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Kinetics of catalyzed and non-catalyzed oxidation of soot from a diesel engine

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Abstract

To comply with the new regulations on particulate matter, car manufacturers more and more commonly use diesel particulate filters (DPF). The working of these systems needs to periodically burn soot that has been accumulated during the loading of the DPF. This paper describes the kinetics of the non-catalytic and catalytic oxidation of real diesel soot with oxygen. From these experiments, mechanisms for catalyzed and non-catalyzed soot oxidation have been proposed.

Keywords: Diesel soot; Oxidation; Catalyst; O_2; Kinetics

1. Introduction

Soot abatement in diesel exhaust conditions commonly consists in a two-step technology. The first step is the separation of carbonaceous particles from the gas phase by mechanical filtration using a so-called diesel particulate filter (DPF). The second step is the burning of soot particles inside the filter in order to avoid this drawback. However, diesel soot elimination is known to be a hard task, since this material burns at roughly 550–600 °C with oxygen, while diesel exhaust gases temperature most of the time lies between 200 and 400 °C. Therefore, some artifice is needed to promote soot oxidation. Very often this is carried out by the use of an oxidation catalyst. Catalyzed oxidation of carbonaceous materials has been studied for a long time [1]. This study deals with catalyzed and non-catalyzed oxidation, respectively (CSO and NCSO) of diesel soot in laboratory conditions, using a ceria–zirconia based catalyst. We mainly focused on the kinetics of particle oxidation and on the influence of catalyst upon kinetics. We investigated soot oxidation via temperature programmed oxidations (TPO), temperature programmed desorptions (TPD) and isothermal reactions at ambient pressure in a fixed bed reactor.

2. Experimental

Here is a brief description of our experimental conditions that have already been described elsewhere [2]. Diesel soot was provided by Renault S.A. Soot was produced from a diesel common rail engine on a bench test. Particles were collected on a SiC diesel particulate filter, and then they were flushed out with air. A ceria–zirconia supplied by Rhodia was used as catalyst support. Catalyst was calcined in air 2 h at 500 °C, after temperature had been raised at 3 °C/min. Then, small amounts of platinum were added by wet impregnation to ensure a catalyst composition of 0.4% $Pt/CeZrO_2$. As contact between soot and catalyst has a great impact on soot oxidation, we carefully paid attention to the mixture of these two compounds. We used a 10 mg soot sample, which we mixed with a spatula to our catalyst, to obtain a ''loose contact'' as defined by Van Setten et al. [3]. Initial catalyst to soot weight ratio was between 0:1 and 20:1. Our sample was diluted with 490 mg of silica carborandum (SiC), to avoid any thermal effect during oxidation [4]. The reactor is fed with UHP grade gases supplied by Air Liquide (pure O_2 and pure He). Soot samples and mixtures of soot + catalyst diluted with SiC were put in a quartz micro reactor (inner diameter 8 mm) containing quartz wool supporting the sample, and were placed in the oven. Gases from the reactor were analyzed using a CO, CO_2 Maihak S710

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analyzer. Gas analyses were then used to calculate the carbon mass evolution during the oxidation runs, using the following equation:

$$-\frac{dm}{dt} = (CO + CO_2) \times Q \times M_C \quad (1)$$

in which CO and CO_2 are the measured molar fraction of these species in the gas phase, Q is the molar flow of gases through the reactor and M_C is the molar mass of carbon. TPO were conducted with 5, 10 and 20% O_2 in the gas phase. The heating rate was 5 °C/min. Gas flow rate was 300 mL/min. TPD were conducted with 300 mL/min of He alone in the gas phase. The heating rate was 10 °C/min. Isothermal runs were conducted at temperatures between 480 and 560 °C, with a gas flow rate of 300 mL/min. P_{O_2}/P_0 was varied between 5 and 20%. Sample was heated in He from room temperature (RT) to run temperature.

