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Thermal Oxidation of Carbonaceous Nanomaterials Revisited: Evidence of Mechanism Changes

Emmanuel Picheau, Ferdinand Hof, Alain Derré, Barbara Daffos, and Alain Pénicaud*

Abstract: Kinetic data, for example, activation energy and reaction order, are crucial for the understanding of chemical reactions and processes. Here, we describe a novel method for obtaining kinetic data based on thermogravimetric measurements (TGA) that exploits in each measurement multiple successive isothermal steps (SIS). We applied this method to the notoriously challenging carbon combustion process for vastly different carbons for oxygen molar fractions between 1.4% and 90%. Our obtained apparent E_A values are within the wide range of results in the literature and vary in a systematic way with the oxygen partial pressure. The improved accuracy and large amount of obtainable data allowed us to show that the majority of experimentally obtained apparent data for apparent E_A are neither in a kinetic regime nor in a diffusion-controlled one but rather in a transition regime.

The combustion of fossil fuels has been studied for centuries and is still a major source of energy production for humanity. Consequently, a very large number of studies have focused on the combustion process of all sorts of different carbon materials such as charcoal and cokes,^[1,2] carbon black,^[3] and soots.^[4] These studies have been performed under various gases, temperatures, pressures, and other experimental conditions^[5–8] as well as from a theoretical point of view.^[9] The main motivation is to reveal the fundamental reaction mechanism, identify the rate-determining step, and estimate kinetic parameters such as activation energy (E_A) and reaction order (n) (see discussion about E_A in The Supporting Information). The activation energy and reaction order are central parameters that directly impact the energy efficiency, especially from an industrial point of view. Lately, the field has been revisited and has regained attention due to its importance in the design of optimal thermal annealing processes in the synthesis or purification of novel materials such as soot,^[4] synthetic graphite,^[10] and carbon nanotubes.^[11]

Despite an impressive number of studies, a consensus about the combustion of carbon materials is still elusive (see Table S1 in the Supporting Information) both in terms of activation energy and reaction order. The variability of the literature data reveals the complexity of this reaction, which may be related to its solid–gas nature. Mass transport through the gas phase and within the particles, active free sites and adsorption/desorption processes are of essential importance.^[12] In 1959 Walker et al. modelled the combustion of carbon particles.^[13] They proposed that there are three different temperature zones, one in the kinetic regime at low temperature and two others under the influence of internal and/or external diffusion. All three zones are separated by intermediate regimes. As a result, only apparent reaction orders and activation energies can be determined experimentally for all zones, except the kinetic one. A discussion of this model and its consequences can be found in Figure S1.

Thermogravimetric analysis (TGA) is the most commonly applied technique to measure kinetic data, using either isothermal or constant heating rate experiments. Both of those have their own limitations^[14–20] and to improve accuracy Gou et al.^[21] recently proposed combining the two methods. Many experimental parameters influence the precision and the results of TGA experiments and they have consequently been studied in detail in several studies in the last decades.^[3,4,22,23] The most crucial parameters are the reactor geometry, the initial mass and the carbonaceous material, namely its structure, porosity, and purity since metallic species can catalyze the reaction.^[24] Typically, multiple heating rates or multiple isothermal profile experiments are requisite to obtain consistent kinetic data.^[25]

In this report, we describe a novel experimental TGA technique, based on successive isothermal steps (SIS) that allows the construction of an Arrhenius plot for one partial pressure in one measurement only (Figure 1), drastically diminishing the time required to experimentally explore the parameter space (P_{O_2}, T) of carbon combustion. We applied this technique to four carbon materials (two carbon blacks (CB, Ketjenblack and Ensaco), one sample of multiwalled carbon nanotubes (MWCNTs, MER Corp.), and one sample of natural graphite (Asbury)) under atmospheric pressure and constant flow rate. The oxygen molar fraction was varied from 1.4% to 90%. We were able to show three important points: 1) Variable apparent activation energies can be obtained, depending on O_2 partial pressure, explaining the widely scattered reported activation energies for carbon combustion (from 17 to 291 kJ mol^{-1} , Table S1); 2) There is a systematic and general evolution of the reaction order with temperature; and 3) The vast majority of our experimentally obtained data

