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# Catalytic combustion of diesel soot: Experimental design for laboratory testing

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ABSTRACT

In order to abate diesel soot particles many catalysts have been studied at several industrial and academic laboratories. However, the comparison of kinetic data obtained with such catalysts is not straightforward, due to the different experimental conditions used in the activity measurement carried out by each research group. Temperature-programmed analysis is the most common technique used to determine catalytic activity for soot oxidation. For a given catalyst, the temperature-programmed oxidation profile depends on variables such as heating rate, oxygen partial pressure, gas flow rate, catalyst:soot weight ratio, type of contact between the catalyst and the soot, and existence of energy and/or mass transfer limitations during the analysis. This work presents a systematic study of the influence of all these testing variables on the TPO profile, and the optimum testing conditions to obtain good reproducibility during the kinetic study. Both experimental and computer simulation results are included to assist researchers in the comparison of results obtained under different experimental conditions.

## 1. Introduction

Soot and $NO_x$ are the main pollutants in diesel engine exhausts; both could be abated catalytically. The catalytic solution is one of the most desirable ones [1,2]. It consists of a porous support coated with a catalyst in order to trap the soot particles and oxidize them at sufficiently low temperatures, thus avoiding pressure drop build-up due to soot accumulation. Therefore, the system works as a self-regenerating trap.

In order to study this catalytic system at a laboratory level, different ways of mixing the soot with the catalyst have been used. This is a relevant issue, since this system is formed by two solids and a gas, and therefore the level of physical interaction between the soot and the catalyst determines the reaction rate. There are two main procedures to mix these solids. In one of them, both phases are mixed by hand-grinding in a mortar or with a ball mill. This procedure leads to what is called 'tight contact' mode [3,4]. The other procedure consists in shaking the soot and the catalyst in a vial [5] or mixing them with a spatula [4]. This leads to the 'loose' contact mode. Depending on the objective of the study, one of these procedures is selected. For example, if the goal is to compare intrinsic catalytic activities, the tight contact mode is used. Temperature-programmed oxidation (TPO) is one of the techniques most widely used to carry out this comparison. However, each research group selects different experimental conditions for catalyst evaluation, such as heating rate, oxygen partial pressure, gas flow rate, catayst:soot weight ratio, soot composition and particle size, and catalyst mass loaded into the analysis cell. The TPO profile is affected by all these variables and, therefore, in order to compare catalysts used in different laboratories it is necessary to take into account these effects. A similar observation can be done for other temperature-programmed techniques, such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). This work analyzes both experimentally and by simulation the influence of these variables upon catalytic results as obtained by TPO.

Neeft et al. [6] reported that in addition to the above mentioned variables, the reaction rate of catalyzed soot oxidation reactions depends on a number of other intrinsic parameters such as the sample pretreatment. For example, it is known that the amount of hydrocarbons adsorbed on the soot decreases as a function of time; an initial heating in inert gas leads to hydrocarbon desorption and this can also have other effects such as a change in the contact between the soot and the catalyst or a reaction between the soot and a metallic oxide, thus reducing the catalyst.

Since the aim of comparing intrinsic catalytic activities is to work under a kinetic controlled regime, a fundamental aspect to take into account is the absence of mass transfer limitations. In the particular case of soot combustion reactions, only external mass transfer limitations can take place since only the external catalytic surface may be in contact with soot given the typical size of these particles.

The soot combustion reaction is very exothermic and because of this, at low catalyst/soot weight ratio, a reaction runaway could take place [7]. Depending upon the technique being used, and the temperature sensor position, this phenomenon could lead to a result misinterpretation, as discussed below.

A particular difficulty in this reaction system is that the soot forms agglomerates of small particles, and it is likely that some of them are not in contact with the catalyst. In this case, there is

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a non-catalytic contribution to the overall reaction rate, mainly at high temperatures. Typically, this appears in the TPO profile as a shoulder or a broadening of the peak on the high temperature side, since the non-catalytic reaction is much slower than the catalytic path. Because of this, a shift of the TPO profile to higher temperatures can be observed. This situation has to be taken into account during kinetic parameters estimation, and is a source of uncertainty and non-reproducible results. The situation worsens when the experiments are carried out under a loose contact mode.

During the last 10 or 15 years, several catalytic systems have been studied by different research groups [3,4,6–15] which have mainly used temperature-programmed techniques to evaluate catalytic activity [16]. The use of one contact mode or the other has depended on whether the main goal of the work was to gather fundamental knowledge about the kinetics and mechanisms, or to evaluate the catalysts under more realistic conditions [7]. A different ranking of activities was obtained in either case. Nevertheless, as a general trend it was found that the samples tested under loose contact mode have a lower activity than in tight contact mode, as indicated by a shift of the TPO profile towards higher temperatures. Typically, the temperature of the maxima in the TPO profile ($T_{\max}$) is higher than in the former case. It is quite difficult to incorporate the physical contact grade effect in a model, and accordingly, the catalysts comparison should be done following a single mixing procedure.

