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# Effect of thermal aging upon the regeneration kinetics of a coked $Cr_2O_3$–$Al_2O_3$ catalyst

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**Abstract**

The effect of thermal aging on the combustion kinetics of coke deposited on a commercial $Cr_2O_3$–$Al_2O_3$ catalyst has been studied. Catalyst aging was produced in several operation and regeneration cycles involving high temperatures and the alternate use of reducing or steam-containing oxidizing atmospheres. As a consequence of aging, the intrinsic regeneration constant decreased, while the activation energy remained unchanged compared with that of the fresh catalyst. This indicates that the regeneration mechanism is not modified, and the effect of catalyst aging is to reduce the number of active regeneration sites on the surface through a partial sintering process.

*Keywords:* Catalyst aging; Coke combustion; Regeneration kinetics

## 1. Introduction

Catalyst coking has great economic importance because of the large number of processes affected in the chemical and petrochemical industry [1–3]. Due to coking, the activity, and often the selectivity, of a given catalyst decreases with time on stream, to values which make it necessary to replace or to regenerate the catalyst. Therefore, a fixed bed reactor in which coking takes place must be used in operation and regeneration cycles. The moment at which regeneration should take place must be determined for each particular process. It is clear that in addition to process economics

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the kinetics of the main reaction and of the coking and regeneration processes play a fundamental role in determining the relative durations of the operation and regeneration cycles.

The preferred method of regeneration of coked catalysts involves the combustion of the coke deposits with oxygen-containing mixtures [4]. The rate of combustion, and hence the heat released in the exothermic combustion of coke, depends on the concentration of oxygen in the reactor feed, which must be carefully controlled. Air diluted with nitrogen or steam is usually employed in order to bring the oxygen concentration down to a sufficiently low level. Otherwise, the large exothermicity of the process would cause a high temperature rise, which can lead to the sintering of the catalyst and/or damage to the reactor.

In view of the above, a suitable regeneration strategy is needed; this should be capable of achieving sufficiently fast regeneration while at the same time limiting the maximum temperature increase in the reactor. This has given rise to numerous theoretical studies in which catalyst regeneration is simulated, with the aim of determining the optimum process conditions. The $Cr_2O_3$–$Al_2O_3$ catalyst in particular is a well studied system from this point of view [5, 6].

In the development of operation strategies it must be taken into account that, as the catalyst ages in successive operation–regeneration cycles, its kinetic behaviour may undergo considerable changes in respect of the fresh catalyst. This means that the reaction kinetics determined in the laboratory with fresh catalyst samples may no longer be valid after the catalyst has been used for some time. Thus, for a $Cr_2O_3$–$Al_2O_3$ catalyst used in the dehydrogenation of butene to butadiene it has been shown that the kinetics of the main reaction [7], and of the coking reaction [8], are significantly different for fresh and aged catalysts. In both cases, the kinetic variations were related to the sintering processes that take place during catalyst aging.

In addition to the kinetics of coking and of the main reaction, the coke combustion kinetics must also be known in order to plan reactor operation in general and the regeneration part of the cycle specifically. Because of this, many investigations have dealt with kinetic studies of the combustion of coke on different types of catalyst. Two different situations can be considered. The first involves the burning of the coke deposited on catalysts that do not catalyze the combustion of the coke deposits, such as silica–alumina catalysts (e.g. Ref. [9, 10]). The second situation arises when, in addition to the main reaction, the catalyst is also active in promoting coke combustion. This has been found for a number of studies on catalysts containing transition metals (e.g. Refs. [11–14]), some of them directly on $Cr_2O_3$–$Al_2O_3$ catalysts.

Despite the experimental evidence showing that catalyst aging can significantly change the performance of a given catalyst, the possible modification of the coke combustion kinetics for aged catalysts has gone largely unresearched. In this work, the kinetics of combustion of the coke deposited on an aged commercial $Cr_2O_3$–$Al_2O_3$ catalyst have been determined, and compared to those observed for the fresh catalyst. The results presented are also a useful means to illustrate how different fitting methods can be used to obtain the kinetic parameters of a relatively difficult system in which high reaction rates are taking place.

