

Kinetics of catalytic carbon black oxidation

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Abstract

Kinetics of the catalyzed oxidation of carbon black (CB) in the presence of Ce–Al oxides is studied. The activation energies for CB combustion are determined from the DTA–TG data. The catalysts performances are compared on the basis of thermal analysis and calculated kinetic parameters. In this investigation, a convenient method for the rapid calculation of the kinetic parameters from single DTA–TG curves is proposed.

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1. Introduction

The emission of carbon particles in the atmosphere has led to serious environmental problems. Catalytic oxidation of the soot is one of the solutions proposed for the reduction of particulate emissions. Catalyst can be added either through the fuel, in which case it is incorporated into the soot spherules as they form, or physically mixed in after collection of soot. The latter would correspond to the case of a soot filter whose surface is impregnated with catalyst via a wash coat [1,2]. Ceria oxide (CeO₂) is an important constituent of the redox catalysts [3]. Three main properties make ceria an essential component in such catalysts: its oxygen storage capacity (OSC) [3], its redox properties (Ce⁴⁺/Ce³⁺) and its thermal stabilizing influence on alumina [4,5]. Moreover, literature data show that ceria oxide is very active for catalytic soot combustion [1,2,6–9]. The presence of cerium additives favors the reactivity of the doped soot and shifts the combustion reaction towards low temperatures [8,9]. Cerium-coated traps are also found to be effective for catalytic soot oxidation [1].

Some research has been performed on the kinetics of non-catalytic and catalytic soot oxidation [2,9–13]. Data from kinetics and mechanism studies of the catalyzed oxidation of soot might help in developing more active or selective soot oxidation catalysts. Differential thermal analysis and thermogravimetry (DTA–TG) has been widely studied by many investigators in order to evaluate kinetic parameters [11–17]. Most of the methods are very complicated and have to be solved by a trial and error approach to obtain the values of activation energy and pre-exponential factor of Arrhenius equation [14–17]. Some of them require a supplementary experiments and variations of different parameters, such as heating rate. In this work, we propose a convenient method for the rapid calculation of the kinetic parameters from single DTA–TG curves. The objective of this study is to compare the Ce–Al–O catalysts for CB oxidation according to its activity and kinetic parameters.

2. Experimental

2.1. Catalysts preparation

Alumina is synthesized by sol–gel method [18]. Secondary aluminum butylate (Al(OC₄H₉)₃, Fluka, ~11.0 wt.%)

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Table 1
Composition of the solids^a

Sample	CeO ₂ (wt.%)	Specific area (m ² /g)
Al ₂ O ₃	–	360
1Ce10Al	25.23	241
3Ce10Al	50.31	144
10Ce10Al	77.14	99
CeO ₂	100	53

^a The number before chemical symbol represents the atomic content in the solid.

Al) is dissolved in butan-2-ol (Fluka, purity $\geq 99.5\%$) at 85 °C. Then, complexing agent (butan-1,3-diol, Fluka, purity $\geq 98\%$) preliminarily heated at 60 °C is added before hydrolysis. Hydrolysis is performed by addition of water to the solution at 85 °C. The gel is dried and calcined at 500 °C for 6 h with a temperature rate of 0.5 °C/min before used as support for preparing the Al₂O₃-supported CeO₂ catalysts. With this method, alumina is characterized with specific area of 360 m²/g and pore volume of 2.3 mL/g. The diameter of alumina grains varies between 0.6 and 4.7 μm . There are also a lot of little grains of 0.1 μm .

Ceria is prepared by precipitation of Ce(NO₃)₃·6H₂O (Prolabo, total amount of rare earth oxides is 99.5%) in an ammonia aqueous solution (0.7 mol/L). The solid is filtered, washed, dried at 100 °C and calcined at 600 °C for 4 h with a temperature rate of 0.5 °C/min.

Different Ce–Al oxides are prepared by incipient wetness of cerium nitrate solution onto alumina pre-calcined at 500 °C. Then the sample is dried at 100 °C and calcined for 4 h in a flow of dry air at 600 °C. Cerium-containing solids are denoted 1Ce10Al, 3Ce10Al and 10Ce10Al where the number before chemical symbol represents the atomic content in the solid. Table 1 summarizes the composition of Ce–Al–O catalysts.