3. Results and discussion

The following equation has been used to derive the kinetic parameters of our diesel soot oxidation:

$$-\frac{dm}{dt} = r = A \times e^{-E_a/RT} \times (x_{O_2})^{\alpha} \times m_0 \times \left(\frac{m}{m_0}\right)^{\beta} \quad (2)$$

In this equation, x_{O_2} is the partial pressure of oxygen in the gas phase; m_0 and m are respectively the initial and instantaneous soot mass in the reactor. This equation is derived from the one proposed by Neeft et al. [4].

3.1. Non-catalyzed soot oxidation (NCSO)

Non-catalyzed soot oxidation leads to CO and CO_2 formation, in a molar ratio close to 0.4 and quite constant upon the O_2 molar fraction and temperature ranges we have investigated. The following expression describes satisfactorily our results: $CO/CO_2 = A_0 \times (x_{O_2})^n \times e^{-Tr/T} = A_0 \times (x_{O_2})^{-0.1} \times e^{-400/T}$. Concerning kinetics of the reaction, we determined the values of A, E_a, α from our isothermal runs (Fig. 1). β has been determined by plotting $\ln(r/m_0)$ versus $\ln(m/m_0)$. In the 15–90% conversion range, a mean β-value of 0.5 has been found, which is close to the shrinking core model value ($\beta = 2/3$). E_a has been obtained by plotting the classical $\ln(r)$ versus $1/T$ curve for a given conversion degree and for several temperatures. E_a is roughly 164 kJ/mol. This high value is in good agreement with literature's data and it excludes any thermal diffusion effect [5–7]. Partial order versus oxygen is close to one (0.9), which is also in agreement with literature's results and could denote a control by adsorption of oxygen on active carbon sites [8]. A has been