## 2. Experimental

The kinetics of combustion of the coke deposited on fresh and aged catalysts were determined in a thermobalance (C.I. Instruments MK2), fitted with automatic control of flow (Brooks mass flow controllers) and temperature. The weight data were acquired at regular intervals using a computer-controlled data logging system. Weight data were automatically collected at regular intervals with an accuracy of $10^{-5}$ g. In a typical run, several hundred data points relating coke weight and time were obtained. Catalyst samples around 40 mg were used, with particle diameters between 100 and 200 microns.

Prior to the regeneration kinetics experiments, catalyst coking was achieved during the dehydrogenation of butene to butadiene, carried out in a separate reaction system over either fresh or aged $Cr_2O_3$–$Al_2O_3$ catalysts, at temperatures of 580°C. The usual coke loadings at the start of the regeneration kinetic experiments were between 2.5 and 3.6% by weight.

Given the high reaction rates encountered in this system, special precautions were taken to ensure the absence of significant interference from transport processes. These have been explained previously [14], and affected the ranges of particle diameter, oxygen partial pressure, total flow rate and sample weight employed, as well as the design of the sample holder.

The aging of the catalyst was accelerated in a separate unit, by using a procedure similar to that described in previous work [7, 8]. It consisted of several (seven to twelve) operation and regeneration cycles in a fixed bed reactor, using 8% oxygen in the feed during the regeneration stage. Under these conditions, the exothermic combustion of the coke deposits gave rise to temperatures in excess of 850°C, i.e., a 400°C increase over the initial regeneration temperature of 450°C. In addition to the high temperatures reached, the alternation of oxidizing and reducing atmospheres during the operation and regeneration stages, and the evolution of steam during regeneration are thought to contribute to the rapid aging of the catalyst.

## 3. Kinetic model

The coke weight–time data gathered in the regeneration experiments have been fitted to a power-law model:

$$-\frac{\mathrm{d}W_C}{\mathrm{d}t} = k p_{O_2}^n W_C^m \tag{1}$$

where $k$ is the intrinsic regeneration constant, for which an Arrhenius-type dependence on temperature has been assumed:

$$k = k_m \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]; \quad k_m = k_0 \exp\left(-\frac{E_a}{R T_m}\right) \tag{2}$$

where $k_0$ is the preexponential factor, $E_a$ the activation energy and $T_m$ the reparametrization temperature, which was taken as 698 K, which was the average temperature in the range investigated. Defining coke conversion as:

$$X_C = \frac{W_{C_0} - W_C}{W_{C_0}} \tag{3}$$

Eq. (1) can be rewritten as:

$$\frac{dX_C}{dt} = k' W_{C_0}^{(m-1)}(1 - X_C)^m \tag{4}$$

where:

$$k' = k p_{O_2}^n \tag{5}$$

Depending on the value of $m$, the integration of Eq. (1) yields different results:

$$X_C = 1 - \exp(-k't); \qquad m = 1 \tag{6}$$

$$X_C = 1 - [1 + (m-1) W_{C_0}^{(m-1)} k' t]^{1/(m-1)}; \quad m \neq 1 \tag{7}$$

These equations can be linearized as follows:

$$f_1(X_C) = \ln\left(\frac{1}{1 - X_C}\right) = k't; \qquad m = 1 \tag{8}$$

$$f_m(X_C) = \frac{(1 - X_C)^{(m-1)} - 1}{(m-1) W_{C_0}^{(m-1)}} = k't; \quad m \neq 1 \tag{9}$$

The above expressions were used to fit the $X_c$–$t$ data obtained in experiments carried out at a given temperature and partial pressure of oxygen in order to calculate $k'$. On the other hand, taking into account the dependence of $k'$ on temperature and on the partial pressure of oxygen (Eqs. (2) and (5)), for a given value of $m$, the values of $E_a$, $k_0$ and $n$ can be obtained from plots of $k'$ versus temperature and partial presure of oxygen, respectively. Alternatively, $E_a$, $k_0$ and $n$ can be calculated directly from $X_c$–$t$ data using a non-linear multivariable fit.