2.2. Activity tests

Commercial available carbon black (CB) (N330 Degussa: 97.23 wt.% C, 0.73 wt.% H, 1.16 wt.% O, 0.19 wt.% N, 0.45 wt.% S) is used as a model soot. The average diameter of the CB spherical particle is 0.08–0.25 μm . Before the catalytic test, CB (10–20 wt.%) and catalyst (90–80 wt.%) are mixed in alumina ball miller for 40 min. It was shown that under practical conditions the contact between soot and catalyst is poor [19,20]. In our paper, we used the preparation method of the mixture of carbon black with the catalyst which gives more tight contact than in real conditions. It was chosen to use a mechanical mill to establish close contact between soot and catalyst in order to define an intrinsic catalytic activity under optimal conditions. The objective of this study is to rank the CB oxidation catalysts according to its activity and kinetic parameters, thus it is necessary to obtain the reproducible and comparable results. For this reason, some authors use the most reproducible method to prepare the

CB/catalyst mixtures for the kinetics studies of carbon black combustion [21]. In real conditions, the soot-to-catalyst ratio varies widely from 1/2.1 to 1/35, which is attributed to irreproducibility in the collection of soot on the catalyst powder and probably to the inhomogeneity of the layer of the catalyst on the filter [19]. In our study, we use carbon black-to-catalyst ratio of 1/5. This ratio is close to that for cerium-coated traps and the practical application for our results is rather justified.

The catalytic tests towards the combustion of CB are studied by simultaneous gravimetric and differential thermal analysis (TG–DTA) with a NETZSCH STA 409 apparatus. 10–50 mg of the CB/catalyst mixture is loaded in an alumina crucible and heated from room temperature to 700 °C (5 °C/min) in airflow (75 mL/min). In the experiments performed under isothermal conditions, the mixture of 20 mg was heated (5 °C/min) up to the reaction temperature (370, 380 and 390 °C) under airflow (75 mL/min) and then the oxidation was carried out at constant temperature till the total CB combustion.

3. Results and discussion

3.1. Carbon black catalytic combustion

Fig. 1 shows an example of TG–DTA curves. A weight loss of ~ 20 wt.% is observed on TG curve, corresponding to the combustion of the total mass of carbon black. The TG curve gives the temperature values T_i (beginning of the carbon black combustion) and T_f (complete conversion of carbon black). The maximum of DTA curve (T_m) corresponds to the temperature of the highest combustion velocity. The value $\Delta T = T_f - T_i$ determines the reaction velocity. Catalytic properties of the solids are evaluated by comparing the values of T_m and ΔT with those of CB combustion without catalyst in the same conditions.

According to the literature data, the sample mass can significantly influence the results of TG–DTA [22–25]. For this study, the mixture of 10 wt.% CB with 90 wt.% CeO₂ is prepared and five sample masses are used: 10, 20, 30, 40 and

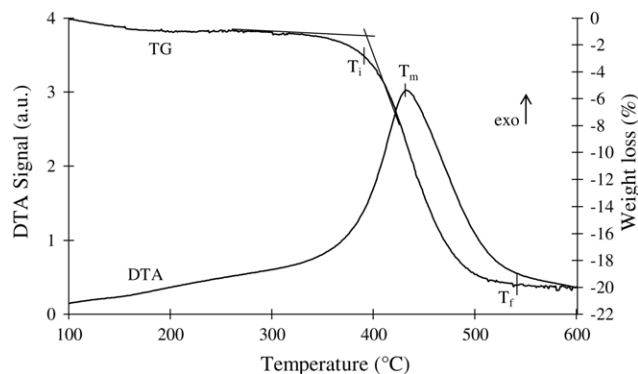


Fig. 1. Example of DTA–TG curves.