In a recent work, Schmal and co-workers [31] reported on the use of statistical experimental design in order to select the variables to be used in catalytic activity tests for soot oxidation. The study included the evaluation of the effect of ramp rate, catalyst:soot mass ratio, and gas flow rate.

The purpose of this work is to carry out a systematic study of the effect of the experimental variables on the TPO profile, in order to select the most appropriate experimental conditions to obtain reliable kinetic data for catalytic soot combustion. In each case, several experiments are carried out by changing one variable at a time in a wide range of values, in order to see the changes in the TPO profile and to detect when mass and energy transfer limitations becomes important. An experimental design to determine if all the soot particles are in contact with the catalyst is presented. The study also includes an estimation of the effect of each of the experimental variables on the TPO profiles by computer simulation, using a power-law kinetic model. Even though the model is quite simple, it is useful to quantify the effect of variables such as oxygen concentration, total gas flow rate, and catalyst and soot mass loaded into the cell, using a global activation energy obtained by fitting the experimental TPO. The very well known kinetic expression used in this work has to be taken as fully empirical, used only with the purpose of estimating the effect of the above mentioned variables on the TPO.

## 2. Experimental

### 2.1. Soot and catalyst preparation

The soot used in this work was prepared by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. After being collected from the vessel walls, it was dried in a stove at 120 °C for 24 h. Its specific surface area was 55 $m^2/g$. Temperature-programmed experiments performed using helium as carrier gas provided information regarding the amount of partially oxidized groups of the soot surface and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, the amount of carbon released as CO, $CO_2$ and hydrocarbons represented 9.3% of the soot [17]. Soot from diesel engine has adsorbed hydrocarbons that could be 10% or higher, and the specific surface area was reported to be in the order of 100 $m^2/g$ [32]. Therefore, the soot used in this study has parameters similar to those of a real soot.

The Ba,K/$CeO_2$ catalysts were prepared from a $CeO_2$ (Sigma, p.a.) support to which the precursors solutions containing $Ba(AcO)_2$ and $KNO_3$ were added, in order to obtain loads of 0 or 22 wt.% of Ba and 7 wt.% of K. The suspension was evaporated while being vigorously stirred until achieving a paste, which was dried in a stove at 120 °C for 24 h and calcined at 400 °C for 2 h.

These catalysts have been previously studied, including catalyst characterization, and activity and stability measurements [33–35].

### 2.2. Activity test

The catalytic activity for the combustion of soot was determined by temperature-programmed oxidation (TPO). The soot and the different catalysts were mechanically mixed in an agate mortar so as to obtain different soot/catalyst ratios (wt./wt.). Different gaseous flow rates with 5% oxygen in nitrogen were used and the temperature was increased at a rate of 12 °C/min. A modified TPO technique [18] was employed which consisted in passing the gases coming from the reactor through a methanation reactor, where CO and $CO_2$ were converted into $CH_4$. Afterwards, methane was measured continuously with an FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C. Unless otherwise stated, in the experiments described in Sections 2.3–2.8, the carrier gas flow rate was 40 ml/min, and the catalyst and the soot were mixed in a mortar with a glass rod for 6 min (tight contact) [6]. The selectivity of the soot combustion reaction to $CO_2$ was as an average approximately 99%.

### 2.3. Reproducibility

Repeated TPO experiments were performed, as described in Section 2.2, so as to determine the reproducibility of the technique. The catalysts used were different batches of K/$CeO_2$. In these experiments 10 mg of catalyst–soot mixtures in 20:1 ratio were used.

### 2.4. Mass transfer limitations analysis

In order to verify that there are no external mass transfer limitations, TPO experiments were performed using 10 mg of catalyst–soot mixture in a 20:1 ratio and using different flow rates of carrier gas ($Q$). The catalyst used to perform these experiments was K/$CeO_2$.

As will be shown below, the 20:1 ratio is an appropriate one since with this ratio and under certain conditions (flow rate, particle size, etc.), the runaway is not produced and, in addition, all the soot particles are in contact with catalyst.

### 2.5. Reaction runaway analysis

The verification was performed by TPO experiments using different catalyst/soot ratios ($R$), with $R$ between 5 and 60. In all the experiments, 10 mg of catalyst–soot mixture were used. The catalyst used to perform these experiments was K/$CeO_2$.

### 2.6. Verification that all the soot particles are in contact with the catalyst

The verification was performed by TPO experiments using different catalyst/soot ratios ($R$), with $R$ between 5 and 60, and always loading the *same soot quantity*, this quantity being equal to 0.47 mg. The catalyst used to perform these experiments was K/$CeO_2$.

### *2.7. Effect of the catalyst–soot mixing time*

In order to study this effect, TPO experiments were performed with 10 mg of catalyst–soot mixtures (20:1) prepared with glass rod and mortar (tight contact) and with different mixing times: 2, 4, 6, and 8 min. The catalyst used to perform these experiments was Ba,K/$CeO_2$.

