

Combustion of Active Carbon as a Model Carbon Material: Comparison of Non-catalytic and Catalytic Oxidation

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Original scientific paper
Received: September 23, 2010
Accepted: August 29, 2011

Kinetics of non-catalytic and Pt-catalysed oxidation of active carbon, selected as a model carbon material was investigated using thermogravimetric analysis (TGA). Investigations were performed in the temperature range from 40 °C to 1000 °C at different heating rates (5–25 °C min⁻¹). The influence of Pt-based catalyst on the combustion kinetics was examined as well.

Values of the kinetic parameters, such as activation energy, E_a and Arrhenius pre-exponential factor, A were determined using isoconversional method proposed by Kissinger-Akahira-Sunose. The obtained values were in good agreement with the literature data.

Key words:

Combustion, carbon material, kinetics, isoconversional method

Introduction

The use of diesel engines has increased recently due to their reliability, durability and efficiency and low consumption of fuels.¹ However, they are the main source of emission of soot particles into atmosphere.^{2,3} It is well known that these particles are very harmful to human health, due to their carcinogenic effect.⁴ Thus, their subsequent oxidation is of great significance for pollution control. One of the available technologies for the control of diesel particulate emissions employs filters that capture the soot particles from the exhaust stream. However, the filters must be regenerated periodically or continuously by combustion/oxidation of the trapped soot to prevent back-pressure build-up. Soot oxidation takes place at high temperatures (> 600 °C) while the temperature of diesel exhaust gases for small engines may be as low as 200 °C.⁵ Therefore, catalysts are used to prevent accumulation of soot on the monolithic filter. Catalysts may be incorporated by addition of oxidation catalyst precursors as fuel additives or by impregnation of the filter walls with the oxidation catalyst. Many materials active in soot oxidation catalysis have been studied over the last twenty years as coating of a particulate filter. In this study, we have used a powder catalyst, based on noble metal Pt, mixed with soot sample to enhance the oxidation rate.

Our primary aim was to investigate the influence of the applied catalyst on the oxidation rate of the model soot particles. Thermo-oxidative deg-

radation and catalytic oxidation were investigated applying dynamic thermogravimetric analysis. Kinetic parameters, activation energy and pre-exponential factor were evaluated by the Kissinger-Akahira-Sunose isoconversional method.^{6,7} The second aim was to provide useful information about regeneration steps in filters used for diesel soot abatement.

Experimental

Active carbon, supplied by Kemika, was selected as a model carbon material to simulate diesel soot combustion. Chloride, sulphate, heavy metals, zinc, iron and carbon content of the manufacturer's sample were (w/%): 0.001; 0.01; 0.005; 0.0005 and 91.969 respectively. Moisture content after heating at 120 °C was 8 %. A model sample was used for non-catalytic oxidation without further modifications. A commercial, Pt-based catalyst (code F 105 R/W; w = 5 % of Pt), supplied by Degussa-Huls AG, (particle diameter 23 µm) was thermally pre-treated at 60 °C for 24 hours. Thermo-oxidative degradation and catalytic oxidation of active carbon were investigated by dynamic thermogravimetric analysis under excess air and employment of PerkinElmer Thermobalance TGS-2. The initial mass of the sample was the same (10 mg) in all experiments. Due to the fact that contact between model carbon material and catalyst has a great influence on oxidation, we paid attention to the mixture of these two compounds. Catalyst and active carbon were loosely mixed with a spatula. The appropriate amount of

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active carbon or a mixture of active carbon and catalyst (mass ratio of 1:1) was loaded in the crucible and heated from 40 °C to 1000 °C. The experiments were carried out at constant heating rates (5, 10, 15, 20 and 25 °C min⁻¹). Mass loss and sample temperature were monitored by a computerised data system. The oxidant was dry air (30 cm³ min⁻¹) flowing downward the cylindrical sample holder.

