Thermochimica Acta, 227 (1993) 19–26
Elsevier Science Publishers B.V., Amsterdam

Characterization of the catalytic oxidation of carbon black by TPD [1]

P. Ciambelli [a,*], A. Di Pietro [b], V. Palma [a] and S. Vaccaro [b]

[a] *Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, via Ponte Don Melillo, 84084 Fisciano, Salerno, Italy*
[b] *Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Naples, Italy*

(Received 28 January 1993; accepted 17 February 1993)

Abstract

Temperature-programmed desorption (TPD) of carbon oxides from partially oxidized carbon black has been performed to investigate the uncatalysed and catalysed carbon–oxygen reactions (Walker, Jr., et al., Carbon, 29 (1991) 411–421 [1]). TPD data have been elaborated to obtain the distribution function of the desorption energies of carbon–oxygen surface complexes. The catalysed oxidation of carbon black was carried out in the presence of a potassium–copper–vanadium catalyst which substantially decreases the temperatures of carbon black burn-off. TPD measurements of carbon oxides and elaborations of the results have shown that the presence of catalyst noticeably increases the number of surface complexes, giving rise to gaseous carbon dioxide, and dramatically modifies the desorption energy distribution functions of carbon–oxygen surface complexes by lowering the peak energy values.

INTRODUCTION

Stringent standards for emissions from combustion systems [2] require the development of new technologies to remove carbon particulate from exhausts. A promising way to achieve this target is to employ a catalytic filter/post-combustor in which the catalyst acts by lowering the combustion temperature, while the filter acts by collecting the carbonaceous particles when operating conditions are not favourable for soot ignition, even in the presence of catalyst [3].

In previous papers, we have reported on the performances of a Cu–V–K-based catalyst (catalyst 137AA) [4, 5] that shows promising application for the catalytic control of particulate emissions from diesel

---

* Corresponding author.

[1] Presented at the 14th National Conference on Calorimetry and Thermal Analysis, Udine, Italy, 13–17 December 1992.

engines [3] as well as from oil-fuelled power stations [6]. Catalyst development for post-combustor design purposes implies the study of the interactions between catalyst, carbon particulates and gaseous oxygen, and the definition of the role the catalyst plays in modifying C–O complexes or in promoting the formation of new complexes on the carbon surface.

In this paper, temperature-programmed desorption (TPD) of carbon oxides from a carbon surface was employed to characterize the uncatalysed and catalysed oxidation of carbon black.

EXPERIMENTAL

The carbonaceous materials investigated were commercial samples of carbon black (CB-330, DEGUSSA) and of partially graphitized carbon black (Graphpac-GB, Alltech), having specific surface areas of 86 and 110 $m^2 g^{-1}$, respectively.

TPD experiments were carried out with the apparatus shown in Fig. 1. The main component is a 20-mm-i.d. glass tubular flow reactor. It was loaded with the carbonaceous material, alone or mixed with the catalyst, and fed by a mixture of 500 N $cm^3 min^{-1}$ of cylinder air and nitrogen (99.999% purity). Outlet gas concentrations were determined by Hartmann & Braun continuous analysers: URAS 10E (for carbon monoxide and carbon dioxide) and Magnos 6G (for oxygen). The signals from the analysers were sent to a personal computer for data processing.

Typical TPD runs were performed on CB-330 or on Graphpac-GB after uncatalysed or catalysed partial oxidations had been carried out. After a given oxidation time at fixed temperature and oxygen concentration (see captions to Figs. 3–6), the reaction was frozen by lowering the temperature to 200°C. When neither carbon monoxide nor carbon dioxide were detected by the analysers, the oxidizing stream was replaced by a nitrogen stream and the temperature was increased at the rate of