### *2.8. Different modes of catalyst–soot contact: tight contact and loose contact*

The effect of the different modes of contact was evaluated by TPO of 10 mg of K/$CeO_2$ and Ba,K/$CeO_2$ catalysts. The carrier gas flow rate was 40 ml/min. The catalyst–soot mechanical mixtures (20:1) were prepared in two different ways. One type of mixture was performed mixing for 6 min with a glass rod in a mortar (tight contact). The other type of mixture was performed by agitating the catalyst and soot in a bottle for 2 or 6 min (loose contact).

### *2.9. Kinetic model*

The kinetic model chosen to make the simulations is a pseudo-homogeneous model which follows a power-law kinetics. In the literature several papers have been published on the combustion of carbonaceous materials that mention this kind of model [19–29]. It is well known that the system under study is very complex, which is due to different phenomena that occur on the gas–solid (gas–soot and gas–catalyst) and solid–solid (catalyst–soot) interfaces. The reaction involves many steps, such as redox reactions, and/or the formation of intermediate compounds such as carbonates, surface diffusion of active components, and other [36]. Even though the model based on the power-law expression, is a simplification of the real reacting system, it is able to provide a global representation of the kinetic behavior and allows the analyses of the influence of the experimental variables on the TPO profiles, without being necessary the estimation of several parameters. It is important to emphasize, that this kinetic model is used here, only to help in the estimation of the effect that several variables have on the TPO profile.

Elemental analysis of soot [17–30] indicates that carbon is the main component, and therefore the stoichiometry proposed for the global reaction is:

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

The kinetic expression derived from Eq. (1) considering surface carbon concentration is [19]:

$$r = A_s \exp\left[-\frac{E}{RT}\right] C^0(1-X)^n P_{O_2}^m \qquad (2)$$

in which '$r$' is the reaction rate (mol $s^{-1}$ $g^{-1}$), '$A_s$' is the surface pre-exponential factor, '$E$' is the global activation energy, '$R$' is the gas universal constant, '$T$' absolute temperature ($K$), '$C^0$' is the initial carbon concentration (mol $g^{-1}$) and can be calculated from the TPO profile, '$X$' is the carbon conversion, '$n$' is the carbon reaction order, '$P_{O_2}$' oxygen partial pressure (atm) and '$m$' oxygen reaction order.

To formulate the reactor mass balance, a tubular reactor without either axial or radial dispersion was considered (1D model). The balance for solid face (carbon) is

$$\frac{\partial C}{\partial T} = \frac{A_s}{\beta} \exp\left[-\frac{E}{RT}\right] C^0(1-X)^n P_{O_2}^m \qquad (3)$$

where $\beta$ is the heating rate of the TPO test. For the gas phase, pseudo-steady-state was assumed, and therefore:

$$F_n^0 \frac{\partial y_{CO_2}}{\partial w} = A_s \exp\left[-\frac{E}{RT}\right] C^0(1-X)^n P_{O_2}^m \qquad (4)$$

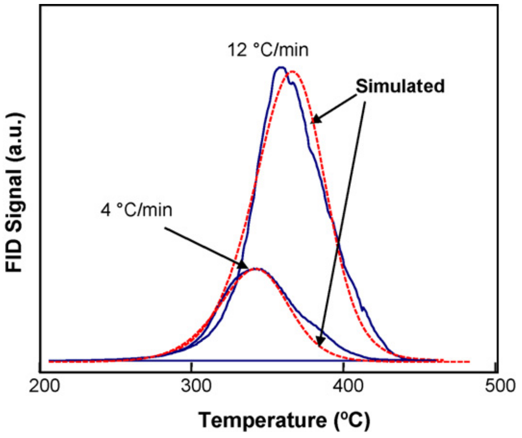

**Fig. 1.** Experimental and simulated TPO profiles, obtained with K(7)/$CeO_2$ catalyst, at 12 and 4 °C/min. Kinetic parameters determined from the TPO obtained at 12 °C/min.

where '$F_n^0$' is the total gas flow rate at the cell inlet (mol $s^{-1}$), '$Y_{CO_2}$' is the carbon dioxide mole fraction and '$w$' is the mass of catalyst:soot mixture employed in the TPO test (g).

The model presented has 4 parameters, $A$, $E$, $n$ and $m$. In this work the oxygen reaction orders was assumed to be 1. Simulations were made using the MicroMath®Scientist® software for Windows™.

As an example of the model capability to predict reasonably well the kinetic response of this system, Fig. 1 shows the result of TPO profiles obtained with a K(7)/$CeO_2$ catalyst mixed with soot, using two different heating rates, 12 and 4 °C/min. Continuous lines correspond to experimental results. The profile obtained at 12 °C/min was used to obtain the kinetic parameters, and then these values were used to predict the profile at 4 °C/min. It can be seen that the fitting of the profile obtained at 12 °C/min is quite good, and also the prediction of the profile obtained at 4 °C/min is very good. Similar quality of prediction was obtained using 8 and 16 °C/min (results not included for clarity reasons).