A different possibility is given by dynamic experiments in which the temperature is varied following a known pattern, as opposed to isothermal experiments carried out at different but constant temperatures. If a temperature ramp of constant heating rate $\beta$ (°C min$^{-1}$) is used, the temperature of the system at time $t$ is given by:

$$T = T_0 + \beta t \tag{10}$$

where $T_0$ is the initial temperature. Under these conditions Eq. (4) does not have an analytical solution. The corresponding parameters can be calculated by coupling a numerical integration routine to the optimization algorithm employed. The value of $k$ is now replaced by:

$$k = \frac{k_0}{\beta} \int \exp(-E_a/RT) \, dT \tag{11}$$

which can now be used in Eq. (5), and then $k'$ can be used in Eqs. (6) and (7) to obtain the corresponding kinetic parameters. In the literature [15, 16], numerous alternative methods have been proposed for an approximate evaluation of Eq. (11).

## 4. Results

A set of isothermal experiments was carried out with fresh and aged catalysts at temperatures from 380 to 470°C, using oxygen partial pressures between 0.03 and 0.16 Atm. Eq. (6) gave the best fit of the conversion–time data, thus confirming $m = 1$, in agreement with previous results for this system [14]. Table 1 gives the values of $k'$ obtained by using Eq. (6) to carry out non-linear regression of experimental data at different temperatures and partial pressures of oxygen. Some of the conversion–time data obtained, corresponding to the fresh catalyst at different temperatures, are shown in Fig. 1. Fig. 2 shows the comparison of the conversions obtained with fresh and aged catalysts at three different temperatures. The corresponding fit of the data by Eq. (6) is also shown in Figs. 1 and 2. It can be seen that a very good fit was obtained for both catalysts at all the temperatures investigated.

The comparison of the performance of both catalysts at a given temperature in Fig. 2 shows that the combustion of the coke deposited on fresh catalyst always proceeds at a much faster rate. This indicates the influence of catalyst sintering on the regeneration kinetics, thus confirming previous reports in the literature about the catalytic nature of the combustion of coke deposited on $Cr_2O_3$–$Al_2O_3$ catalysts [11, 12, 14].

Table 1
Values of the apparent kinetic constant $k'$, obtained in isothermal experiments at different temperatures and partial pressures of oxygen

| Oxygen partial pressure/Atm | Temperature/°C | $k' \pm$ S.E./$s^{-1}$ | |
|---|---|---|---|
| | | Fresh catalyst | Aged catalyst |
| 0.03 | 380 | $1.15 \times 10^{-3} \pm 10^{-5}$ | – |
| 0.03 | 390 | $1.62 \times 10^{-3} \pm 10^{-5}$ | – |
| 0.03 | 400 | $3.01 \times 10^{-3} \pm 4 \times 10^{-5}$ | – |
| 0.012 | 405 | $1.73 \times 10^{-3} \pm 3 \times 10^{-5}$ | – |
| 0.015 | 420 | $3.86 \times 10^{-3} \pm 6 \times 10^{-5}$ | – |
| 0.03 | 420 | $5.52 \times 10^{-3} \pm 8 \times 10^{-5}$ | – |
| 0.05 | 420 | $1.155 \times 10^{-2} \pm 3.8 \times 10^{-4}$ | – |
| 0.065 | 420 | $1.298 \times 10^{-2} \pm 4 \times 10^{-4}$ | – |
| 0.105 | 420 | $2.123 \times 10^{-2} \pm 1.5 \times 10^{-3}$ | – |
| 0.12 | 420 | $2.993 \times 10^{-2} \pm 6.1 \times 10^{-4}$ | – |
| 0.16 | 420 | $4.507 \times 10^{-2} \pm 1.9 \times 10^{-3}$ | – |
| 0.012 | 435 | $4.51 \times 10^{-3} \pm 1.2 \times 10^{-4}$ | – |
| 0.03 | 440 | $1.511 \times 10^{-2} \pm 1.8 \times 10^{-4}$ | – |
| 0.03 | 455 | $1.848 \times 10^{-2} \pm 3.9 \times 10^{-4}$ | – |
| 0.03 | 470 | $2.14 \times 10^{-2} \pm 6.5 \times 10^{-4}$ | – |
| 0.03 | 390 | – | $4.43 \times 10^{-4} \pm 4.2 \times 10^{-6}$ |
| 0.03 | 410 | – | $8.91 \times 10^{-4} \pm 5.3 \times 10^{-6}$ |
| 0.03 | 420 | – | $1.45 \times 10^{-3} \pm 2 \times 10^{-5}$ |
| 0.03 | 430 | – | $2.21 \times 10^{-3} \pm 10^{-5}$ |
| 0.03 | 440 | – | $3.16 \times 10^{-3} \pm 3 \times 10^{-5}$ |
| 0.03 | 450 | – | $4.12 \times 10^{-3} \pm 4 \times 10^{-5}$ |