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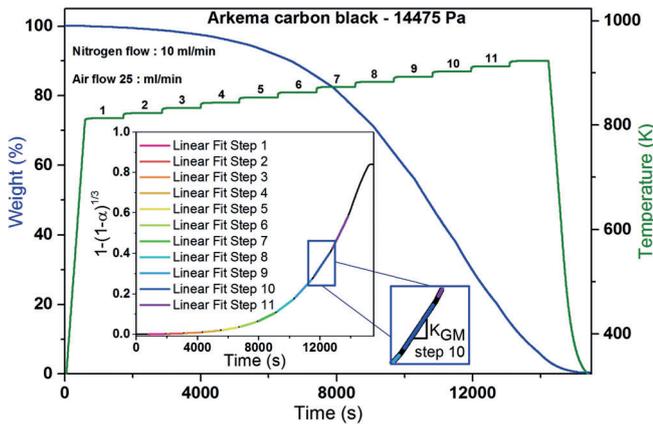


Figure 1. Example of SIS measurement and analysis (insert) of Ensaco carbon black at the partial oxygen pressure of 14475 Pa with 12 successive isothermal steps of 20 minutes each, spaced by 10 K: Weight loss (blue, left axis) and temperature (green, right axis) vs. time. Insert: Data analysis exploiting the shrinking core model to derive the apparent rate constant K_{GM} .

for apparent E_A are neither in the kinetic regime nor in the diffusion-controlled zones but in one of the two transitions. Up to now, to the best of our knowledge, this change of mechanism has not been experimentally observed for the combustion reaction of different carbon materials. We attribute this fact to the time requirements of conventional isothermal measurements. In contrast, the SIS technique provides a precise and extended dataset, is reliable, quick, and generates data with high precision, thus allowing a deeper understanding of the notoriously difficult carbon combustion reaction.

The SIS technique exploits a temperature profile involving successive isothermal steps (Figure 1). Many kinetics models have been developed to describe the combustion of carbon materials. One of the main models, notably in the char literature,^[26] is the shrinking core model. The obtained mass loss on each individual step was analyzed by a graphical solution using the shrinking core model coupled with the grain model (see rationale for this choice and a discussion of those and other models in the Supporting Information) as described by Morin et al.^[26] [Eq. (1)] with α the conversion

$$\frac{d\alpha}{dt} = A_{SCM} \exp\left(\frac{-E_a}{RT}\right) P_{O_2}^n (1 - \alpha)^{2/3} \quad (1)$$

rate, t the time, T the temperature, R the universal gas constant, and A_{SCM} a constant (see the Supporting Information for more details).

Integration of Equation (1) yields Equation (2):

$$1 - (1 - \alpha)^{1/3} = K_{GM} t \quad (2)$$

With

$$K_{GM} = A_{SCM} \exp\left(\frac{-E_a}{RT}\right) P_{O_2}^n \quad (3)$$

K_{GM} values are obtained from the slopes in the insert of Figure 1. From these values, an Arrhenius plot allows one to

obtain E_A for the oxygen partial pressure of the experiment. Similarly, n is deduced from the evolution of $\ln(K_{GM})$ with the partial oxygen pressure at a given temperature [cf. Eq. (3)] (data for all carbon materials: Figure S2; details, model, reference experiments, formulas, Matlab details, data extraction are given in the Supporting Information). It is noteworthy that the fitted curves are perfectly straight lines. This behavior serves as a proof that the temperature is constant within one step and the influence of internal burning processes, known to impact the determination of kinetic data,^[22] is not an important factor in these experiments. The SIS technique was developed by postulating that the change of conversion rate does not affect the kinetics of the reaction, whereas the contrary had been shown by Wang-Hansen et al.^[27] The rationale for this assumption is based on the applied shrinking core model, which considers that the carbon aggregates are a conglomerate of smaller nonporous particles, and that the combustion occurs at the outer shell by continuously shrinking the respective particles (Scheme S2). In order to validate this assumption, the SIS program was directly compared with classical isothermal measurements, and its validity was verified (Figure S3). The reproducibility of the method was also investigated (Figures S4–S6) and shows a variation of the obtained kinetic data of less than 3.5%.

