

DEVELOPMENT OF A NEW EQUIPMENT FOR APPLYING THE CONSTANT RATE THERMAL ANALYSIS (CRTA) TO TEMPERATURE PROGRAMMED OXIDATION (TPO) OF CATALYSIS

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A new equipment has been developed in order to apply the constant rate thermal analysis method (CRTA) to Temperature Programmed Oxidation (TPO) processes. The exhausted gases flow through an electrochemical oxygen sensor after leaving the reactor in order to monitor the oxygen consumption in the reaction. The control of the sample temperature is carried out by interfacing both the furnace and the electrical signal of the oxygen sensor to a PID controller that allows to monitor the sample temperature in such a way that the consumption of oxygen is a constant value previously selected by the user.

Keywords: constant rate thermal analysis, new equipment, Temperature Programmed Oxidation

Introduction

The Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO) have been extensively used [1–3] for characterizing supported catalysts. Conventional TPR and TPO techniques imply to follow the trend of either the hydrogen or the catalyst as a function of the temperature that is increased at a constant rate β . It has been reported in previous papers [4, 5] that the change in the concentration induced by the consumption of the reactive gas leads to large distortions in the shape of the TPR profiles. Therefore, it is difficult to get reliable kinetic information from the above experiments. This conclusions would be easily extended to conventional TPO method. The application of the Constant Rate Thermal Analysis (CRTA) to the study of TPR and TPO processes would allow to overcome these problems, provided that in this

method, the concentration of the reactive gas all over the process is held at a constant value selected by the user [6].

The CRTA tool developed by Rouquerol *et al.* [7] is basically constituted by a conventional vacuum apparatus, equipped with a vacuum gauge interfaced to the sample heater through a controller. The constant rate is attained both by controlling the residual pressure in the close vicinity of the sample or by maintaining a constant value of the pumping rate that can be selected by means of a vacuum leak valve. It has been reported [8–10] that this system has been successfully used for discriminating the kinetics of thermal decomposition of solids. On the other hand, it has been claimed that CRTA allows to yield solids with homogeneous structure and low particle size [11–13]. However, the described equipment requires to work at very low pressures and, therefore, it can not be used for studying reactions taking place under flowing gases. CRTA equipments under gas flow using either catharometer [6, 14] or an IR detector [15] have been previously described. However it would be necessary to develop a new equipment using the analogical output of an electrochemical sensor of oxygen for controlling the reaction rate in order to apply CRTA method to the study of TPO processes.

Experimental

The apparatus developed in this work is outlined in Fig. 1. A mixture of helium and oxygen has been used as reactive gas. Both the flow rate of the carrier gas and its initial concentration in oxygen at the input of the quartz reactor containing the sample, have been selected by means of a two mass flow controller.

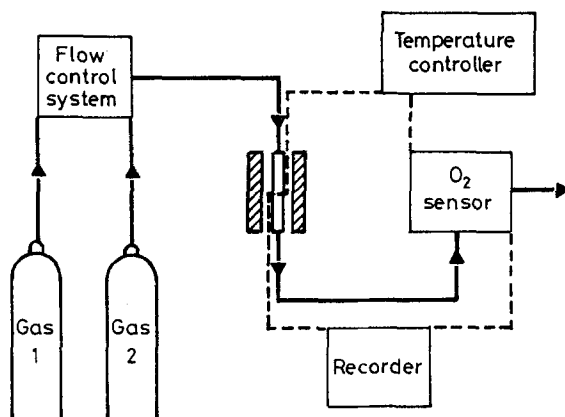


Fig. 1 A plot of the experimental system. The arrows show the gas flow way

The exhausted gases flow through an electrochemical oxygen sensor Teledyne, model 320 P, after leaving the reactor in order to monitor the oxygen consumed in the reaction. The oxygen sensor has three selectable ranges: 0–5%, 0–25% and 0–100% associated to a linear analogical output of 1 V f.s.d. This output has been interfaced to the furnace through a PID controller designed for monitoring the sample temperature in such a way that the output of the oxygen sensor remains constant all over the process; in other words, the starting oxygen concentration is decreased to a constant value previously selected by the user. The reaction rate will be constant provided that both the oxygen partial pressure and the flow rate of the carrier gas are constant.

The oxidation of an active carbon from Aldrich with a specific surface of $1500 \text{ m}^2/\text{g}$ has been studied for checking the equipment described above. The percentage of CO has been measured at the output of the reactor by means of an electrochemical CO sensor, Teledyne, model 426 R.