## 3. Results and discussion

### *3.1. Reproducibility*

The reproducibility of the TPO profiles obtained with catalyst/soot mixtures prepared as described in this work was such that the maximum difference between two TPO maximum temperatures ($\Delta T_M$) was the following:

- When comparing two profiles obtained with the same catalyst–soot mixture, and when the TPO experiments were performed with a maximum difference of 8 days, $\Delta T_M$ was 3 °C.
- When comparing two profiles obtained with the same catalyst–soot mixture, and when the TPO experiments were performed with a maximum difference of 15 months, $\Delta T_M$ was 10 °C.
- When comparing two profiles obtained with different mixtures carried out with the same catalyst, and when the TPO experiments were performed with a maximum difference of 15 months, $\Delta T_M$ was 11 °C.
- When comparing two batches of catalysts $\Delta T_M$ was usually 10 °C, and that is why a given set of experiments is always done with the same batch of catalyst.

It is important to take into account these values. Small differences in $T_M$ can be ascribed to technique errors, to sample

**Table 1**
$T_M$ values for different $Q$ values of carrier gas. $R$ = 20 (tight contact). Catalyst: K/CeO$_2$. Oxygen partial pressure at the maximum reaction rate (at $T_M$).

| Q (ml/min) | $T_M$ (°C) experimental | $T_M$ (°C) simulated | $P_{O_2}$ at $T_M$ simulated (bar) |
|---|---|---|---|
| 43 | 353 | 350 | 0.024 |
| 38 | 351 | 355 | 0.022 |
| 33 | 358 | 360 | 0.019 |
| 23 | 397 | 370 | 0.012 |
| 18 | 394 | 380 | 0.008 |
| 14 | 405 | 400 | 0.004 |
| 8 | – | 425 | 0.0005 |
| 4 | – | ND | 0.00001 |

heterogeneity, and to catalyst variability during storage, and not necessarily to differences in catalytic performance.

### 3.2. Mass transfer limitation analysis

The soot is deposited on the external surface of the catalyst, since as above indicated; soot particles are larger than the pore diameter of typical catalysts. Even though the reaction mechanism is very complex, involving the redox capacity of cerium support among other steps, it can be expected that only external mass transfer limitation may occur, since no significant oxygen consumption takes place inside the pores. To determine if such limitation is present, the effect of gas flow rate on the TPO profile was determined. Note that the model can predict the effect of the gas flow rate and oxygen concentration, changing the variables $F_n^0$ and the value of the initial oxygen partial pressure used to integrate these equations.

Fig. 2A shows the experimental TPO profiles for different carrier gas flow rates. The TPO experiments were performed using 10 mg of catalyst:soot mixture with a weight ratio of 20:1. In Fig. 2B the simulated TPO profiles are shown. The simulations were made using the same conditions as the experimental tests (10 mg of sample, catalyst:soot mass ratio 20:1, heating rate 12 °C/min). Two additional simulations with $Q$ values of 8 and 4 ml/min were carried out to calculate the oxygen consumption in a wider range of flow rates. The values of $E$ and $A$ were 89.9 kJ/mol and $7 \times 10^6$ atm$^{-1}$ s$^{-1}$, respectively, inlet oxygen partial pressure was 0.05 atm. Table 1 shows the values of the gas carrier flow rates ($Q$), the temperatures corresponding to the TPO maxima ($T_M$) shown in Fig. 2A (experimental) and B (simulated), and the estimated oxygen partial pressure at the reactor outlet at $T_M$. There is a very good agreement between the experimental and predicted values of TM at high flow rates, where the mass transfer limitations are less likely to occur. Predicted values agree very well with the experimental at flow rates of 33 ml/min or higher. Then, as the flow rate decreases, and the mass transfer become the limiting step due to the high oxygen consumption, the predicted value is lower. This is consistent with the fact that the system is working under mass transfer limitation, and therefore the overall reaction rate is slower than in the pure kinetically controlled case. Table 1 shows the oxygen partial pressure at the maximum of the TPO profile, calculated with the kinetic model above described. It can be seen that the calculated oxygen concentration decreased to less than one fourth of the initial value when the carrier gas flow rate is 23 ml/min, and because of this the simulated TPO profile becomes flat at the maximum rate. In Fig. 2B the mass limitation regime is more evident for low flow rates (8 and 4 ml/min), the TPO profiles are predicted to be lower in height (reaction rate) and the TM values are less defined than those obtained with high flow rate. This shape of a flat maximum is a clear indication that the oxygen is becoming the limiting reactant, and because of this the reaction rate cannot increase with the temperature. The experimental values show that the TPO profiles become wider at low flow rates than at high flow rate. At a very low flow rate, such as 4 ml/min the combustion did not finish at 700 °C. Based on these results, it can be concluded that the system is under chemical controlled regime or with a negligible effect of mass transfer, at flow rates higher than 33 ml/min, when the catalyst:soot weight ratio is 20:1, the heating rate is 12 °C/min, the sample mass is 10 mg, and the gas phase contains 5% oxygen. Therefore, a flow rate of 40 ml/min was chosen as a standard value to carry out the kinetic experiments. Another very useful conclusion that can be obtained from these data is that the simulation is very helpful to assist in the experimental design, thus reducing the number of experiments to be carried out. It is true that the simple model being used does not include diffusion phenomena. However, it is still valid to determine the oxygen consumption under chemical controlled and therefore, it can be known if this concentration reach a level where the mass transfer might becomes a limitation, due to the very low oxygen concentration. The shape of the profile is an indication of such behavior.