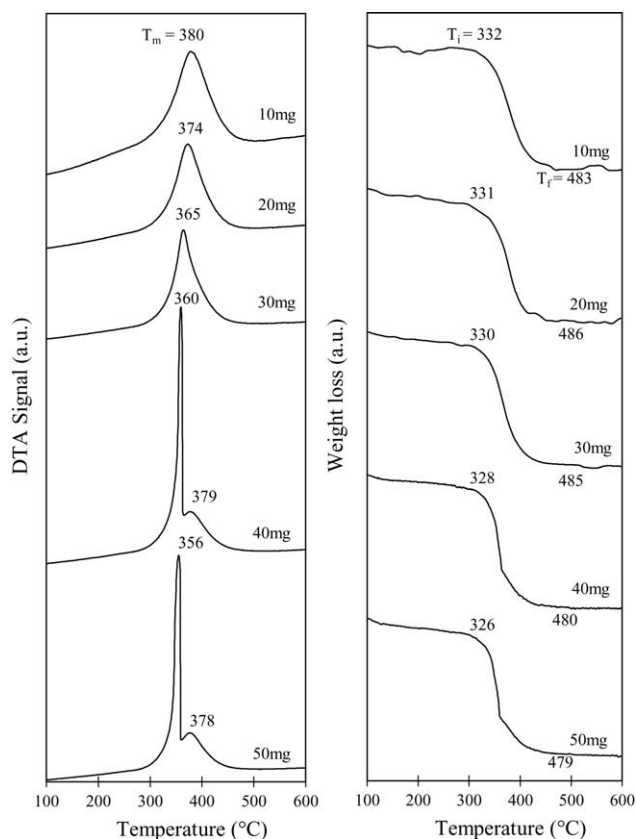


Fig. 2. Evolution of the DTA–TG curves as a function of sample mass for the mixture of 10% CB + 90% CeO₂.

50 mg. Fig. 2 presents the results of TG–DTA obtained during the combustion of the samples. As shown in this figure, the form of the signals varies with the sample masses. For the sample masses below than 30 mg, one exothermic peak is observed on DTA curve which is accompanied by the weight loss in one stage. For higher sample masses, two peaks are observed and the weight loss passes into two stages. The first peak is steep and sharp, whereas the second peak is broad and smooth. The temperatures at the maxima of these second peaks coincide reasonably well with the temperatures at the maxima of the peaks obtained for the smaller samples without the runaway peak. Thus, part of the carbon black is burned fastly in a steep runaway peak, while the second part combustion is slower and takes part at higher temperatures. This phenomenon can be explained by mass and heat transfer limitations [7,22–25]. Indeed, the oxygen diffusion influences significantly the kinetics of carbon black combustion. The more larger the sample mass, more higher is the level of the sample placed in the crucible. Thus, oxygen of air has more difficulties to diffuse in the bulk of the mixture. In addition, during the combustion of the sample center, the heat flow limits the oxygen transfer.

Fig. 3 shows the reactivity of Ce–Al–O catalysts in CB combustion. For the non-catalyzed reaction, the combustion

of CB occurs between $T_i = 540^\circ\text{C}$ and $T_f = 630^\circ\text{C}$ and insignificant difference is observed when the reaction is performed in the presence of Al₂O₃. For the other samples, combustion temperature decreases, showing the reactivity of ceria-based catalysts. Ceria oxide is the most reactive sample with a combustion temperature T_m of 389°C . For the Ce–Al oxides, reactivity increases with increasing ceria content. Thus, the temperature T_m decreases from 584°C for the 1Ce10Al sample to 473°C for the 3Ce10Al sample and to 411°C for 10Ce10Al sample. Comparing the ΔT values, the slight increase of the reaction rate can be observed with the increase of ceria content in the catalyst. Thus ΔT falls from 170°C for 3Ce10Al to 130°C for CeO₂. However, non-catalyzed CB combustion occurs within more narrow temperature range with ΔT of 90°C . Nevertheless, all the characteristic temperatures of non-catalyzed CB combustion are higher than those for CB combustion in the presence of catalyst.

3.2. The kinetic parameters calculation

3.2.1. Non-isothermal conditions

The temperature T_m depends on heating rate and sample mass, thus it is more reasonable to characterize the catalyst activity using the rate constant. At different temperatures, the rate constant is determined by Arrhenius equation:

$$k = k_0 e^{-(E_a/RT)} \quad (1)$$

where k is the rate constant, k_0 the pre-exponential factor, E_a the activation energy, R (8.314 J/mol K) the gas constant and T the temperature of the reaction.

In this paper, the convenient method is proposed to calculate the activation energy and pre-exponential factor using one TG and one DTA curve. This method allows to obtain the exact solution according to the model proposed without any complementary approaches. The method can be described here as follows.