Results and discussion

Catalytic and non-catalytic oxidation

Understanding the phenomena involved in regeneration of diesel filters is essential to the successful development of a new emission control technology based on catalytically activated diesel particulate filters. Thermal analysis methods are commonly used in the investigation of diesel soot oxidation behaviour and the determination of kinetic parameters. This study is focused on the experimental investigation of kinetic parameters for the thermal and catalytic oxidation of model soot material.

Fig. 1 shows comparison of the results obtained for non-catalytic and catalytic oxidation of the soot at constant heating rate of 20 °C min⁻¹. The overall results indicate that the presence of the Pt in model soot material significantly lowers the activation energy of oxidation. Maximum temperature for catalytic oxidation of the soot-Pt catalyst mixture was reduced by approximately 180–200 °C compared to non-catalyzed oxidation. The conversion-temperature curves for non-catalytic and Pt-catalysed oxidation on sample, recorded at varying heating rate are shown in Figs. 2 and 3. From Fig. 3 we can conclude that soot shows heterogeneous reactivity. At lower temperatures, some more reactive part of the model soot material (which is

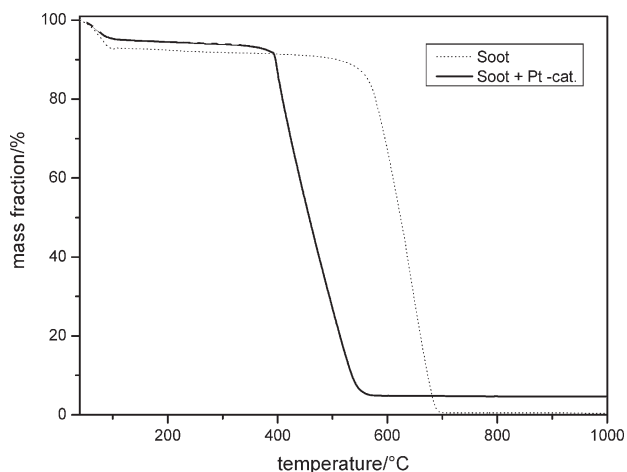


Fig. 1 – Experimental data obtained at constant heating rate of 20 °C min⁻¹ for non-catalytic and catalytic oxidation of soot

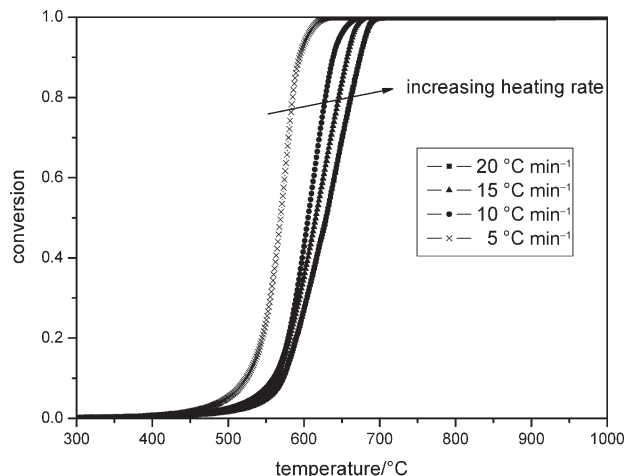


Fig. 2 – Experimental conversion vs. temperature curves obtained at different heating rates for non-catalytic oxidation of sample

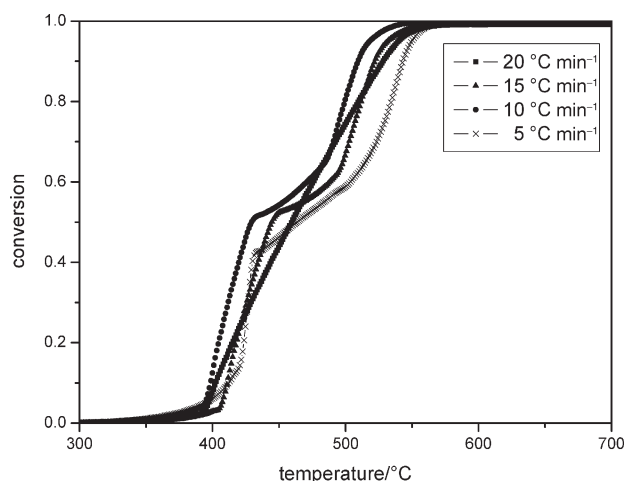


Fig. 3 – Experimental conversion vs. temperature curves obtained at different heating rates for catalytic oxidation of sample