The TPO profile is predicted to shift to lower temperatures as the oxygen concentration increases, even if there are no mass transfer limitations as seen in Fig. 3. In this case the simulations were performed using a flow rate equal to 40 ml/min, the rest of parameters being the same as those used in the simulations presented in Fig. 2B, except the oxygen partial pressure that was varied between 0.005 and 1 atm. It is worth noting that the simulated TPO profiles observed in Fig. 2B slightly shift to lower temperatures as the flow rate increases, even when there are no mass transfer limitations. This is due to the variations of

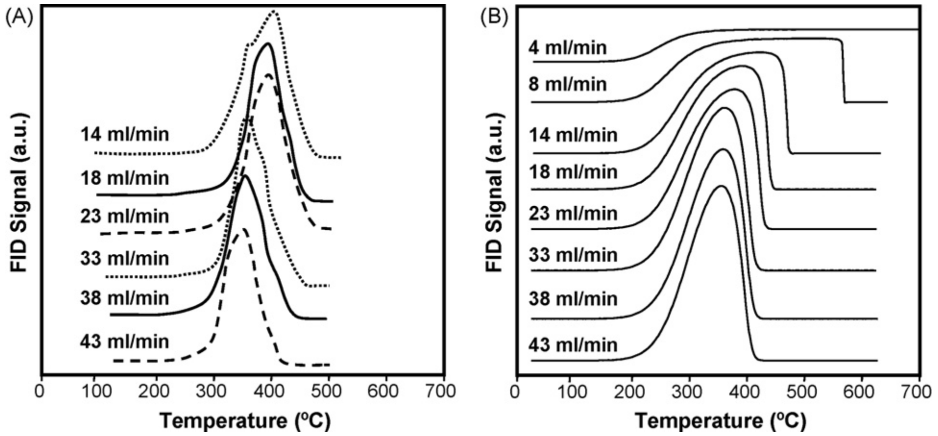

**Fig. 2.** (A) TPO profiles for 10 mg of 20:1 mixtures of K/CeO$_2$ + soot (tight contact). $Q$ values from 14 to 43 ml/min. (B) TPO simulated for $Q$ values from 4 to 43 ml/min.

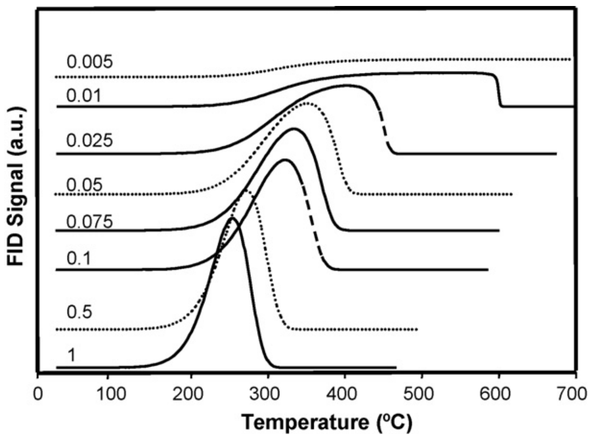

**Fig. 3.** TPO profiles simulated for different oxygen partial pressure. $Q = 40$ ml/min.

the oxygen partial pressure provoked by the different flow rates employed.

### 3.3. Reaction runaway analysis

**Table 2**
$T_M$ values for different $R$ values. $Q = 40$ ml/min. Mixture mass = 10 mg (tight contact). Catalyst: K/CeO$_2$.

| $R$ | $T_M$ (°C) experimental | $T_M$ (°C) simulated |
|---|---|---|
| 60:1 | 379 | 370 |
| 40:1 | 381 | 375 |
| 20:1 | 380 | 380 |
| 10:1 | 373 | 405 |
| 5:1 | 380 | 460 |

When the amount of soot mixed with catalyst is very high, a strong local heating might occur due to the heat generated during the reaction. To verify at which catalyst:soot weight ratio ($R$) this occurs, experiments were carried out changing this parameter, but loading the same total mass (10 mg) in all cases. Thus, when loading a mixture of lower $R$, a higher soot quantity is charged into the analysis cell. Under this condition, higher oxygen consumption takes place and therefore, as above discussed, a shift of the TPO profile towards higher temperatures should be observed, as long as a reaction runaway does not occur. In the experiments we are presenting in this work, the TPO cell is a U-shape reactor as described in Ref. [18]. The thermocouple is located in a symmetrical position as compared to the bed, each of them in a different arm. Under normal operation conditions, the thermocouple registers the same temperature as that of the bed. In case of a reaction runaway, the catalytic bed temperature will be higher than that registered by the thermocouple; and therefore, the apparent effect will be that of shifting the profile to lower temperatures. These phenomena must be avoided in order to obtain reliable kinetic data.