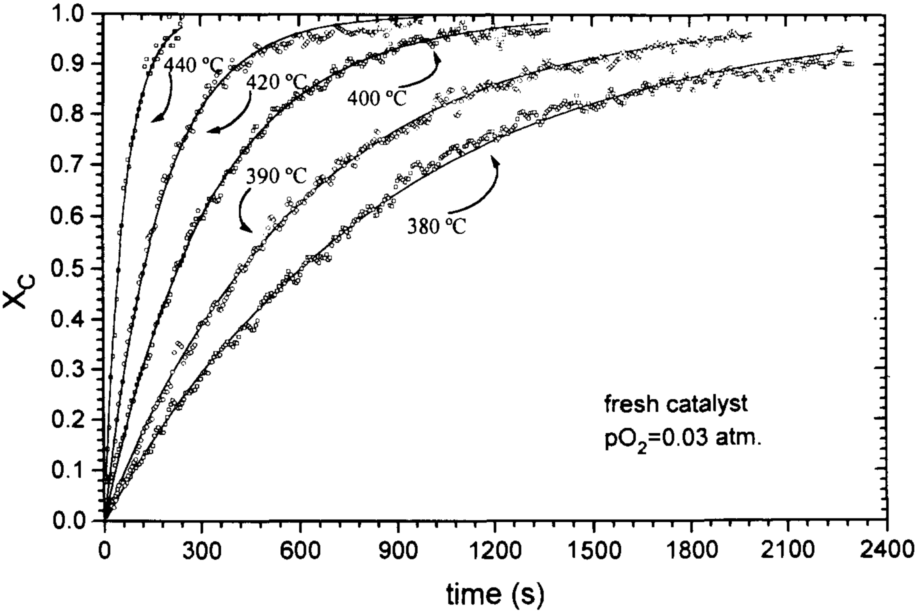
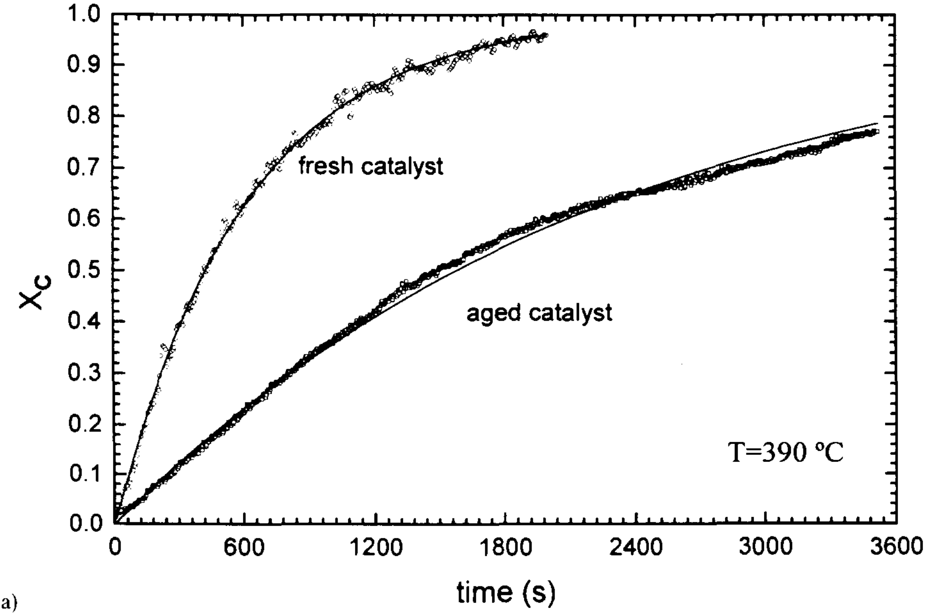


Fig. 1. Coke conversion versus time at different temperatures for the fresh catalyst.



(a)

Fig. 2. Comparison of coke conversion versus time at different temperatures for fresh and aged catalysts. $pO_2 = 0.03$ Atm. 2a: $T = 390$°C. 2b: $T = 420$°C. 2c: $T = 440$°C.