probably in better contact with the catalyst) reacts with oxygen and decompose. Then, at temperatures above 420–450 °C the low-reactive part of soot is oxidised. This may be also explained by the loss of contact between soot and catalyst when one part of soot is oxidized.⁸

On the other hand, the obtained results could be interpreted in terms of the change in the reaction mechanism. At high reaction temperatures, the transfer of oxygen molecules to the soot surface is usually the limiting step of the overall reaction rate. However, at lower temperature the reaction is probably under control of chemical reaction.

Influence of gas flow rate

The experiments were also performed with varying flow rate of dry air (30 and 150 cm³ min⁻¹) in order to investigate the influence of the external

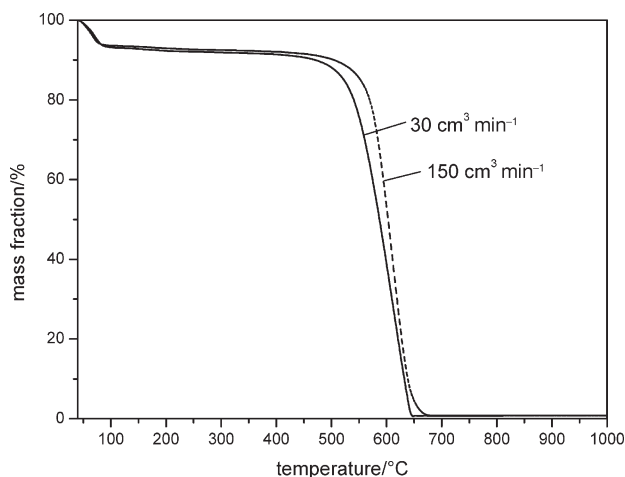


Fig. 4 – Influence of gas flow rate on the oxidation rate for non-catalytic oxidation of soot at constant heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

mass transfer limitations on the results of thermo-analytical measurements (Fig. 4). Under the experimental conditions employed in this study, the weight versus temperature curves remained unchanged within the range of experimental uncertainty. Due to a small fraction of the used soot sample, the intraphase mass transfer was neglected also.

Isoconversional kinetic analysis

Isoconversional methods have been known for many years.^{6,7,9,10} Recently, these methods have been widely used to study the kinetics of chemical or physical processes, and allow drawing important conclusions on the mechanisms of various chemical reactions, cross-linking, polymer crystallization, glass transition kinetics, etc.^{11–14} Isoconversional kinetic methods differ from the classical ones in that the former assume a kinetic model $f(\alpha)$ and then determine activation energy (E_a) for such a process by directly calculating E_a . Their result is E_a dependence on conversion (α). Complexity of that dependence indicates a complex reaction mechanism. Dependence analysis of E_a on α often enables identification of the scheme of a kinetic process and can be used in modelling the reaction kinetics outside the temperature range of a particular experiment.

Thermogravimetric analysis (TGA) used to determine the kinetics of composites degradation, gave the integral curves, showing dependence of mass loss on temperature. Thus, integral isoconversional methods such as Flynn-Wall-Ozawa (FWO)^{9,10} and Kissinger-Akahira-Sunose (KAS) method^{6,7} are commonly used. Differential isoconversional methods such as Friedman method¹⁵ are not very suitable for analysis of TGA curves because they require numerical derivation of experimental results which contributes to experimental error. A detailed analysis of the various isocon-

versional methods (i.e. the isoconversional differential and integral methods) for the determination of the activation energy has been presented by Budrugeac *et al.*¹⁶ and Sbirrazzuoli *et al.*¹⁷

KAS method is a mathematical equivalent to FWO method but it is more accurate for a wider interval of E_a values.¹⁸ Therefore, KAS method was chosen in this study for isoconversional (model-free) calculation of E_a . Conversion, α , is calculated after the eq. (1), where m_0 is the initial and m_{∞} is final mass of a sample, ignoring the initial loss at the temperatures below $150\text{ }^{\circ}\text{C}$ attributed to evaporation of adsorbed moisture.