The expression for the solid-state oxidation reaction under the constant oxygen concentration can be written as

$$\frac{dm}{dt} = -k_0 e^{-(E_a/RT)} m^n \quad (2)$$

where m is the mass of the substance, t the time and n the reaction order. The unit for the pre-exponential factor k_0 in the system SI is kg^{1-n}/s . But in our paper the unit for k_0 was selected as mg^{1-n}/s in order to be consistent with the sample mass units.

Mass transfer and oxygen depletion can influence the results and lower the apparent activation energy [22–26]. However, the purpose of our calculations is to compare the apparent kinetic parameters for different catalysts for CB combustion. These parameters are useful for the mathematical modeling of combustion process as far as for the analysis of catalysts activity at different temperatures. The catalytic tests for every catalyst were carried out at the same conditions, thus we can provide the catalysts comparison even without

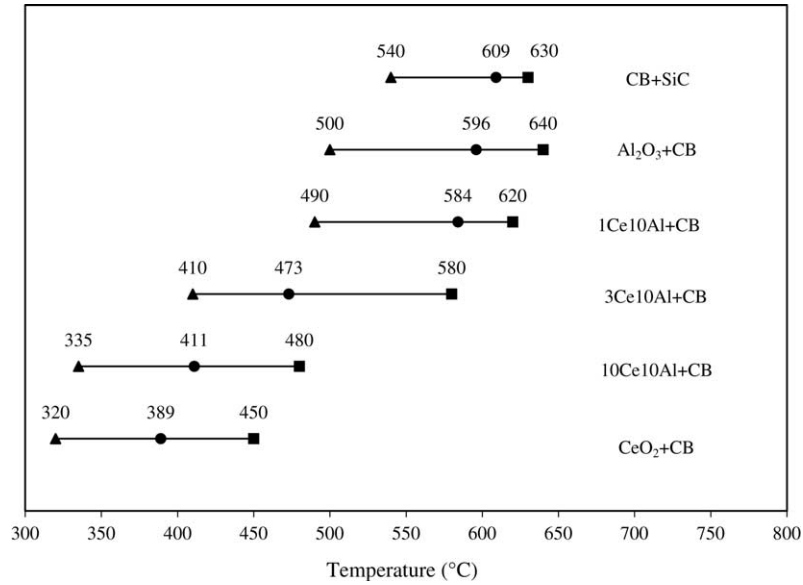


Fig. 3. The characteristic temperatures of carbon black combustion in the presence of Ce–Al oxides: (▲) T_i (beginning of the carbon black combustion); (●) T_m (temperature of the maximum of the DTA curve); (■) T_f (complete conversion of carbon black).

information about the detail mechanism of the process, as oxygen transfer limitations and oxygen depletion. Apparent parameters can be the functions of elementary stages rate constants and contain, for example, the diffusion coefficient and oxygen mass transfer coefficients. If oxygen concentration also influences the rate of oxidation, equation for k_0 can be written as

$$k_0 = k'_0 f(CO_2) \quad (3)$$

In this case, the unit for k_0 rests the same (mg^{1-n}/s), but the unit for k'_0 is $mg^{1-n}/(s f(\text{mol/L}))$. Even if the oxygen diffusion limitations and oxygen depletion take place, they will influence all of the apparent kinetic parameters at the same time and our results are comparable.

Under constant heating rate, the temperature is a linear function of the time during the experiment:

$$T = T_0 + \beta t \quad (4)$$

where T_0 is the initial temperature and β the heating rate.

In this case

$$dT = \beta dt \quad (5)$$

and Eq. (2) takes the following form:

$$\frac{dm}{dT} = -\frac{k_0}{\beta} e^{-(E_a/RT)} m^n \quad (6)$$

The point of inflection on TG curve occurs when

$$\left(\frac{d^2m}{dT^2}\right)_{\text{inf}} = 0 \quad (7)$$

Substitution of Eq. (6) into Eq. (7) yields

$$\frac{k_0}{\beta} \left[nm_{\text{inf}}^{n-1} \left(\frac{dm}{dT}\right)_{\text{inf}} e^{-(E_a/RT_{\text{inf}})} + m_{\text{inf}}^n e^{-(E_a/RT_{\text{inf}})} \times \left(-\frac{E_a}{R}\right) \left(-\frac{1}{T_{\text{inf}}^2}\right) \right] = 0 \quad (8)$$

where m_{inf} is the mass of the substance in the point of inflection on TG curve.