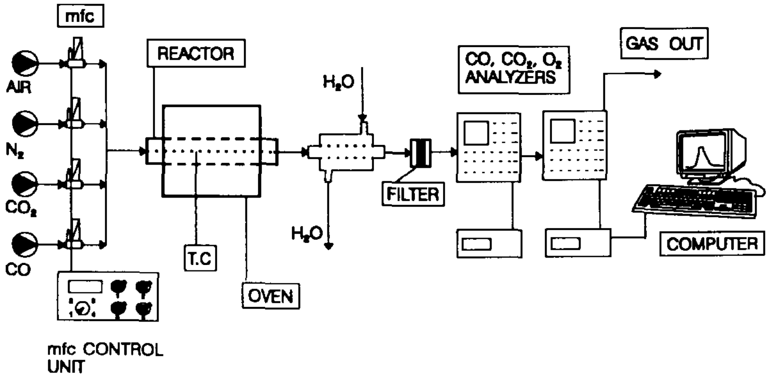

Fig. 1. Scheme of the experimental apparatus; mfc, mass flow controllers.

900°C h^{-1}. TPD data were processed as suggested in the literature [7] to find the distribution function $F(E)$ of the activation energy E of desorption of carbon–oxygen complexes from the carbon surface. In particular, experimental data were treated following a model based on the mass conservation balance and on the rate equation for the generation of carbon oxides [7].

The initial mass of particulate carbon was about 200 mg, while the initial mass ratio between carbon black and catalyst was always 0.1. During the oxidation, the molar fraction of oxygen in the gas fed to the reactor was kept to 0.1, if uncatalysed, and to 0.05, when catalysed; in all cases, the reactor was operated under differential conditions with respect to the oxygen. The oxidation rate, as well as the conversion degree of carbon, were calculated from concentrations of carbon oxides in the outlet gases. Carbon mass-balance was verified in the 95–100% range for all kinetic tests.

The catalyst 137AA was obtained by impregnating non-porous α-alumina powder with aqueous solutions of NH_4VO_3, $CuCl_2 \cdot 2H_2O$, and KCl, drying at 120°C and calcining at 700°C. More details on catalyst features and preparation procedures are reported elsewhere [2–4].

RESULTS AND DISCUSSION

The uncatalysed oxidation of carbonaceous materials for practical purposes requires high temperatures and/or high oxygen concentrations. The presence of the catalyst 137AA allows a much lower carbon burn-off temperature because it strongly promotes the carbon oxidation rate. This is shown by the comparison in Fig. 2 of Arrhenius plots for uncatalysed and catalysed oxidations of both tested materials. Data are reported as the rate of change of carbon conversion degree x as a function of the reaction temperature

$$x = (m_0 - m)/m_0 \qquad (1)$$

where m and m_0 are respectively the current and the initial value of the mass of carbon in the sample of carbon black. Figure 2 shows that, under the same operating conditions, the catalysed reaction rate would be several orders of magnitude faster than the uncatalysed rate. The apparent activation energy E_a for the uncatalysed oxidation, evaluated from data in Fig. 2, yields 52 and 40 kcal mol^{-1} for Graphpac-GB and CB-330, respectively. Both values are reduced to 17 kcal mol^{-1} in the presence of catalyst, confirming [3] the capability of the catalyst in attenuating the differences in reactivity between different carbon particulates. The values of dx/dt in Fig. 2 were computed at the same overall conversion degree $x = 0.3$. Similar values of E_a were obtained in the 0.2–0.7 range of the overall conversion degree x.

The large differences between the rates of catalysed and uncatalysed

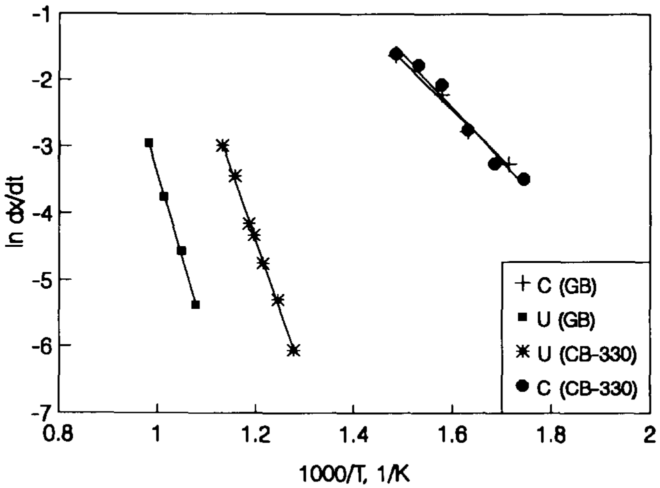

Fig. 2. Comparison of Arrhenius plots for catalysed (C, $PO_2 = 0.05$ atm, Graphpac GB or CB-330/cat.mass ratio = 0.1) and uncatalysed oxidation of Graphpac GB and CB330 (U, $PO_2 = 0.1$ atm).

