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CALORIMETRIC EVIDENCE FOR A DUAL MECHANISM IN THE LOW TEMPERATURE OXIDATION OF COAL

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Calorimetry linked with GPC analysis has allowed the measurement of the heat of reaction against the oxygen coverage for three french coals ranging from subbituminous to semianthracite. At low oxygen coverage, a complex evolution of the enthalpy is observed mainly attributed to a chemisorption located on radical sites formed and accumulated during the outgassing pretreatment, whereas at higher coverage, the enthalpy becomes independent of the oxygen coverage where the removal of hydrogen as water vapour predominates. At low coverage the degassing pretreatments influence in a persistent way the enthalpy measurements, and in consequence it is generally only at high oxygen coverage, that enthalpy measurements coming from differently pretreated samples may be usefully compared.

Introduction

Coal, like many other carbonaceous materials, can undergo oxidation during its aerial storage, transport and handling. Low temperature oxidation is generally detrimental and leads to a severe alteration of its physical and chemical properties. Certain changes have an economic importance as well such the decrease of heat content for plain coal and the destruction of coking properties for coking coal. The coal oxidation can lead to the self heating, and, in some cases, to its spontaneous ignition. Also, most calorimetric studies are concerned rather with safety problems aiming mainly to measure the rate of heat evolution [1–3] in contrast, only a small number of papers have been devoted to the study of the oxidation mechanism itself [4, 5]. As a rule, such studies are concerned with the problem of weathering and are, in consequence, carried out at low temperature where, unfortunately, the reversible adsorptions of both unreacted oxygen and evolved water vapour are superimposed on the chemical reaction and

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chemisorption of oxygen making the interpretation of enthalpy measurements difficult.

Although our long range objective was also to reach a better understanding of the weathering mechanism, as a first step, the study of the low temperature oxidation of coal has been examined at 423 K in order to remove doubts caused by reversible adsorptions and also for kinetic reasons. In a second step, not shown here, the weathering will be studied near ambient temperature and the role of water will be emphasized.

Experimental

The experimental device and the procedures followed have previously been described [6–8], and are only briefly reviewed here. The experimental device consists of a Tian-Calvet calorimeter connected to a static apparatus allowing the oxygen introduction and measurement (Fig. 1). During the oxygen reaction a dry-ice mixture allowed the water vapour formed to be trapped in T_2. Then, after the removal of the freezing mixture, the maximum water vapour pressure was manometrically measured in a control volume V, and finally absorbed in T_2 on P_4O_{10}.

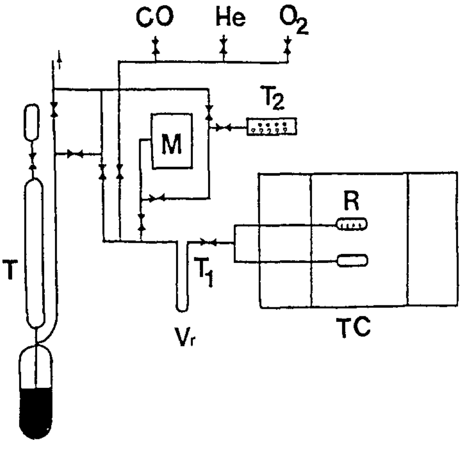

Fig. 1 Schematic diagram of the volumetric apparatus and the calorimeter: T_1, trap; T_2, P_4O_{10} absorber; M, micromanometer; R, reactor; TC, Tian-Calvet calorimeter; T, Toeppler gauge

To take into account water adsorbed on the walls, a calibration curve ($N = f(P_{max})$) was obtained by introducing int V, known micromole doses of liquid water and measuring P_{max} after the removal of the dry-ice mixture. This procedure allowed the measurement of water quantities between 5 and 300 μmoles with a precision of 5–7% [8].

After a pressure measurement with the micromanometer M, all of the unreacted or desorbed gases were sampled with the Toeppler gauge T and analysed by GPC (O_2, N_2, CO, CO_2, CH_4).