The transformation of Eq. (8) gives

$$\frac{E_a}{n} = -\frac{RT_{\text{inf}}^2}{m_{\text{inf}}} \left(\frac{dm}{dt}\right)_{\text{inf}} \quad (9)$$

The dependence of DTA curve from the temperature is described by the following equation:

$$E = \alpha \frac{dm}{dT} \quad (10)$$

where α is the proportionality constant and E the DTA signal.

The maximum of DTA curve will occur when

$$\left(\frac{dE}{dT}\right)_m = 0 \quad (11)$$

Taking into consideration Eqs. (7) and (11), it is possible to demonstrate that

$$T_{\text{inf}}(\text{TG}) = T_m(\text{DTA}) \quad (12)$$

and Eq. (9) is changed for

$$\frac{E_a}{n} = -\frac{RT_m^2}{m_{\text{inf}}} \left(\frac{dm}{dT}\right)_{\text{inf}} \quad (13)$$

Thus, when the peak temperature and the sample mass in the point of inflection are known, the relation E_a/n can be

calculated. It is necessary to find T_m on the DTA curve (the temperature of maximum), which according to Eq. (12) coincides with T_{inf} on TG curve (the temperature of inflection). After this the value of m_{inf} (the mass of inflection) on TG curve can be found. Then linear approximation of the TG curve near the point of inflection gives $(dm/dT)_{inf}$ and accordingly E_a/n by Eq. (13).

Taking into account Eq. (10), the kinetic equation (2) for the curve DTA is transformed as

$$E = \alpha k_0 e^{-(E_a/RT)} m^n \quad (14)$$

Eq. (14) is divided by m^n and taking the logarithm gives

$$\ln\left(\frac{E}{m^n}\right) = \ln(\alpha k_0) - \frac{E_a}{RT} \quad (15)$$

The approximation of the dependence of $\ln(E/m^n)$ versus $1/T$ by linear function gives the value of activation energy E_a according to Eq. (15).

From Eqs. (6) and (12), the expression for k_0 is following:

$$k_0 = \frac{\left(\frac{dm}{dT}\right)_{inf} e^{(E_a/RT)} \beta}{m_{inf}^n} \quad (16)$$

The shrinking core model, used for CB combustion processes, requires that reaction order n be $2/3$. In this model, the rate of combustion is proportional to the surface of the CB spherules [10]. However, some authors conclude that internal burning takes place during the oxidation of CB at the low temperatures [2]. In the case of complete internal burning, the oxidation rate is proportional to the remaining mass, i.e. $n = 1$. Partial internal burning will result in n being between this value and that for the surface burning case, which gives shrinking core behavior ($1 > n > 2/3$). Thus we calculated our data with the both values for n of 1 and $2/3$ in order to compare the values for E_a obtained with those in the literature. For more precise calculations, the fractal character of CB surface should be taken into account [27] that will be done in our future work.

The kinetic parameters derived from the TG–DTA data for CB combustion in the presence of Ce–Al oxides are presented in Table 2. Using the reaction order value of $2/3$ in Eq. (15), the oxidation of CB in the presence of Al_2O_3 has activation energy value of 163 kJ/mol. Since alumina does not present catalytic activity in the reaction of CB combustion, the oxidation of CB in the presence of Al_2O_3 may be comparable with non-catalyzed CB oxidation. Low-temperature

activation energy for non-catalytic CB combustion is found to cover a range, namely between 102 and 210 kJ/mol [2,9,10]. Values between 140 and 170 kJ/mol appear frequently. The activation energy obtained for CB + Al_2O_3 mixture in this work is similar close to the reported experimental values of 168 kJ/mol [10] and 164 kJ/mol [13] for non-catalytic soot oxidation. Probably, in the case of uncatalyzed CB combustion, the contribution of internal burning is less important and the shrinking-core behavior applies with a value of n close to $2/3$ [10].