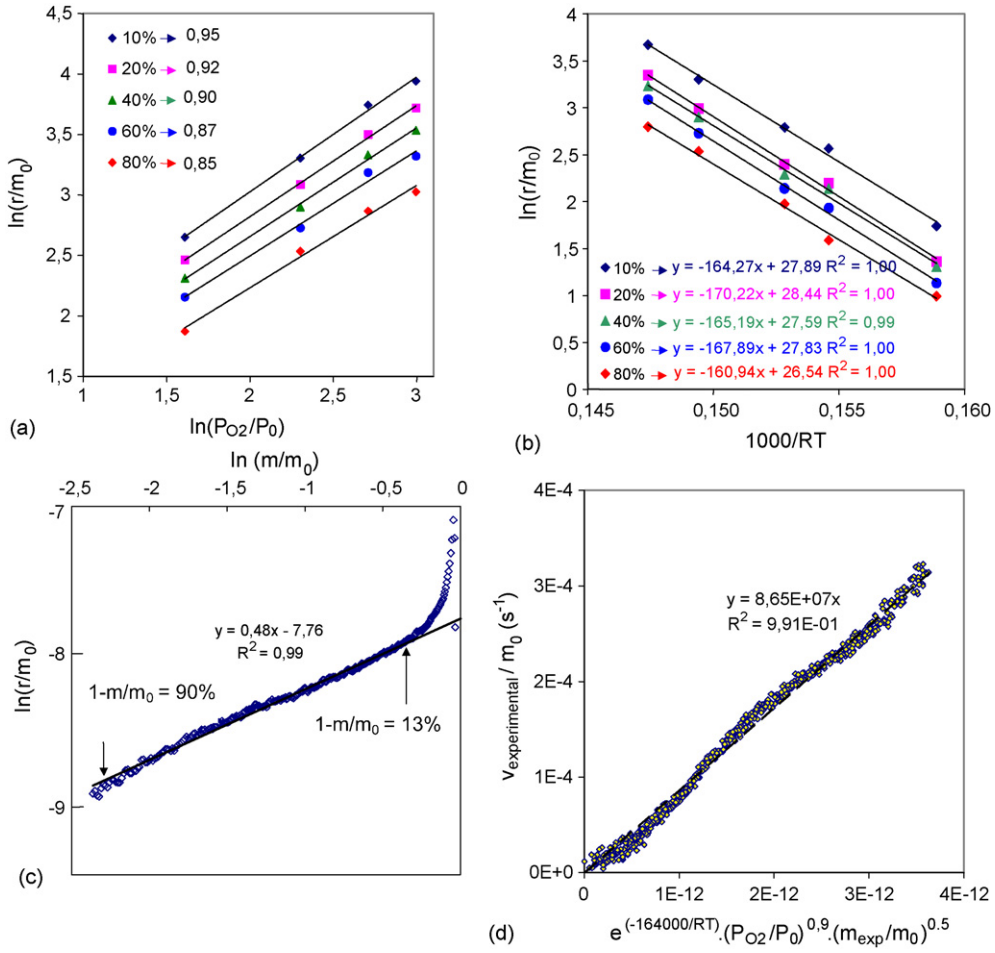

Fig. 1. Kinetic parameters for NC soot oxidation, $T = 500$–560 °C, $P_{O_2}/P_0 = 5 - 20\%$: (a) determination of α partial order for oxygen, (b) determination of E_a, global activation energy for the reaction, (c) determination of β, partial order for the soot, and (d) determination of A, preexponential factor.

determined by plotting the experimental oxidation rate versus $e^{-164{,}000/RT} \times (x_{O_2})^{0.9} \times m_0 \times (m/m_0)^{0.5}$. The reproducibility of our experiments was good (see the A confidence interval in Eq. (3)), so that we can express the oxidation rate as follows:

$$r = 8.5 \pm 0.4 \times 10^7 \times e^{-164{,}000/RT} \times (x_{O_2})^{0.9} \times m_0 \left(\frac{m}{m_0}\right)^{0.5} \quad (3)$$

This Eq. (2) has been used to model our TPO runs. From Fig. 2, it is clear that this model is not appropriate to describe the fresh soot oxidation, especially in the temperature range 300–550 °C. From this figure, we can conclude that diesel soot shows heterogeneous reactivity. At low temperatures, some highly reactive oxygenated species initially present on soot may react with oxygen or decompose. These species are not SOF, since they are not affected by extraction. They consist more likely in the volatile organic fraction of soot (VOF), i.e. oxygenated compounds initially contained in soot [9]. At high temperature, only the low-reactive part of diesel soot (LR), which is composed of almost pure carbon, remains. Another conclusion is that kinetic parameters, which have been determined from isothermal runs, only account for this low-reactive part of soot. To model the TPO run carried out with fresh soot, a specific rate equation for the oxidation of those reactive species is needed. We have used a very simple model, considering that VOF and carbonaceous part of soot "burnt" simultaneously, even if VOF do not just burn, but are probably also subject to decomposition. The oxidation rate has therefore written as:

$$r = r_{VOF} + r_{LR} \quad (4)$$

The oxidation rate of VOF has then been expressed by Eq. (4):

$$-\frac{dm_{VOF}}{dt} = r_{VOF} = A' \times e^{-E'_a/RT} \times (x_{O_2})^{\alpha'} \times m_{VOF,0} \times \left(\frac{m_{VOF}}{m_{VOF,0}}\right)^{\beta'} \quad (5)$$

3.2. Catalyzed soot oxidation (CSO)

The introduction of the catalyst in the reactor strongly modifies the soot oxidation process. The reaction leads only to CO_2, CO being oxidized by the $Pt/CeZrO_2$ catalyst. Kinetic parameters for CSO have been determined from our isothermal runs, in the same way than for the NCSO Those parameters are presented in Fig. 3(a) as a function of the soot conversion degree and they are compared with those obtained for the NCSO Partial order versus O_2 increases from 0.5 to 0.75 and activation energy increases from 120 to 160 kJ/mol. In opposite to our results for NCSO, the kinetic parameters for the CSO change during the soot oxidation process. It seems that CSO parameters migrate towards NCSO parameters as soot is oxidized. Moreover, kinetic parameters for low conversion degree look like catalyzed oxidation parameters. Indeed, we find a lower partial order versus oxygen and lower activation energy than for NCSO The