reactions are reflected in the TPD results of carbon oxides performed on carbon blacks after partially uncatalysed or catalysed oxidations had been carried out. In the case of uncatalysed oxidation, only carbon monoxide was measured during the TPD tests, the carbon dioxide concentration being at the limit of detectability of the equipment. TPD data elaboration yielded a distribuiton function $F(E)$ of the activation energy of the desorption of C–O complexes with a pseudo-Gaussian shape whose characteristics do not change (Fig. 3), or vary only slightly, with the conversion x (Fig. 4). Changing the nature of the material resulted in some shifting of the peak energy values from 69 kcal mol^{-1} with Graphpac-GB (Fig. 3) to 64–67 kcal mol^{-1} with CB-330 (Fig. 4). Therefore the different reactivity of Graphpac-GB and CB-330 parallels the shift of the relevant distribution function $F(E)$.

When carbon black was mixed with the catalyst, the desorption of both carbon monoxide and carbon dioxide was detected, the amount of carbon dioxide being more than six times that of carbon monoxide. According to the literature [8], the presence of carbon monoxide and dioxide in the outlet stream is related to the likely formation of both C–O and C–O_2 complexes on the sample surface. Therefore, carbon monoxide and dioxide data were processed separately to give two different $F(E)$ functions. The distribution functions $F(E)$ for carbon monoxide and carbon dioxide both show a multimodal trend. In particular, the distribution functions evaluated for Graphpac-GB, reported in Fig. 5, show peaks at 41 and 64 kcal mol^{-1}

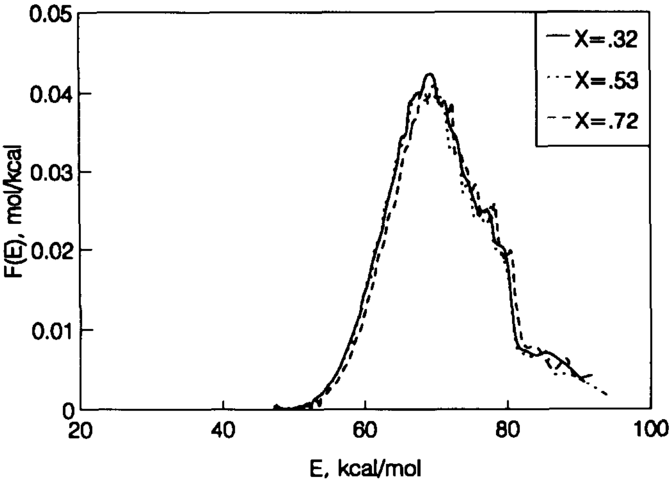

Fig. 3. Distribution functions $F(E)$ of the activation energy for the desorption of C–O complexes from Graphpac GB. TPD performed in the range 200–930°C after different sample conversions at 550°C.

for carbon dioxide and at 41 and 78 kcal mol^{-1} for carbon monoxide. The distribution functions obtained for CB-330, reported in Fig. 6, show peaks at 40, 61 and 78 kcal mol^{-1} for carbon monoxide and at 42 and 61 kcal mol^{-1} for carbon dioxide. In both diagrams, the first peak indicates the presence of a relevant fraction of surface sites or of the total carbon–oxygen surface complexes which have an activation energy that is about 30% lower than that of C–O complexes in the uncatalysed system.