It is evident that the presence of ceria has significant influence on the CB oxidation kinetics. Catalyst reaction mechanisms are evidently different from the uncatalyzed condition. The catalyst generally lowers activation energy, typically by 30–80 kJ/mol, that is from 170 to 120 and 151 to 100 kJ/mol [2]. The rate of the reaction can be influenced by the activation energy and by the pre-exponential factor. The decrease of activation energy and/or the increase of pre-exponential value leads to the increase of the combustion rate, clearly shown in our case by the decrease of T_m and ΔT . From Table 2, we can see that the sample 1Ce10Al has low activity in CB combustion. We assume that the reaction order is also $2/3$ for CB + 1Ce10Al combustion. Activation energy (169 kJ/mol) and $\ln k_0$ (18.1) are also close to those of non-catalytic combustion. The calculation of E_a for the samples 3Ce10Al, 10Ce10Al and CeO_2 with a value for n of 1 in Eq. (15) gives the results more close to literature data, than with a value for n of $2/3$. It is possible that the internal burning takes place during catalytic oxidation of CB. These catalysts are active in the reaction of CB combustion and they change the kinetics of the process. In the case of 3Ce10Al catalyst, the activation energy (119 kJ/mol) is lower than for non-catalytic CB combustion and the value of $\ln k_0$ is also low (12.7). The most active catalysts are 10Ce10Al ($E_a = 90$ kJ/mol, $\ln k_0 = 9.4$) and CeO_2 ($E_a = 90$ kJ/mol, $\ln k_0 = 10$). The activation energy for these systems is rather low and the value of k_0 is significantly high. The choice of n ($n = 2/3$ or 1) in Eq. (13) leads to values for E_a which agree with those derived from Eq. (15) (Table 2). It means that our method is useful for DTA–TG data obtained.

Using the activation energy and k_0 we can evaluate the dependence of catalyst activity from the temperature due to Arrhenius equation in logarithmic form. The linear dependence of $\ln k_0$ versus $1/T$ for the Ce–Al–O systems is presented in Fig. 4. From this figure, it is possible to create the following row of activity increase $Al_2O_3 \approx$

Table 2
Kinetic parameters of carbon black catalytic combustion in the presence of Ce–Al oxides^a

Catalyst + CB	T_m (°C)	E_a/n (kJ/mol) (Eq. (13))	E_a (kJ/mol) (Eq. (15))		$\ln k_0$ (Eq. (16))	
			$n = 2/3$	$n = 1$	$n = 2/3$	$n = 1$
Al_2O_3 + CB	595	252	163	251	19.2	31.4
1Ce10Al + CB	584	233	169	250	18.1	29.5
3Ce10Al + CB	473	117	75	119	5.9	12.7
10Ce10Al + CB	411	83	63	90	5.0	9.4
CeO_2 + CB	389	78	65	90	5.7	10.0

^a Standard deviation is 20%.

Table 3
Kinetic parameters of carbon black combustion in the presence of cerium oxide^a

Kinetic parameter	Equation	Sample		
		80% CeO ₂ + 20% CB (20 mg)	80% CeO ₂ + 20% CB (40 mg)	90% CeO ₂ + 10% CB (20 mg)
T_m (°C)	–	385	389	374
E_a/n (kJ/mol)	(13)	78	78	93
E_a ($n=1$) (kJ/mol)	(15)	89	90	105
$\ln k_0$ ($n=1$)	(16)	8.6	10.0	11.7

^a Standard deviation is 20%.

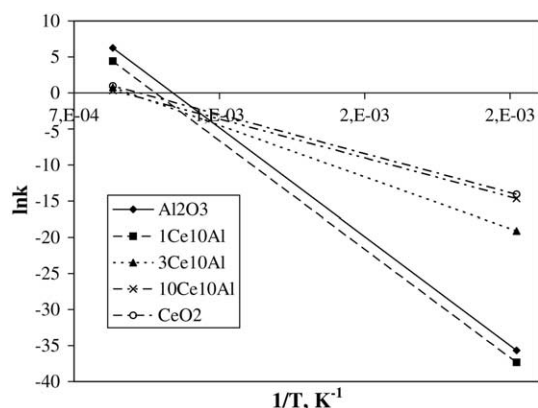


Fig. 4. Arrhenius plots of carbon black combustion in the presence of Ce–Al oxides.

$1\text{Ce}10\text{Al} < 3\text{Ce}10\text{Al} < 10\text{Ce}10\text{Al} \approx \text{CeO}_2$. These data are in accordance with those obtained for catalytic tests. Thus, the activity of the catalyst revealed from TG–DTA data (Fig. 3) and from the kinetic parameters (Table 2) correlate with each other.