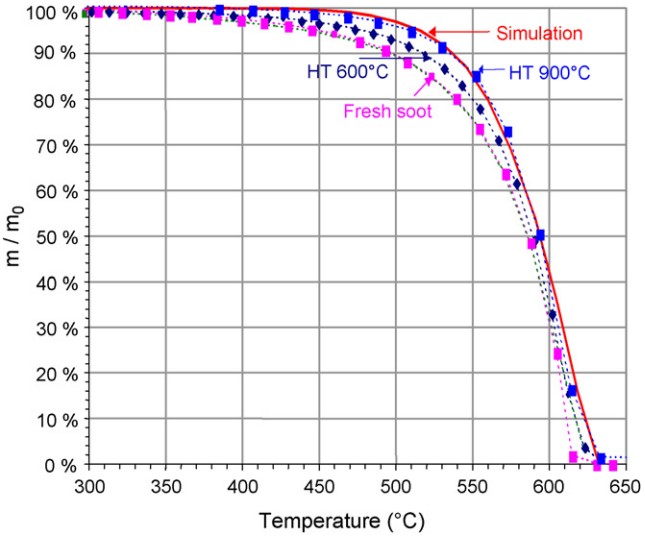

Fig. 2. Simulation of TPO run on fresh and heat-pre-treated soot at 600 or 900 °C under He (HT 600 °C HT 900 °C).

determination of partial order versus soot conversion degree (β) is shown in Fig. 3(c). We can remark that the partial order versus soot conversion degree is the same than for slow oxidation, meaning that the active carbon sites evolution is the same in the whole sample. The evolution of the rate versus the time on stream is presented Fig. 3(d). From these three results Fig. 3(d), we conclude that the presence of the catalyst induces the existence of two distinct soot oxidation processes: a fast-catalyzed oxidation occurs at low conversion degrees, when catalyst and soot are still in close contact, while at high conversion degrees, only a slow-non-catalyzed oxidation remains, due to a loss of contact between soot and catalyst. Neeft et al. have already explained their results by a loss of contact between catalyst and soot when soot is oxidized [10]. Thus, we propose a kinetic model based on the following assumptions: (i) a fast oxidation process only concerns carbon sites that are subject to the catalyst influence. It occurs on part of the soot mass ($m_{catalyzed}$); (ii) a slow oxidation process occurs between soot and molecular oxygen. It does not depend on the presence of the catalyst and therefore every carbon sites are concerned by this reaction (m_{total}). Based on this hypothesis, we have expressed the oxidation rate as the sum of two components, according to Eq. (5):

$$r_{total} = r_{slow\,oxidation}(m_{total}) + r_{fast\,oxidation}(m_{catalyzed}),$$

$$\left.\frac{r}{m_{total,t=0}}\right|_{slow\,oxidation} = A \times e^{-E_a/RT} \times (x_{O_2})^{\alpha} \times \left(\frac{m_{total,t}}{m_{total,t=0}}\right)^{\beta} = k \times \left(\frac{m_{total,t}}{m_{total,t=0}}\right)^{\beta},$$

$$\left.\frac{r}{m_{catalyzed,t=0}}\right|_{fast\,oxidation} = A' \times e^{-E'_a/RT} \times (x_{O_2})^{\alpha'} \times \left(\frac{m_{catalyzed,t}}{m_{catalyzed,t=0}}\right)^{\beta'} \quad (6)$$