Fig. 4A and B shows the TPO profiles obtained experimentally and by simulation, respectively, for different $R$ values. Table 2 shows the different temperatures corresponding to the TPO maxima ($T_M$) of profiles shown in Fig. 4A and B. To perform the simulations, the same conditions and parameters were used, except carbon initial concentration (varied from 60:1 to 5:1 mass ratios) and activation energy, that had been slightly increased to fit the maximum temperature (93.0 instead 89.9 kJ/mol). This had been done because the catalyst used in this set of experiments was different from that used before. In Fig. 4A it can be observed that the $T_M$ values practically do not change as $R$ is modified. However the TPO profiles shapes for $R = 10$ and $R = 5$ are different as compared with the corresponding ones for higher $R$ values. For $R = 10$, the profile shape is slightly different and the $T_M$ value is 7 °C lower, which suggests that the runaway phenomena are beginning to take place. The TPO profile shape for $R = 5$ indicates that the runaway occurred, which is evidenced by the very sharp shape of the TPO peak, with a very fast increment in the production of CO$_2$ (FID signal), practically at constant apparent temperature. Note that the sharper peak has an almost vertical signal growth, which would be indicating a very fast reaction rate increase at a given temperature. On the other hand, the TPO shift to lower temperatures is incompatible with the reaction being carried out under chemical control, as was previously explained. The runaway phenomena cannot be reproduced with the kinetic model, simply because no energy balance was included in the model, assuming that the bed temperature is that of the oven.

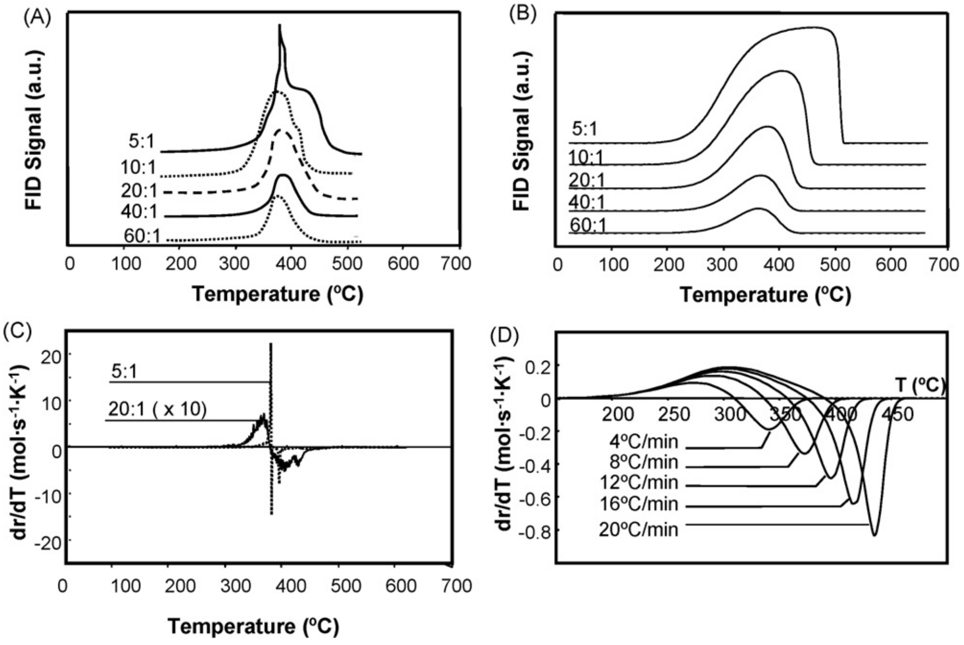

**Fig. 4.** TPO profiles for K/CeO$_2$ + soot (tight contact) mixtures. $R$ values from 5 to 60. Mass loaded: 10 mg. (A) Experimental profiles, (B) simulated profiles, (C) slope of the experimental TPO profile, and (D) slope of the simulated TPO profile.

Nevertheless, it has to be emphasized that the goal of the simulation is to predict what should be observed in the TPO profile when working under a kinetic controlled regime. If the experimental result differs significantly from this prediction, it can be concluded that the system is not under this regime. Based on these experiments, in order to obtain kinetic data, a 20:1 catalyst/soot ratio was selected as a standard ratio to determine catalytic activities. Fig. 4 and Table 2 shows that the model prediction agrees very well with the experimental results, as long as the system is working under a kinetic controlled reaction.

