurs (Fig. 2). Instead, with uncatalytic filter the CO_2/CO ratio increases monotonically with X (Fig. 3) and does not show any maximum corresponding to that shown by the dX/dt-temperature profile (Fig. 2).

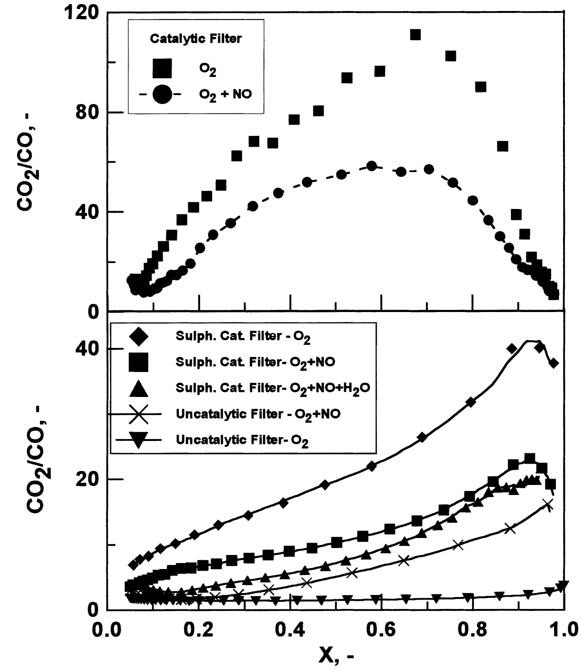

Fig. 5. CO_2/CO ratio as function of carbon conversion for uncatalytic, fresh and sulphated catalytic filters (feeding gas, 10 vol.% O_2, 0 or 1000 ppmv NO, 0 or 10 vol.% H_2O, balance N_2; gas flow rate=500 N cm^3/min; heating rate 10 K/min).

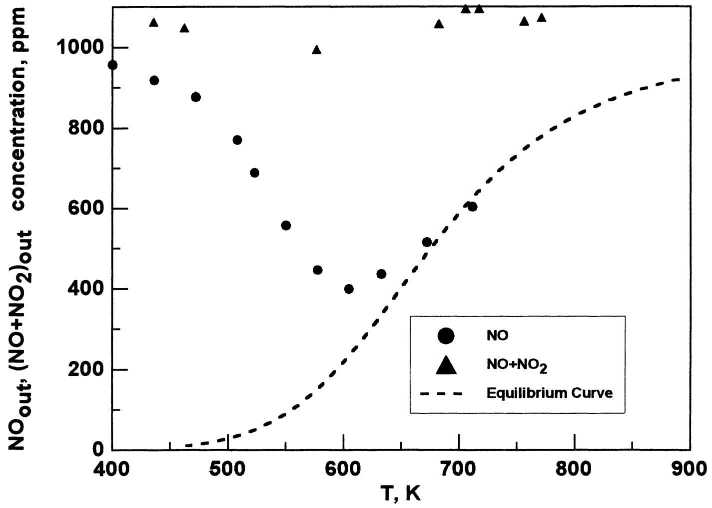

Fig. 6. Outlet concentration of NO and NO+NO_2 in the presence of catalytic filter as function of temperature and relevant NO equilibrium concentration (feeding gas, 10 vol.% O_2, 1000 ppmv NO, balance N_2; gas flow rate=500 N cm^3/min; heating rate 10 K/min).

The CO_2/CO ratios obtained with sulphated catalytic filter show an intermediate behaviour between uncatalytic and catalytic filter. In particular (Fig. 5), in the presence of NO, or NO and H_2O in the reactant gas mixture the CO_2/CO ratio profile is lowered, like in the case of unsulphated catalytic filter, but it also shows typical features of uncatalysed combustion such as the lack of a maximum and the slightly increasing slope with carbon conversion or temperature increase.

In Fig. 6, the concentration curves of NO_{out} and $(NO+NO_2)_{out}$, obtained with the catalytic filter fed by 10% O_2 and 1000 ppm of NO in N_2, but in the absence of soot, are plotted. The figure shows that the total concentration of ($NO+NO_2$) is substantially constant during the test, while that of NO_{out} changes due to the catalytic conversion of NO to NO_2.

4. Discussion

The above findings give clear evidence that NO enhances the oxidation of soot in the presence of the Cu/V/K/Cl/Ti catalyst. In addition, we have found that NO depletion at temperature as low as 500 K is due to the presence of catalyst since no conversion is obtained before 800 K during the uncatalysed combustion of soot (Fig. 3). Specifically, Fig. 6 shows that NO depletion is due to NO conversion to NO_2 and that the catalyst strongly enhances the rate of such a reaction. Moreover, the comparison of NO data in Fig. 3 shows that NO depletion is smaller when also carbon is present, suggesting that carbon favours the formation of NO by NO_2 reduction. As a result, the higher values of NO concentration in the TPO tests with respect to the thermodynamic equilibrium concentrations of NO oxidation to NO_2 are likely due to carbon oxidation by NO_2. This result conforms to that found in previous work [22] in which, in addition to the direct catalytic soot oxidation, an indirect contribution to soot oxidation was hypothesised, due to the reactions:

$$2NO_2 + C \rightarrow 2NO + CO_2 \qquad (1)$$

$$NO_2 + C \rightarrow NO + CO \qquad (2)$$

$$NO_2 + (C\text{–}O) \rightarrow NO + CO_2 \qquad (3)$$

where (C–O) is a carbon–oxygen surface complex, and NO_2 is formed by catalytic oxidation of NO. This interpretation is in agreement with recent studies performed with similar systems [19].