The apparent E_A of the four materials (obtained from the Arrhenius plots (Figure S2)) have been plotted vs. oxygen molar fraction in the range between 1.4% and 90% in Figure 2 a–d. Different apparent E_A values are observed for the two CBs, the MWCNTs, and the graphite. Furthermore, for three samples, two values of apparent E_A can be found per partial pressure, at high and low temperatures. This is directly related to the shape of the Arrhenius plot (Figure S2), exhibiting a profile which needs to be fitted with two different linear slopes (high (circles) and low (squares) temperature). For the MWCNTs only one apparent E_A can be found. It is remarkable how much the value of apparent E_A varies for each of the four measured materials as a function of $p(O_2)$. On

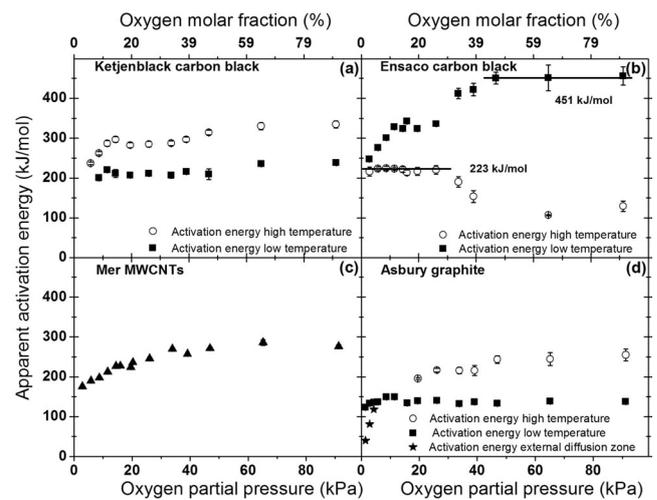


Figure 2. Evolution of the activation energy with the partial pressure for thermal oxidation of a) Ketjenblack carbon black, b) Ensaco carbon black, c) MER MWCNTs, d) Asbury graphite.

a more global level, this is compatible with the scattering of apparent E_A values reported by different groups for similar materials over the last 45 years (Table S1). To the best of our knowledge, there is to date no study showing the evolution of the apparent E_A with experimental parameters (e.g. $p(\text{O}_2)$). How much the values change is best outlined with the MWCNT sample (Figure 2c), exhibiting the smallest change, but nonetheless with a difference between the extreme values of more than 100 kJ mol^{-1} and a mean value around 250 kJ mol^{-1} . On the other end of the spectrum, the Ensaco CB exhibits the largest variation in apparent E_A (about 300 kJ mol^{-1}). Interestingly, two plateaus can be clearly identified for this sample (Figure 2b). One plateau is for low temperature and high partial pressure showing a value of 451 kJ mol^{-1} , and the other for high temperature and low partial pressure with a value of 223 kJ mol^{-1} . According to Walker's model, those two values correspond to a reaction in the kinetic regime (E_A : 451 kJ mol^{-1}) and in the internal diffusion regime (E_A : 223 kJ mol^{-1}), respectively. All the other data points of the Ensaco CB are in the transition regime (over 70% of all data points of the Arrhenius plot, Figure S2). In the graphite sample, Figure 2d, a striking behavior can be seen for low oxygen partial pressures and high temperatures (represented by green stars). The apparent E_A values range from 118 kJ mol^{-1} to 40 kJ mol^{-1} and can be related to partial external diffusion control. This assumption has been validated by performing experiments varying the total flow rate of gas (Figure S7). In contrast, flow rate variation experiments realized on the MWCNTs and Ensaco CB (Figure S8) reveal that they are far from external diffusion, because the obtained kinetic data at varied flow rates are constant. Moreover, the majority of all data points, over 90% of all measured values, can be assigned to either of the two transition zones under our experimental conditions. This observation serves as an important reminder of how challenging and complex the determination of kinetic data for carbon combustion processes is, and urges caution in assigning the experimental data to either the kinetic or diffusion-controlled regime. A further intriguing observation is that the apparent activation energy is higher at higher temperatures for Ketjenblack and graphite, while the opposite behavior is visible for the Ensaco CB. While Walker's model fits perfectly for the Ensaco CB it failed to explain this behavior for the two other materials. However, the confidence in the data is high, because the trend is observed on two different materials at two completely different temperatures.