To verify our method, for the most active catalyst CeO₂ we calculated the kinetic parameters for the TG–DTA data of the mixtures of 40 and 20 mg (80% CeO₂ + 20% CB) and 20 mg (90% CeO₂ + 10% CB). The values for activation energy and $\ln k_0$ calculated from Eqs. (13), (15) and (16) for these systems are presented in Table 3. It should be noted that for the sample of 40 mg the calculations were carried out for the second exothermic peak. From Table 3, we can conclude that for the mixtures of CB with the same catalyst CeO₂ but with different sample mass (20 and 40 mg) the value for E_a/n is the same (78 kJ/mol). For the systems with the dif-

ferent percentage of CB (10 and 20%) the value for E_a/n differs at 20% that could be regarded as comparable results (78 and 93 kJ/mol). The values of E_a calculated from Eq. (15) correlates with those calculated from Eq. (13) taking $n=1$. In addition, the values of activation energy for different systems CeO₂ + CB are close to each other (taking into consideration 20% error). It indicates that the method proposed is useful for CB combustion.

3.2.2. Isothermal conditions

To verify the activation energies determined from non-isothermal conditions, the reaction of CB combustion in the presence of CeO₂ was carried out at constant temperatures (370, 380 and 390 °C). The isothermal curves are shown in Fig. 5. For the three isothermal experiments, the loss of CB before reaching the isothermal temperature is negligible, thus the isothermal data are comparable.

The kinetics of soot combustion under isothermal conditions is described by the following differential equation:

$$\frac{dm}{dt} = -km^n \quad (17)$$

where $m(t=0) = m_0$.

If the reaction order is 1, Eq. (17) gives

$$\frac{dm}{dt} = -km \quad (18)$$

The transformation of Eq. (18) gives

$$\frac{dm}{m} = -k dt \quad (19)$$

or

$$\ln m - \ln m_0 = -kt \quad (20)$$

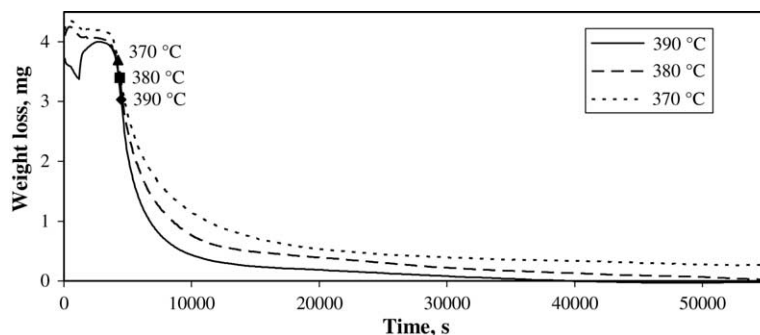


Fig. 5. Isothermal curves for the mixture of 20 mg (20% CB + 80% CeO₂) at 370, 380 and 390 °C.

Thus, the rate constant can be determined with the help of Eq. (20) by the approximation of the dependence $\ln(m(\text{CB}))$ versus the time by the linear function for every isotherm. The region of the linear approximation was chosen as the first 60 min of the curve. Then using the Arrhenius equation, the activation energy was calculated. The values for E_a of 96 kJ/mol and for $\ln k_0$ of 11.3 were obtained. The values for activation energies, obtained for the same sample treated at different conditions (during the TG–DTA analysis and under isothermal conditions) gives the comparable results (89 and 96 kJ/mol). Thus two independent methods give the same values for activation energies. It permits us to conclude that they both adequately describe our experimental data.

4. Conclusion

The catalytic combustion of carbon black has been investigated in the presence of Ce–Al oxides. Catalytic tests show that Al_2O_3 does not influence CB combustion. Cerium oxide is the most reactive catalyst. CeO_2 is capable of lowering the temperature of the maximum of the carbon black combustion from 609 to 389 °C. For the Ce–Al oxides, reactivity increases with increasing ceria content. The kinetic parameters of carbon black catalytic combustion were calculated using the DTA–TG data. The activation energy of non-catalytic CB oxidation is 163 kJ/mol and the order in carbon is 2/3. Ceria lower activation energy to 90 kJ/mol and change the reaction order for 1. The activity of the catalysts correlates with their kinetic parameters.

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