These measurements allowed an oxygen mass balance to be made and also the determination of oxygen reacted, oxygen recovered (as H_2O, CO, CO_2) and, by difference, oxygen irreversibly fixed.

Calorimetric data have been corrected using the relation given by Letoquart *et al.* [9]:

$$Q = Q_m - RT - V_G(P_2-P_1) \tag{1}$$

where Q_m, Q, V_G, P_1, P_2, and $V_G(P_2-P_1)$ are respectively: the heat measured and corrected, the reactor volume, the initial and final oxygen pressures and the work of compression which can be neglected with the differential arrangement used here.

Three french coals from the GRECO-CERCHAR minibank were used: Vouters (high volatile btuminous B coal), Provence (subbituminous A coal), Escarpelle (semi-anthracite). Their compositions are listed in Table 1.

Table 1 Composition of coals

	Ultimate analysis, w%				
	C	H	O	N	S
Provence	67.3	4.6	20.2	5.8	2.0
Vouters	82.8	4.9	10.4	0.5	1.3
Escarpelle	91.1	3.4	2.9	1.0	1.4

Coal samples (0–1g) were crushed for five minutes with an agate mortar and pestle, then introduced into the calorimeter at 313 K briefly evacuated at this temperature, heated under vacuum at 10 deg·h^{-1} to 523 K and degassed for 100 h.; then, the temperature was fixed at 423 K before oxygen admission.

For the oxygen coverage calculations, microporous volumes and surface area values were derived from adsorption measurements at 298 K using CO_2 as adsorbate and the Dubinin-Raduskevitch method for the data treatment. The area per adsorbate molecule was taken for CO_2 and O_2 respectively as 0.253 nm^2 and 0.16 mn^2 [10].

Results and discussion

For the three coals studied the enthalpy of oxygen reaction against the oxygen coverage exhibited the same qualitative behaviour (Fig. 2). At low coverage the enthalpy first decreased, passed through a minimum, then increased and tended toward, at higher coverage, similar values for all three coals and a quasi independence of the oxygen coverage. To our knowledge it is the first time that a such behaviour has been observed at low coverage (very likely because of the careful control of conditions used for the outgassing treatment). The quasi independence of enthalpy against the oxygen coverage has been already observed by Sevenster on several South African coals [5], but at an unprecised oxygen coverage (which is presumed low). The enthalpies measured at the plateau (330–360 kJ/mole) are difficult to compare with the value of 290 kJ/mole found by Sevenster after different pretreatment conditions (385 K) and reaction temperature (343 K).

In the low oxygen coverage region the decreasing enthalpy is characteristic of a dissociative chemisorption located on radical sites formed during the degassing treatment at 523 K [8]. Such behaviour has been already observed with different carbonaceous materials such as graphite [11] and charcoal [12].

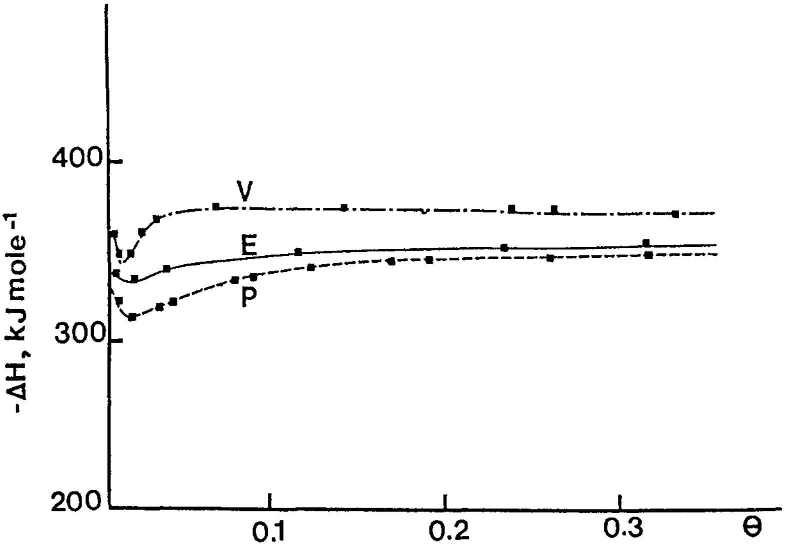

Fig. 2 Calorimetric isotherms at 423 K for the three coals Vouters (*V*), Provence (*P*) and Escarpelle (*E*) showing the enthalpy variation against the oxygen coverage Θ