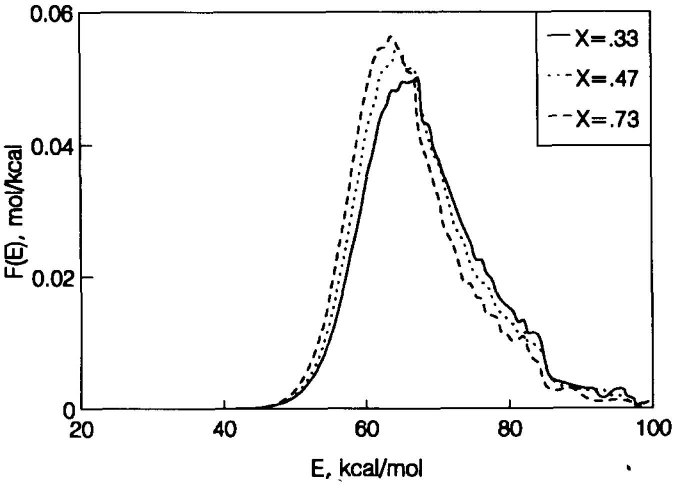

Fig. 4. Distribution functions $F(E)$ of the activation energy for the desorption of C–O complexes from CB-330. TPD performed in the range 200–930°C after different sample conversions at 550°C.

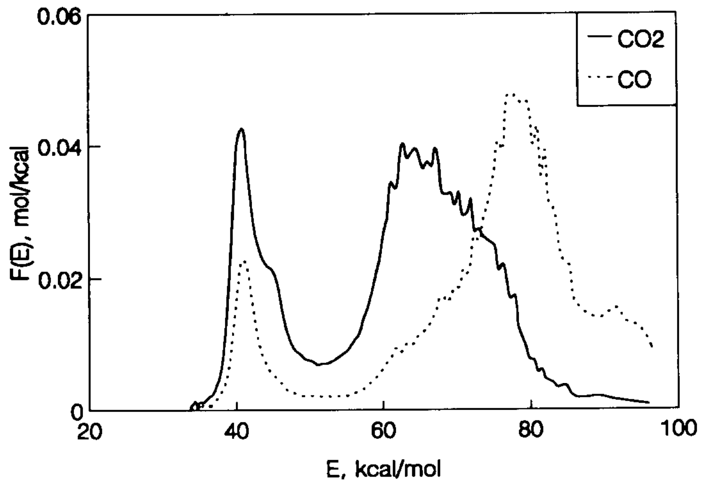

Fig. 5. Distribution functions $F(E)$ of the activation energy for the desorption of $(C–O)_x$ complexes from Graphpac GB mixed with catalyst. TPD performed in the range 200–1000°C after a sample conversion of 37% at 310°C.

Even in the presence of catalyst, the application of the TPD technique to samples oxidised at different conversion degrees leads to the conclusion that the $F(E)$ functions remain practically unchanged during the reaction.

The comparision of the $F(E)$s from uncatalytically and catalytically oxidised samples could provide an explanation for the marked difference between the oxidation reaction rates, which depend on the rate of

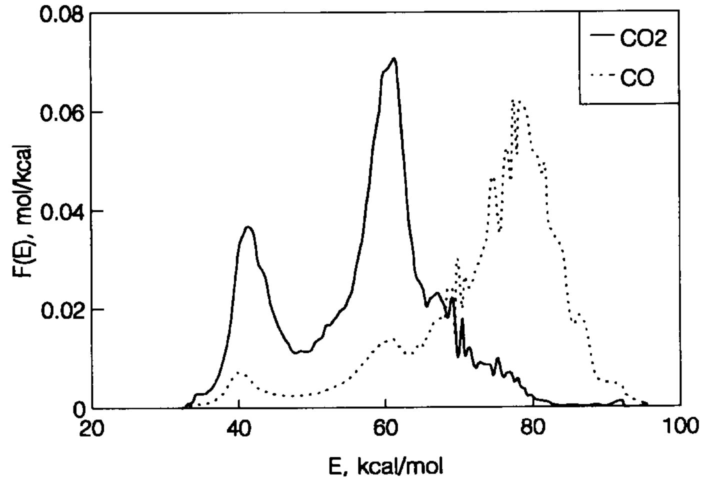

Fig. 6. Distribution functions $F(E)$ of the activation energy for the desorption of $(C–O)_x$ complexes from CB-330. TPD performed in the range 200–1000°C after a sample conversion of 55% at 320°C.