The enhancing effect of NO on the catalyst performance has also been observed in the case of sulphated catalytic filter. The activity loss caused by the sulphation treatment is partially recovered when NO is present and strongly reduced by the combined effect of NO and H_2O (Fig. 4).

Concerning the selectivity of the carbon oxidation reaction, we have found that for the uncatalysed filter, the presence of NO increases the CO_2/CO ratio, whereas for the catalytic filter, either fresh or sulphated, any increase of activity associated to the presence of NO and H_2O results in a decrease of the CO_2/CO ratio. The present results suggest that the reaction (2) is faster than the others since the presence of NO in the gas phase makes lower the CO_2/CO concentration ratio.

While the role of NO in enhancing the catalytic soot combustion is quite clear, the mechanism by which water vapour in the presence of sulphated catalytic filter promotes the reaction is less evident. Recently, it has been suggested that H_2O as well as SO_2 may have a role in the decomposition of carbon surface species formed by partial oxidation of the reacting carbon surface by NO_2 attack [19]. These species would be highly stable to further oxidation, while their decomposition by H_2O and SO_3 should accelerate the overall combustion process. Our results do not contradict this hypothesis, but do not allow to confirm it either. Furthermore, since in the present experiments the reactor inlet gas does not contain SO_2 or SO_3, it can be argued that the increase of catalyst activity, observed upon water addition to the feed stream, may be related to the decomposition of adsorbed sulphated species. Nevertheless, the results of three replicated TPO runs, carried out with sulphated catalyst and with water in the feed stream but without catalyst sulphation among the various runs, seem to be in contrast with the above hypothesis since the soot reactivity profile does not change.

It is worth noting that both NO and H_2O are present in a diesel exhaust. Therefore, if their presence results in accelerating the catalytic combustion of soot, less severe effects of sulphation on the performance of the catalytic filter should be expected in the treatment of a real exhaust. Preliminary results of simultaneous soot loading and regeneration performed at the exhaust of the gas-oil burner confirm this assumption. On the other hand, the planned reduction of sulphur content in diesel fuel should strongly limit the negative effects on the activity of soot oxidation catalysts.

5. Conclusions

The presence of NO in the reactant oxidising gas increases the activity of the Cu/V/K/Cl/Ti catalytic filter in the soot combustion. This effect may be attributed to carbon oxidation by NO_2 in turn produced by NO oxidation on the same catalyst.

Severe catalyst sulphation dramatically reduces the activity in O_2–N_2 flow, but when NO and H_2O are present in the gas, as in a real exhaust, the catalyst activity is recovered almost completely.

Sulphated catalytic filters show intermediate behaviour between catalytic and uncatalytic filters as inferred from selectivity and reactivity data of carbon oxidation.

References

[1] E. Koberstein, H.D. Pletka, H. Volker, SAE Paper 830,081 (1983).
[2] E.S. Lox, B.H. Engler, E. Koberstein, Stud. Surf. Sci. Catal. 71 (1991) 291.
[3] A.F. Ahlström, C.U.I. Odenbrand, Appl. Catal. 60 (1990) 143.
[4] E. Xue, K. Seshan, J.G. van Ommen, J.R.H. Ross, Appl. Catal. B 2 (1993) 183.
[5] G. Mul, J.P.A. Neeft, F. Kapteijn, M. Makkee, J.A. Moulijn, Appl. Catal. B 6 (1995) 339.
[6] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B 8 (1996) 57.
[7] G. Saracco, C. Badini, N. Russo, V. Specchia, Appl. Catal. B 21 (1999) 233.
[8] P. Ciambelli, P. Parrella, S. Vaccaro, Thermochim. Acta 162 (1990) 83.
[9] P. Ciambelli, V. Palma, S. Vaccaro, Catal. Today 17 (1993) 71.
[10] P. Ciambelli, P. Corbo, M. Gambino, V. Palma, S. Vaccaro, Catal. Today 27 (1996) 99.
[11] J.P.A. Neeft, O.P. van Pruissen, M. Makkee, J.A. Moulijn, Appl. Catal. B 12 (1997) 21.
[12] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, Stud. Surf. Sci. Catal. 116 (1998) 635.
[13] B.J. Cooper, H.J. Jung, J.E. Thoss, US Patent 4,902,487 (1990).
[14] P.N. Hawker, Platinum Met. Rev. 39 (1995) 2.
[15] P. Hawker, N. Myers, G. Hütwohl, H. Vogel, B. Bates, L. Magnusson, P. Bronnenberg, SAE Paper 970,182 (1997).
[16] S.J. Jelles, B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Stud. Surf. Sci. Catal. 116 (1998) 667.
[17] 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.
[18] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, Appl. Catal. B 22 (1999) L5.
[19] J. Oi-Uchisawa, A. Obuchi, A. Ogata, R. Enomoto, S. Kushiyama, Appl. Catal. B 21 (1999) 9.
[20] T. Suzuki, T. Kyotani, A. Tomita, Ind. Eng. Chem. Res. 33 (1994) 2840.
[21] M.J. Illan-Gomez, A. Linares-Solano, L.R. Radovic, C. Salinas-Martinez de Lecea, Energy Fuels 10 (1996) 158.
[22] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, Comb. Sci. Tech. (1999), in press.