Fig. 4C shows the slope of the experimental TPO profiles obtained with different catalyst/soot ratios. These data provide a reference in order to determine whether the increase rate of the TPO signal observed during an experiment, is consistent with a system working under kinetic control or if there might be a reaction runaway taking place. It is important to note that in the case of a catalyst/soot mass ratio equal to 20:1 the maximum change in reaction rate was about 0.5 and when the ratio was 5:1, the value went up to 23, what definitely implies that a reaction runaway took place. The simulation (Fig. 4D) indicates that the maximum increase in reaction rate as a function of temperature is $0.2\,\mathrm{s}^{-1}\,\mathrm{K}^{-1}$ and corresponds to the highest heating rate used in this study (20 °C/min). This is a useful guide to judge the regime in which the experimental setup is operating.

### 3.4. *Verification of the soot–catalyst particles contact extent*

In order to verify that all the soot particles are in contact with the catalyst, several TPO experiments were carried out using mixtures with different catalyst/soot ratios (*R*), loading the same soot mass, instead of the same total mass of catalyst/soot mixture. Under this condition, if all the soot particles are in contact with catalyst, the temperature corresponding to the combustion maximum $T_M$ should be the same in all the experiments, independently of the catalyst–soot ratio used. As the soot amount increases relative to the catalyst, at a certain point there is no more catalyst available to contact the soot particles and, therefore a lower global reaction rate is observed and a shift of the TPO profiles to higher temperatures is displayed.

Fig. 5 shows the TPO profiles for different *R* values, and Table 3 shows the $T_M$ values and the total mass loaded in order to obtain 0.47 mg of soot into the cell. It can be observed that for *R* values between 10 and 60 the $T_M$ valued is the same. When using a 5:1 ratio ($R = 5$) the TPO profile displaces to higher temperatures due to the decrease in the reaction rate. These results indicate that when mixing one part of soot and 5 parts of catalyst, not all the soot particles are in complete contact with the catalyst particles. Based on these results and taking into account the previous ones, a catalyst–soot ratio of 20:1 was selected as the working catalyst–soot ratio. Obviously, when simulating this situation, keeping constant *A* and *E*, varying the *R* value and loading the same soot mass to the cell, all the TPO are the same (not shown).

**Table 3**
$T_M$ values for different catalyst/soot ratios at constant soot mass loaded into the cell. $Q = 40$ ml/min. Soot mass = 0.47 mg (tight contact). Catalyst: K/CeO$_2$.

| *m* (mg) | *R* | $T_M$ (°C) |
|---|---|---|
| 29 | 60:1 | 368 |
| 19.5 | 40:1 | 369 |
| 10 | 20:1 | 372 |
| 5.2 | 10:1 | 369 |
| 2.9 | 5:1 | 388 |

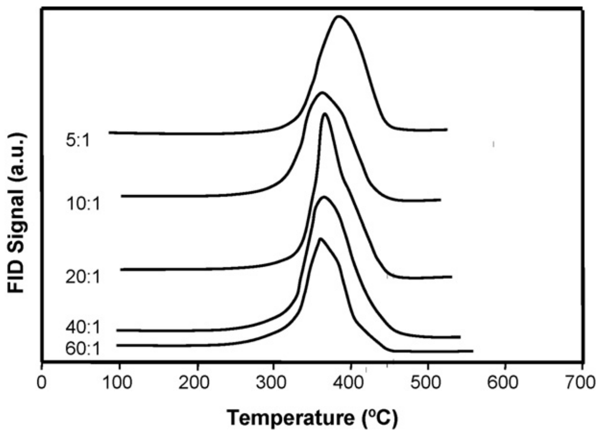

**Fig. 5.** TPO profiles for several catalyst/soot mass ratios at constant soot mass loaded into the cell. Soot mass = 0.47 mg.

### 3.5. *Effect of the catalyst–soot mixing time*

Fig. 6 shows the TPO profiles of catalyst/soot mixtures, which were obtained by mixing soot and catalyst with a glass rod in a mortar (tight contact), for different times. As can be observed, there is a high influence of this variable on the catalytic activity. The higher the mixing time, a more intimate catalyst–soot contact is obtained, and consequently the observed catalytic activity is higher. At low mixing times, e.g. 2 min, it can be observed that the TPO profile presents two maxima. In this case, the temperature range in which combustion occurs is wider, which indicates that an important fraction of the soot particles is not in physical contact with the catalyst. The TPO profile of a mixture of soot with an inert material is included for reference. It can be observed that in the case of the mixture with the catalyst, the second peak is displayed to lower temperature than the uncatalyzed reaction. Most probably, at high temperature the mobility of potassium compounds leads to get them in contact with the soot particles, thus decreasing the combustion temperature.

The profile shape corresponding to a mixing time of 2 min was verified by repeating the experiment. In the case of the sample with 4 min mixing time, the second maximum becomes a shoulder on a single combustion maximum. In the case of the 6 and 8 min mixtures the profiles are very similar, and therefore, a mixing time of 6 min was adopted to study catalytic performance for this reaction.