The apparent reaction order can be calculated by plotting the logarithm of the partial oxygen pressure vs. the logarithm of K_{GM} . Conventionally, this method is applied for a couple of partial pressures at a given temperature.^[26] We extended this method and applied it to all the data obtained from our measurements (Figure S9). The good linearity found in the data provides high confidence in the applied model, the data acquisition, and the analysis. The observed linearity in the points at a given temperature is based on 14 individual TGA experiments. The obtained apparent reaction order of $p(\text{O}_2)$ was plotted vs. temperature (Figure 3a). Strikingly, the apparent reaction order $n(p(\text{O}_2))$ is not constant and varies systematically with temperature for the four materials.

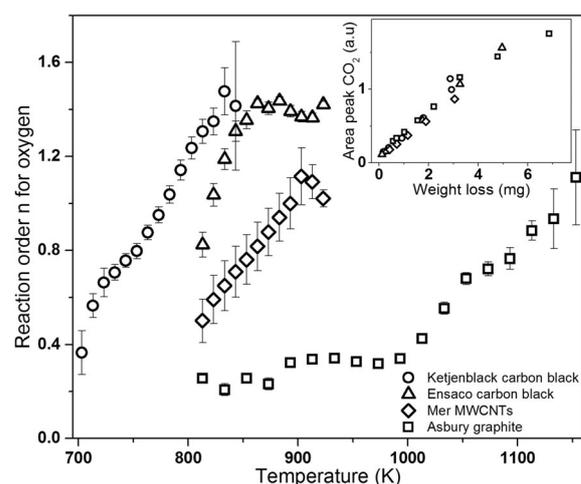


Figure 3. Evolution of the reaction order for oxygen with temperature from the shrinking core model during thermal oxidation. Insert: Correlation between TGA and GC-MS. Residual CO_2 at 0 mg weight loss comes from air.

Furthermore, above a specific temperature, all materials exhibit a linear increase with temperature with quite similar slopes. The overall consensus in the literature is that the reaction order is a constant and exhibits values between 0 and 1 (see Table S1), which is not reflected in the obtained data. The observed range of $n(p(\text{O}_2))$ is found between 0.35 to 1.5 for all four materials. The observed similar linear evolution of the reaction order reveals that similar mechanistic changes occur when the temperature is changed in the combustion process for all materials (Figure 3). Furthermore, the onset temperature for the change of the apparent reaction order varies inversely with the porosity (see Figure S15). In order to further investigate these mechanistic changes, the SIS technique has been used on a TGA instrument that is coupled to a gas chromatograph with mass spectrometric analysis (TG-GC/MS), considering that presumably all products of the primary reaction are gaseous. The same temperature range was investigated and six isothermal steps of 30 minutes each have been applied (Figures S10 and S11). For each isothermal step a gas chromatographic separation has been performed (example elugram in Figure S12). The peaks originating from the balance purge gases, and the peak related to CO_2 are clearly detectable but notably, no trace of CO was found. The mass loss at each step has been plotted vs. the area of CO_2 peak (insert Figure 3).