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_{\infty}} \quad (1)$$

In kinetic analysis, it is generally assumed that the rate of reaction can be described by two separate functions, $k(T)$ and $f(\alpha)$ such that:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (2)$$

where $k(T)$ is the temperature-dependent rate constant, A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant ($8.314\text{ J mol}^{-1}\text{ K}^{-1}$), T is the absolute temperature, and $f(\alpha)$ is the differential conversion function. When a sample is heated at constant rate $\beta = dT/dt$ eq. (2) can be rewritten as:

$$\beta \frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (3)$$

Furthermore, KAS method is based on taking the natural logarithm of eq. (3) giving:

$$\ln\left(\frac{\beta}{T^2}\right) = [\ln(AR/E_a) - \ln G(\alpha)] - \frac{E_a}{RT} \quad (4)$$

Fig. 5 shows an example of isoconversional plots for non-catalytic oxidation of soot. In case of catalytic oxidation, the data for heating rate of 20 K min^{-1} is excluded, Fig. 6. The reason for this is visible from Fig. 3, namely due to the low resolution of TGA scanning (at higher heating rate precision is lower) the effect of heterogeneous kinetic is lost. According to the eq. (4) the activation energy was obtained from the slope of the resulting linear adjunct from plotting $\ln(\beta/T^2)$ versus $1/T$ at several constant conversion extents. The obtained values of E_a for non-catalytic and Pt-based oxidation were in the range from $105\text{--}340\text{ kJ mol}^{-1}$ and $11\text{--}16\text{ kJ mol}^{-1}$, respectively. It has been generally assumed that the apparent activation energy and pre-exponential factor remain constant, however, it has been shown in the solid-state reactions that these kinetic param-

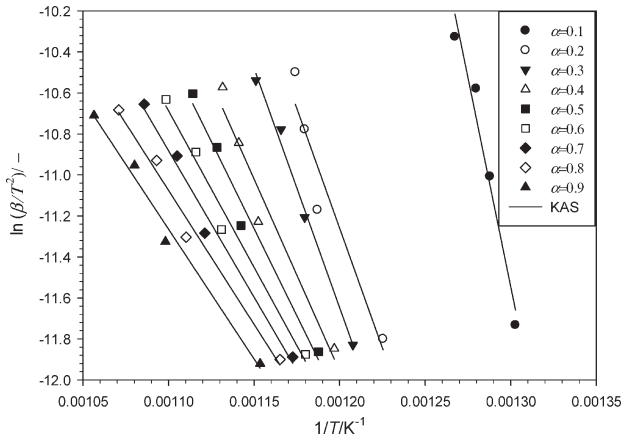


Fig. 5 – Isoconversional plots used to calculate activation energy at listed conversions by Kissinger-Akahira-Sunose method, for non-catalytic oxidation of soot