### 3.6. *Effect of the contact mode: "tight contact" versus "loose contact"*

The effect of the contact mode is very well known [6], and therefore is included in this work to show its relevance on the

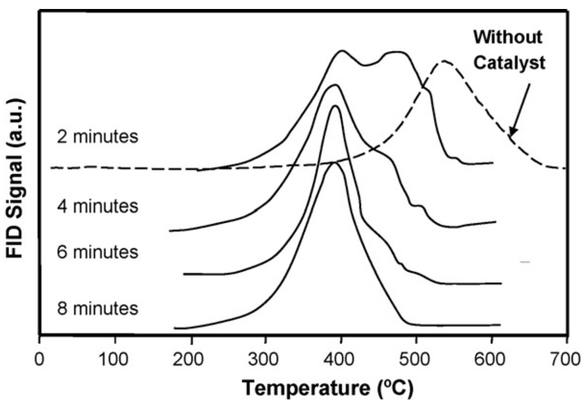

**Fig. 6.** TPO profiles for 10 mg of 20:1 mixtures of Ba,K/CeO$_2$ + soot (tight contact). Mixing time from 2 to 8 min.

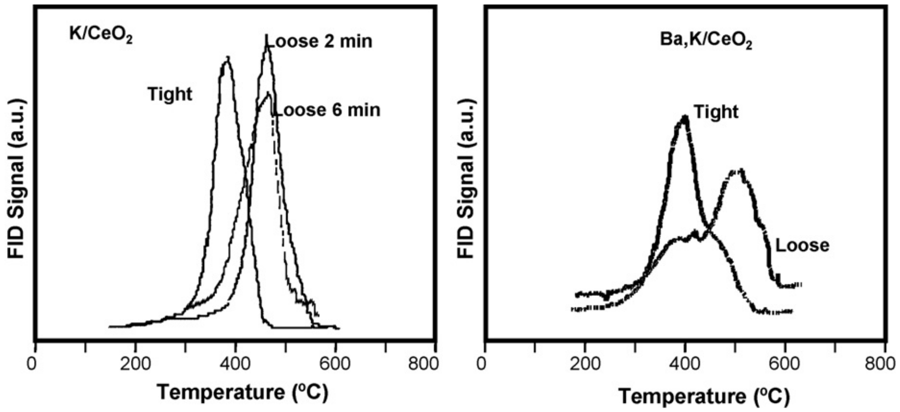

**Fig. 7.** TPO profiles for 10 mg of tight and loose contact of 20:1 mixtures of catalyst + soot. Catalysts: K/$CeO_2$ and Ba,K/$CeO_2$. Mixing time: 6 min if not indicated in the figures.

apparent activity of catalyst for soot combustion. Fig. 7 shows the TPO profiles corresponding to tight contact and loose contact mode for the same catalyst and for 6 min of mixing in both cases. The same results were obtained when using 2 and 6 min of agitation in loose contact. It can be observed a significant difference in activities when comparing both contact modes for the same catalyst. In loose contact, the activities of these catalysts, as the activities of most of the catalysts reported in the literature, are considerably lower than in tight contact mode. These results demonstrate that the reaction mechanism is very complex and that there are many factors to be taken into account when formulating a kinetic model. In this case, the simplified model proposed failed because in loose contact some soot particles react with oxygen with a non-catalytic reaction mechanism and it is extremely difficult to estimate a priori the proportion of soot reacting through this pathway.

## 4. Conclusions

This study shows that in order to compare soot combustion catalyst activities, it is necessary to adopt the appropriate experimental conditions that assure chemical control, runaway absence and that all the soot particles are in good contact with the catalyst.

In this paper the following experimental conditions were adopted in order to obtain intrinsic kinetic data during the soot combustion:

- a catalyst–soot mass ratio of 20:1,
- a flow rate of 40 ml/min, when loading 10 mg of sample, and the oxygen partial pressure is 0.05 bar,
- a mixing time of 6 min.

The importance of this study is to help researchers in selecting the experimental conditions to test catalysts in this complex system, and to facilitate the comparison of catalysts when the experiments are run under different conditions. In the present work it was shown that when using the same contact mode, such as "tight contact", and different mixing times, the catalytic activity considerably increased from 2 to 8 min of mixing.

An important contribution of this study is the demonstration that the power-law kinetic expression is very useful in order to predict the magnitude of the changes, which can be expected to occur in the TPO profile upon changes in the experimental variables, as long as the catalyst and soot are mixed in tight contact mode. These results provide information regarding the effect of flow rate, oxygen partial pressure, catalyst:soot ratio, mass loaded to the cell, and heating rate. A quantitative variable (reaction rate first derivative) has been found to be very useful to determine whether a reaction runaway is taking place in a system, and therefore an energy transfer limitation is masking the results.

The systematic change of each variable at a time, as shown in this work, is very useful in assessing the reaction regime under which the experimental setup is working. The reaction system is quite complex, and therefore this type of verification should be carried out before catalyst evaluation.

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