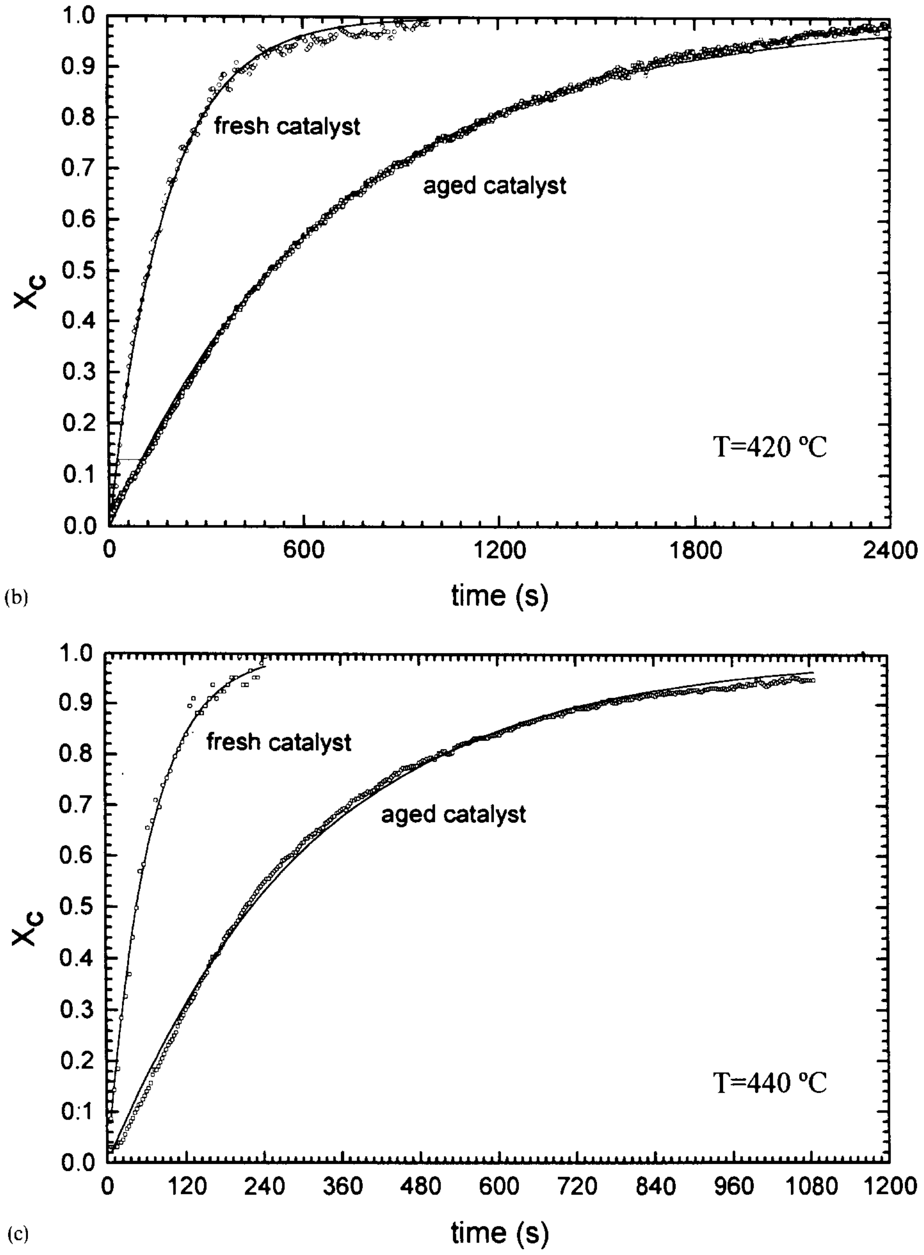


Fig. 2. (*Continued*).