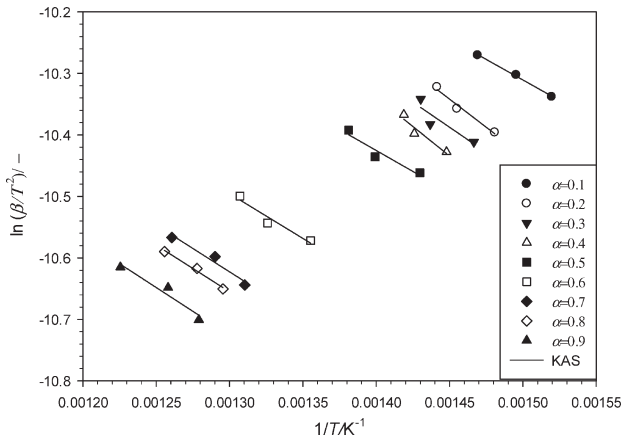


Fig. 6 – Isoconversional plots used to calculate activation energy at listed conversions by Kissinger-Akahira-Sunose method, for catalytic oxidation of soot

ters may vary with the degree of conversion.¹⁹ A complex dependence of the activation energy on the degree of conversion, observed in our reaction system, can be seen in Fig. 7. A variation in apparent

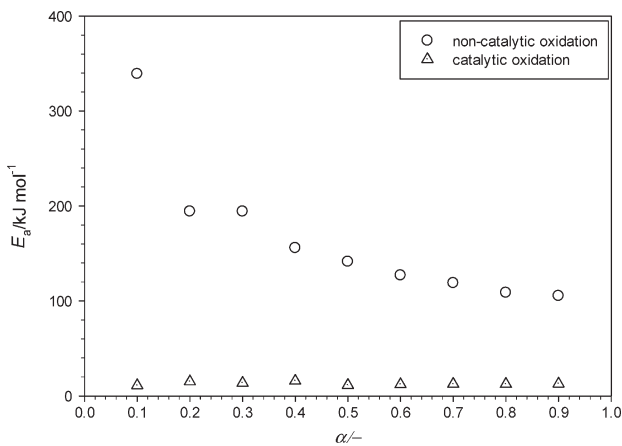


Fig. 7 – Dependence of apparent activation energy on conversion as obtained by Kissinger-Akahira-Sunose method

activation energy could be explained in the terms of the heterogeneous nature of solid sample and/or due to a complex reaction mechanism. It is known that degradation reactions are often very complex and can involve several processes with different activation energies and mechanisms. In such situations, the reaction rate can be described by complex equations, where the activation energy is dependent on the reaction progress.

Conclusion

Non-catalytic and catalytic oxidation of the model carbon material were analysed by dynamic thermogravimetric method in order to gain useful information for modelling of regeneration steps in filters used for diesel soot removal. Values of the kinetic parameters, such as activation energy, E_a and Arrhenius pre-exponential factor, A were determined using isoconversional (model-free) method. It was found that Pt catalyst considerably reduces temperature of active carbon oxidation and decreases activation energy. The results indicate that the carbon material employed in this study was composed of two parts with different reactivity towards oxidation. A variation in apparent activation energy with the degree of conversion was observed. The shape of the dependence has been interpreted in terms of the complex reaction mechanism. The isoconversional Kissinger-Akahira-Sunose method applied in this work appears appropriate, despite numerous approximations used in calculation of the kinetic parameters. More accurate results can be obtained using the advanced integral methods proposed by Vyazovkin,¹⁹ but this will be presented in our future work.

ACKNOWLEDGEMENT

The authors highly appreciate the financial support that the Ministry of Science, Education and Sport of the Republic of Croatia has given for this study.

List of symbols

- A – Arrhenius pre-exponential factor, min^{-1}
- α – conversion, –
- β – heating rate, K min^{-1}
- E_a – activation energy, kJ mol^{-1}
- $f(\alpha)$ – differential conversion function, –
- $G(\alpha)$ – integral conversion function, –
- $k(T)$ – temperature-dependent rate constant, min^{-1}
- m_0 – initial mass of sample, g
- m_∞ – final mass of sample, g

$m(T)$ – temperature-dependent mass of sample, g
 R – universal gas constant, J mol⁻¹ K⁻¹
 T – absolute temperature, K
 t – time, min
 w – mass fraction, %

List of abbreviations

FWO – Flynn-Wall-Ozawa method
KAS – Kissinger-Akahira-Sunose method
TGA – thermogravimetric analysis

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