For all four materials studied, a strict linear correlation can be seen. It can be concluded that the CO_2 proportion of the product is linearly dependent on the mass loss and more remarkably, the curve is identical for all materials. Therefore, the proportion of CO_2 in the product distribution is the same for all materials. Although no quantification of the CO_2 has been performed, the conclusions based on the correlation between two different machines, coupled with the absence of CO in the GC-MS results, strongly suggest that products recorded for the four materials correspond to 100% CO_2 . As a result, no explanation about the change in apparent reaction order can be related to a change in the final product of the

reaction. That does not rule out that, at one point, CO is produced and is oxidized to CO₂ at the carbon surface (or as an homogeneous reaction in the gas phase). On a more general level, there are a few reports discussing hypothetical changes of the mechanism of carbon combustion.^[27] One rationale to understand the observed change of the reaction order is that the formation of CO₂ over CO is thermodynamically favored. At higher temperatures, the reaction of CO with O₂ has a more negative free energy than the reaction of carbon with oxygen forming CO₂ based on Ellingham diagrams.^[28] One may argue that the reaction between adsorbed CO on the carbon surface and oxygen is favored over desorption, and consequently every CO molecule produced is oxidized on the carbon surface to CO₂, thus continuously changing the global reaction order. The observation that the vast majority of the obtained data points lie in the transition regime may be related to the complex relationship between active free sites, mass transport, porosity, oxygen concentration, and adsorption/desorption processes. It is by no means surprising that the parameters need to be carefully adjusted to push the reaction into a pure kinetic regime and that this could be achieved for only one of the four studied materials under the chosen measurement conditions. Furthermore, under specific conditions, that is, at high temperature and high partial oxygen pressures, Walkers' model does not apply for two of the carbon materials. This may be related to the structural evolution (porosity, for example) of the materials with temperature, or the dilated lattice spacing of graphite at higher temperatures and provides guidelines for additional studies.

The thermal oxidation of carbonaceous material is known to be a difficult reaction to study. Until now the existence of some diffusional and possible adsorption/desorption limitation steps were thought to be responsible for the variability of kinetic data in literature. Illekova et al.^[29] actually concluded in 2005 that only apparent kinetic parameters can be reached by thermoanalytical methods due to the complexity of the thermal oxidation of carbon. The present work confirms this conclusion, showing how much the activation energy can differ for the same material. Furthermore, 1) Under specific conditions the true activation energy for one material could be obtained (Ensaco CB); 2) Continuous variation in activation energy has been observed up to five times; 3) There is a systematic evolution of the apparent reaction order with temperature for all materials, indicating a mechanism change; 4) The mechanism change does not influence the final product distribution (CO to CO₂ ratio) in any of the investigated carbon materials, which vary drastically in terms of porosity, crystallinity, aspect ratio, and shape. The successive isothermal step method (SIS) is a technique that allows acquisition of kinetic data in a reliable, fast, and direct way. It can be translated directly to other disciplines and fields for obtaining fast and precise kinetic data from TGA experiments.

Experimental Section

The four carbon materials are composed of nearly 100% carbon and free of ashes: Ketjenblack 600 JD (AkzoNobel), carbon black

250P ENSACO (Timcal), arc-discharge MWCNTs (MER corporation), and graphite Asbury 3061 (Asbury carbons). TGA measurements were performed on a Q5500 from TA Instruments. The temperature profile consisted of 12 successive isothermal steps, spaced from 10 K each. More details are available in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon black · carbon nanotubes · graphite · kinetics · thermal oxidation

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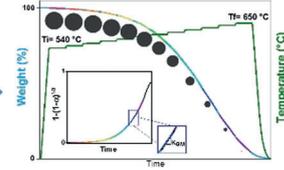
Communications



Kinetic Analysis

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A. Pénicaud* ————— ■■■■-■■■■

Thermal Oxidation of Carbonaceous
Nanomaterials Revisited: Evidence of
Mechanism Changes



Burn, baby, burn! A novel thermogravimetric method has been developed for the rapid extraction of precise kinetic data. Studies on the combustion of carbon show that the mechanism

changes depending on the temperature. This technique can be applied directly to other disciplines and fields for obtaining fast and precise kinetic data from thermogravimetric experiments.