The regression of the $k'$ values corresponding to different oxygen partial pressures in Table 1 yielded the kinetic order for oxygen as $0.944 \pm 0.068$, i.e., at the 95% confidence level the value of $n$ lies between 1.133 and 0.755, close to the value of 1 found in most kinetic studies (e.g. Refs. [9–14]). An Arrhenius plot of the values of $k$ obtained at different temperatures is shown in Fig. 3, and the corresponding Arrhenius parameters are given in column A of Table 2. It can be seen that approximately the same slope was obtained for both catalysts, which indicates that the activation energy remains unchanged, and suggests that the aging process does not affect the coke combustion

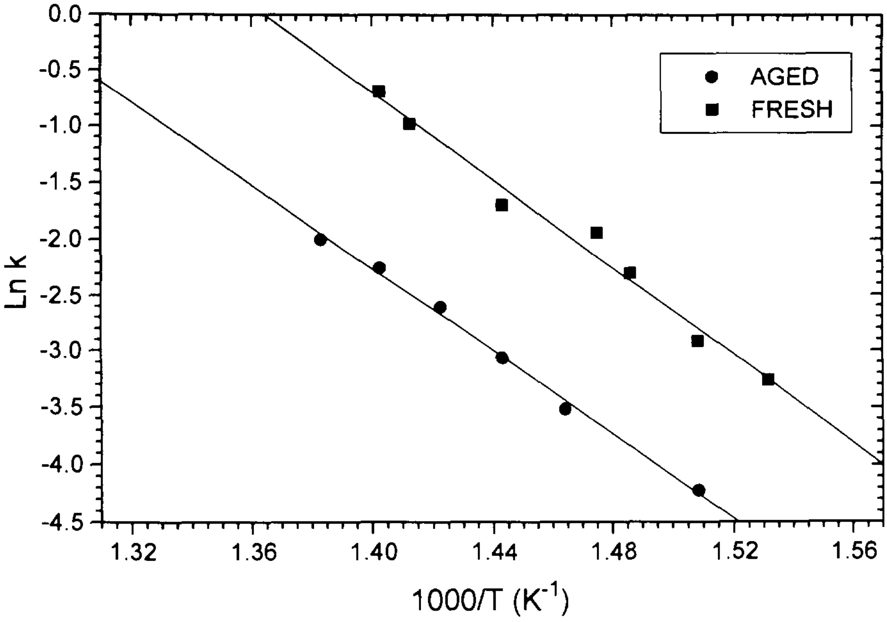


Fig. 3. Arrheius plot of $k$ for fresh and aged catalysts.

Table 2
Kinetic parameters obtained using different methods of data fitting

| | Isothermal experiments | | | | | | Dynamic experiments | |
|---|---|---|---|---|---|---|---|---|
| | A | | B | | C | | D | |
| | Linear regression of $k'$ (Table 1) | | Non-linear regression of $k'$ (Table 1) | | Non-linear, Multivariable regression of raw $X_c$–time data | | Non-linear regression of raw $X_c$–time data | |
| Catalyst | Fresh | Aged | Fresh | Aged | Fresh | Aged | Fresh | Aged |
| $k_m$/($Atm^{-1} s^{-1}$) | 0.25861 | 0.05838 | 0.11292 | 0.02762 | 0.13755 | 0.03116 | – | 0.03513 |
| S.E./($Atm^{-1} s^{-1}$) | 0.011347 | 0.00063 | 0.01106 | 0.00063 | 0.00043 | 0.0004 | – | 0.00014 |
| $E_a$/(kJ $mol^{-1}$) | 164.0 | 157.5 | 181.5 | 164.3 | 160.4 | 152.4 | – | 158.3 |
| S.E./(kJ $mol^{-1}$) | 9.4 | 6.4 | 13.0 | 5.9 | 0.8 | 0.3 | – | 0.5 |

mechanism. Alternatively, Table 2 also shows a non-linear fit of the $k'$ values of Table 1. Again, similar activation energies were found for the fresh and aged catalysts. This is consistent with the behaviour of the catalyst in the main and coking reactions [7, 8], where, despite a considerable reduction of the reaction rate, the activation energy was the same for the fresh and aged catalysts. Based on XPS characterization of both catalysts, [8], it was concluded that, although the same reaction mechanism was operating on the aged catalysts, a sintering process had taken place, which reduced the number of active sites for the reaction. This resulted in the same activation energies but lower values of the preexponential factor for the main and coking reactions on the aged catalyst, the same behaviour found in this work for the regeneration process.