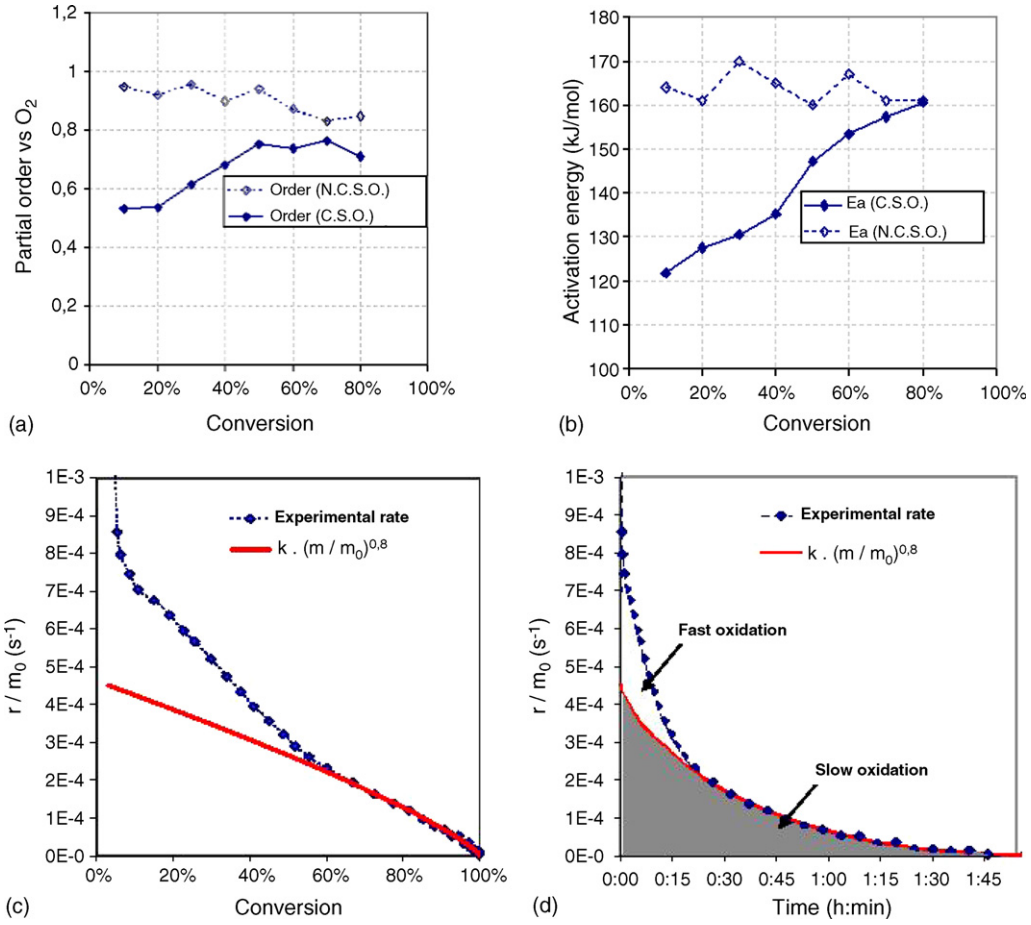

Fig. 3. (a) Dependence of kinetic parameters vs. conversion degree, for NCSO and CSO of diesel soot. Catalyst:soot = 5:1, T = 480–540 °C, $x_{O_2} = 5 - 20\%$. (b) Determination of slow and fast oxidation processes rates from the measured oxidation rate.

As we have already observed, β is close to 0.8, thus we have used this conversion dependence to model the slow oxidation process. Parameter k was adjusted so that the theoretical curve $k \times (m_{\text{total},t}/m_{\text{total},t=0})^{0.8}$ fit the experimental one. Several k were determined, corresponding to several x_{O_2} and temperature run conditions. A and E_a were then determined by plotting the classical $\ln(r) = f(1/T)$ and $\ln(r) = \ln(x_{O_2})$ curves from these k values. $r_{\text{fast oxidation}}$ has been determined by subtracting $r_{\text{slow oxidation}}$ from the experimental rate. Initial catalyzed soot mass in the sample has been determined by integrating $r_{\text{fast oxidation}}$ over the fast oxidation process time. Kinetic parameters of the fast oxidation process have been determined from these new – part experimental and part modelled – curves, with the method, which has previously been presented in the NCSO part of this paper. The kinetic model for our isothermal runs is finally:

$$r_{\text{slow oxidation}} = 6.05 \pm 0.3 \times 10^7 \times e^{-161{,}000/RT} \times (x_{O_2})^{0.7} \times m_{\text{total},t=0} \times \left(\frac{m_{\text{total},t}}{m_{\text{total},t=0}}\right)^{0.8}$$

$$r_{\text{fast oxidation}} = 1.19 \pm 0.06 \times 10^5 \times e^{-114{,}000/RT} \times (x_{O_2})^{0.3} \times m_{\text{catalyzed},t=0} \times \left(\frac{m_{\text{catalyzed},t}}{m_{\text{catalyzed},t=0}}\right)^{0.8}$$

Application of this model to the TPO runs leads to the same observations than for the NCSO (solid line in Fig. 3(b)): a low temperature oxidation rate, accounting for VOF fast oxidation, is needed to fit the experimental soot consumption. Good results have then been obtained using the following rate equation:

$$r_{\text{total}} = r_{\text{VOF}} + r_{\text{fast oxidation}} + r_{\text{slow oxidation}}$$

4. Conclusion

NCSO of diesel soot leads to CO and CO_2 formation, in a molar ratio of roughly 0.4. Isothermal runs have shown that soot particulates are composed of two parts with different reactivity towards O_2: oxygenated species (VOF) are very reactive. They spontaneously decompose under inert atmosphere when they are heated up. Their oxidation in oxygen containing gases occurs at low temperature (300 °C in our experimental conditions). Carbonaceous core of diesel soot is less reactive and is oxidized only above 450 °C. Based on this observation, a simple kinetic model has been proposed for non-catalytic soot oxidation. This model has been successfully used to model our TPO results. CSO with a $Pt/CeZrO_2$ catalyst has also been studied. The oxidation leads to CO_2 production only. Our experiments showed that three mechanisms occur in soot consumption: first, a VOF oxidation, which is catalyzed by our $Pt/CeZrO_2$ catalyst. Secondly,

a catalytic oxidation occurs on a part of the sample. The proportion of catalyzed soot mass increases with the catalyst:soot ratio. Kinetic parameters of this oxidation have been determined. Partial order versus oxygen (0.3) and activation energy (114 kJ/mol) are both lower than for the non-catalyzed oxidation process, whose kinetic parameters are respectively 0.9 and 164 kJ/mol. Finally, the whole soot mass reacts via slow oxidation, which looks like a non-catalytic oxidation (partial order versus oxygen: 0.7, activation energy: 161 kJ/mol). VOF are oxidized first, well below 450 °C. Catalyzed part of soot reacts from 400 °C, with a maximum activity between 520 and 550 °C, while slow oxidation occurs when temperature is 30–40 °C higher and reaches a maximum for temperatures between 570 and 600 °C. Kinetics of these three steps have been determined and successfully applied to our TPO results.

References

[1] D.W. Mc Kee, Carbon 8 (1970) 629.
[2] P. Darcy, P. Da Costa, H. Mellottée, J.-M. Trichard, G. Djéga-Mariadassou, Matériaux carbonés et catalytiques pour l'environnement (2003) 215.
[3] B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, Appl. Catal. B 28 (2000) 253.
[4] J.P.A. Neeft, T.X. Nijhuis, E. Smakman, M. Makkee, J.A. Moulijn, Fuel 76 (12) (1997) 1129.
[5] B. Dernaika, D. Uner, Appl. Catal. B 40 (2003) 219.
[6] R. Lopez-Fonseca, U. Elizundia, I. Landa, M.A. Gutierrez-Ortiz, J.R. Gonzalez-Velasco, Appl. Catal. B 61 (2005) 150.
[7] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Fuel Proc. Tech. 47 (1996) 1.
[8] B. Stanmore, J.F. Brilhac, P. Gilot, Carbon 39 (2001) 2247.
[9] S. Collura, Ph.D. Thesis of Metz University, France, 2004.
[10] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Fuel 77 (3) (1998) 111.