desorption of carbon–oxygen complexes. Many researchers [8–10] agree that the mechanism of uncatalysed carbon oxidation comprises the steps of oxygen chemisorption on the carbon surface, of formation of carbon–oxygen complexes, and of desorption of such complexes as carbon oxides. At a given temperature, a number of complexes are present over the carbon surface (this number can be determined by TPD measurements), as a result of the dynamic equilibrium between the formation and the desorption steps. At this temperature, only a fraction of the above number may be successfully desorbed, i.e. only that fraction which has an activation energy of desorption lower than a certain threshold value dependent on the temperature itself. Therefore the activity of the catalyst promotes the formation of complexes characterized by a relatively low activation energy for desorption (see Figs. 5 and 6), thus favouring this step at a given temperature. Whether this fraction of complexes that is formed in the presence of the catalyst derives from the modification of ordinary complexes (uncatalysed case) or from the formation of new types of complexes, both cases generating carbon monoxide and dioxide by desorption, is a matter to be investigated in future work on this subject. Certainly, the catalyst strongly increases the number of surface complexes (presumably $C–O_2$) which are intermediates in the process of formation of gaseous carbon dioxide.

In the light of this previous explanation, it is also possible to give an interpretation of the attenuation of the differences between the reactivities of the two carbon blacks in the presence of catalyst (Fig. 2). Indeed, the comparison of the $F(E)$s in Figs. 5 and 6 shows that for both CB-330 and Graphpac-GB, the fraction of surface sites with low desorption energy has almost the same peak energy value. If this fraction is really responsible for the strong increase in the oxidation rate with respect to the uncatalysed reaction, only very small differences in reactivity between the two materials can be expected.

CONCLUSIONS

The site energy distribution functions of carbon blacks after partial gasification in oxygen are not influenced by the reaction conversion degree, for both uncatalysed and catalysed oxidations.

The determination of carbon surface activation energies from TPD data appears to be an effective tool for the study of the mechanism of carbon-particulate-catalysed oxidation.

The marked increase in the rate of carbon oxidation in the presence of catalyst could be associated with the strong increase in the number of surface complexes generating gaseous carbon dioxide, and with the decrease in the activation energy of the desorption of carbon–oxygen complexes.

ACKNOWLEDGEMENT

This work was financed by "Progetto Finalizzato Trasporti 2" of the National Research Council of Italy.

REFERENCES

1 P.L. Walker, Jr., R.L. Taylor and J.M. Ranish, Carbon, 29 (1991) 411–421.
2 H. Henssler, Stud. Surf. Sci. Catal., 71 (1991) 35–40.
3 P. Ciambelli, P. Parrella and S. Vaccaro, Stud. Surf. Sci. Catal., 71 (1991) 323–336.
4 P. Ciambelli, P. Corbo, M. Scialò and S. Vaccaro, Italian Patent No. 1221416 (1988).
5 P. Ciambelli, P. Corbo, P. Parrella, M. Scialò and S. Vaccaro, Thermochim. Acta, 162 (1990) 83–89.
6 P. Ciambelli, V. Palma and S. Vaccaro, Catalysis Today, 17 (1993) 71–78.
7 Z. Du, A.F. Sarofim and J.P. Longwell, Energy Fuels, 4 (1990) 296–302.
8 Z. Du, A.F. Sarofim and J.P. Longwell, Energy Fuels, 5 (1991) 214–221.
9 A.E. Lear, T.C. Brown and B.S. Haynes, Proc. Int. Symp. Combust., 23 (1990) 1191–1197.
10 T. Kyotani, H. Yamada, H. Yamashita, A. Tomita and L.R. Radovic, Energy Fuels, 6 (1992) 865–867.