Statistically, it is more rigorous, [17], to carry out non-linear multiple–variable regression using all the data (at different temperatures and partial pressures) simultaneously. Since with the aged catalyst all the experiments were carried out at the same partial pressure of oxygen, the fitting assumed that the same value of $n$ applied for fresh and aged catalysts. This gave a kinetic order for oxygen $n = 0.828 \pm 0.06$, similar to although lower than, that shown previously, [14], obtained from the fit of $k'$. The values of $k_m$ and $E_a$ are given in the third column (C), of Table 2. Again, it can be seen that the value of $k_m$ is considerably lower for the aged catalysts, while the activation energies for fresh and aged catalysts remained very similar. In fact, when the activation energy obtained for the fresh catalyst, (160.4 kJ mol$^{-1}$), was used to fit the data corresponding to the aged catalyst, the value of $k_m$ obtained was $0.03219 \pm 0.00043\,(\text{Atm s})^{-1}$, very similar to that shown in Table 2.

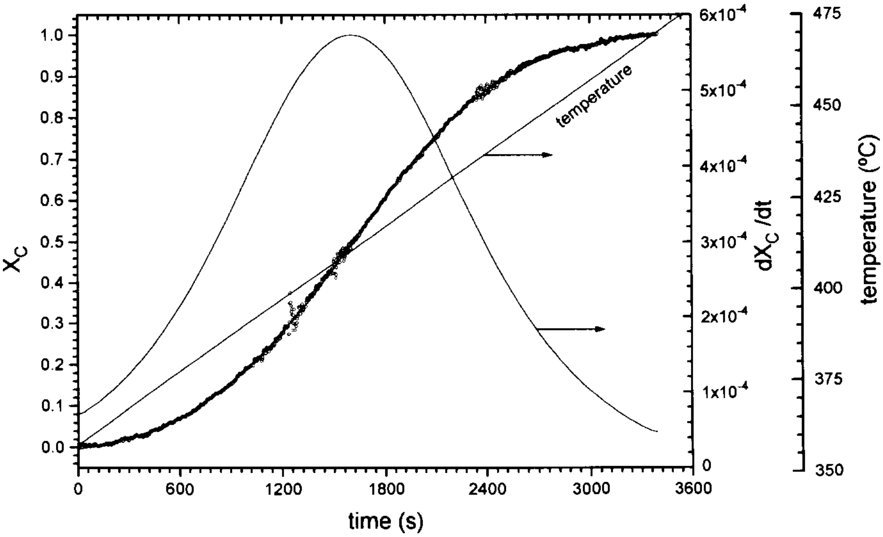


Fig. 4. Coke conversion, temperature and weight derivative in a dynamic experiment.

Finally, a dynamic experiment was also carried out under a temperature ramp of 2°C $\text{min}^{-1}$ and a fixed partial pressure of oxygen of 0.03 Atm. The initial coke content of the sample was 3.6 wt%, and other experimental conditions were the same as those used in isothermal experiments. The evolution of coke conversion with time is shown in Fig. 4, together with the temperature ramp and the calculated derivative of the weight curve, which shows a maximum at a temperature of approximately 410°C. The fit of the conversion–time data (using Eqs. (6), (10) and (11)), was excellent, as evidenced by the narrow standard errors quoted for $k_m$ and $E_a$ in column D of Table 2. The values given for $k_m$ and $E_a$ are very similar to those obtained from isothermal experiments (e.g. column C of Table 2). It must be noted that, given the fast reaction rates encountered and the high exothermicity of the combustion reaction, on an a priori basis, the study presented in this work could be expected to show significant deviation between kinetic and dynamic experiments. The fact that, despite this, very similar parameters are obtained indicates that if relatively simple kinetics are applicable, dynamic experiments can provide an accurate estimate of the kinetic parameters, with considerable economy in experimental effort.

## 5. Conclusions

The results presented in this work confirm the catalytic effect of chromia upon coke combustion kinetics, in agreement with other reports in the literature [11, 12, 14]. However, unlike previous studies, the issue of the influence of catalyst aging on the regeneration kinetics has been addressed in this work. The regeneration of an aged catalyst proceeds with the same activation energy, albeit at a considerably lower rate. This is consistent with a scenario in which the same coke combustion mechanism takes place, while the number of active sites on the catalyst surface has been reduced as a consequence of sintering.

Finally, dynamic experiments yielded kinetic parameters which were very similar to those from isothermal experiments. This is so under conditions that could be regarded as unfavorable for dynamic experiments, i.e., a strongly exothermic reaction and high reaction rates, and shows the potential of dynamic experimentation when (i) they are applied to the determination of relatively simple kinetics, and (ii) a large number of experimental data are gathered, which greatly increases the reliability of the statistics obtained.

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