Results

Figure 2 shows by way of example the CRTA diagram obtained for the oxidation of carbon under a flow of at $200 \text{ cm}^3/\text{min}$ helium with a starting oxygen concentration of 0.5%. The percentage of oxygen maintained constant in the exhausted gases all over the CRTA experiment has been 0.42%, what implies an oxygen consumption of $0.15 \text{ cm}^3/\text{min}$ NTP. It can be observed in Fig. 2 that the CO formation rate has been constant along the experiment. Moreover, the total amount of CO determined from the area under the line representing the concen-

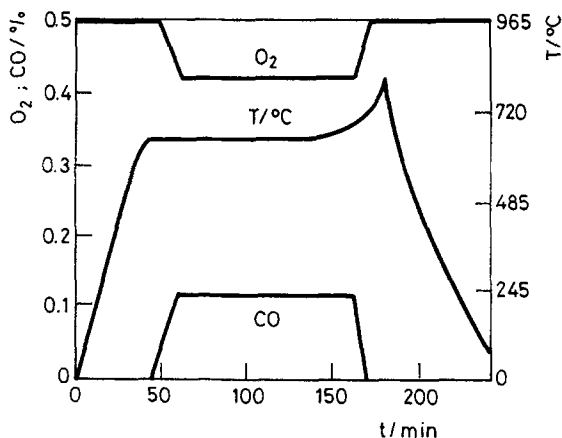
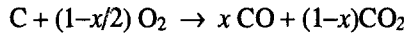


Fig. 2 CRTA plot obtained for the oxidation of carbon at 0.4% O₂ and $8 \cdot 10^{-3} \text{ min}^{-1}$

tration of CO as a function of the time, agrees with the value calculated from the amount of oxygen consumed in the gasification of the carbon sample according with the equations:



The percentage of CO and CO₂ calculated from both methods are included in Table 1.

Table 1

Sample	% O ₂		T / °C	%		C / min ⁻¹
	Starting	Steady State		CO ₂	CO	
Carbon	20.4	18.5	585	57	43	2·10 ⁻²
Carbon	0.5	0.4	660	0	100	8·10 ⁻³
Carbon/1%Pt	0.5	0.4	460	100	0	5·10 ⁻³

It is evident that the fraction of carbon gasified at the time t is given by the ratio between the area enclosed in Fig. 2 by the oxygen sensor output trace at the time t and the total area when the reaction is over. Figure 3 shows a plot of

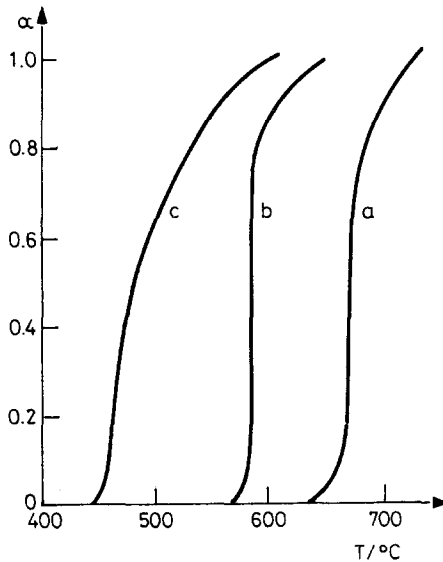


Fig. 3 α - T plots calculated from CRTA. a) carbon $8 \cdot 10^{-3} \text{ min}^{-1}$. b) carbon $2 \cdot 10^{-2} \text{ min}^{-1}$ c) carbon/1%Pt $5 \cdot 10^{-3} \text{ min}^{-1}$

the α value calculated from CRTA plot in Fig. 2 as a function of the temperature.

Figure 3 shows as well the $\alpha-T$ plot obtained by fixing in the starting and exhausted gas flow, the concentrations of oxygen quoted in Table 1 (20.4%, 18.5%). The percentages of CO and CO₂ generated in the reaction are also included in this table. It can be observed that the carbon dioxide percentage increases with the oxygen concentration, as it would be expected.

On the other hand, it has been considered of interest to apply the CRTA technique to study the catalytic activity of platinum in the gasification of carbon. Figure 3 shows the $\alpha-T$ plot corresponding to the gasification of a sample of carbon with 1% of supported platinum. The CRTA trace was recorded under the experimental conditions indicated in Table 1. The percentage of CO and CO₂ generated are also included in this table. It can be observed that the catalytic effect of platinum leads to an enormous diminution of the carbon gasification temperature at the time that the conversion to CO₂ becomes 100% in spite of the low concentration of oxygen.

In summary, it can be concluded that the method here developed could be a general procedure for studying the oxidation of supported catalysts usually studied by temperature programmed oxidation (TPO) methods. Moreover, CRTA allows to determine both the consumption of oxygen and the reaction temperature, at a constant partial pressure of oxygen selected by the user, what is not possible using conventional methods.

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Zusammenfassung — Es wurde eine neue Apparatur zur Anwendung der Konstantgeschwindigkeits-Thermoanalyse (CRTA) auf temperaturprogrammierte Oxidationsprozesse

(TPO) entwickelt. Die abgesaugten Gase strömen nach Verlassen des Reaktors zur Bestimmung der während der Reaktion verbrauchten Sauerstoffmenge durch einen elektrochemischen Sauerstoffsensoren. Die Überwachung der Proben temperatur erfolgt, indem sowohl das Ofen- als auch das elektrische Signal des Sauerstoffsensors an einen PID-Regler weitergeleitet wird, der die Proben temperatur wiederum so regelt, daß der Sauerstoffverbrauch auf einem zuvor vom Anwender wählbaren Wert konstant gehalten wird.