At higher coverage a dehydrogenation reaction dominates over chemisorption as evidenced by the oxygen balance (Fig. 3) which shows, that, less than 50% of the oxygen reacted remains fixed on the coal surface, the major part being restored into the gas phase as H_2O, CO_2 and CO.

For all coals, the main constituent of the gas phase was water vapour, whereas the sum CO_2 + CO represented only a minor part (Figs 4 and 5).

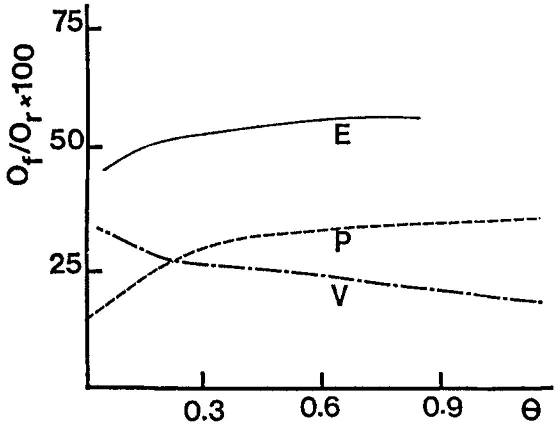

Fig. 3 Variation in the ratios fixed oxygen/reacted oxygen against the oxygen coverage Θ

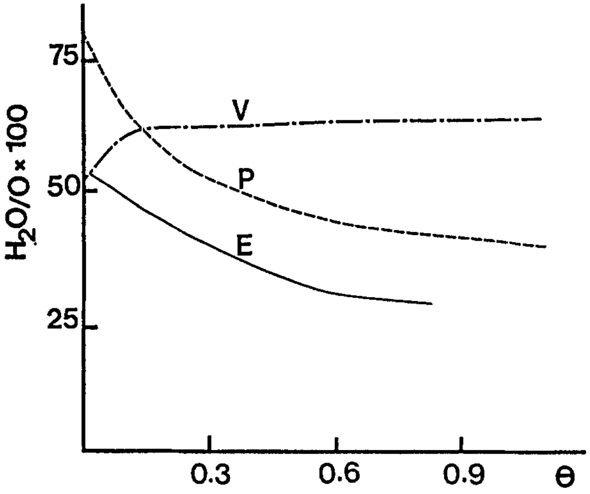

Fig. 4 Variation in the ratios of oxygen restored as water/reacted oxygen against oxygen coverage Θ

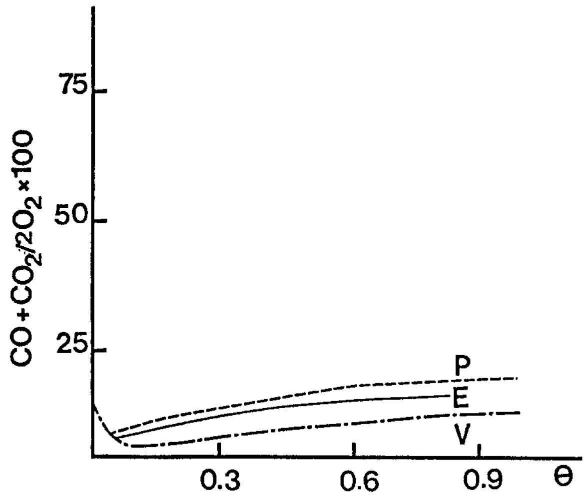

Fig. 5 Variation in the ratios of oxygen restored as CO_2 + CO/fixed oxygen against oxygen coverage Θ

After the complete oxygen consumption a post effect was observed evolving CO_2, CO and H_2O. Whereas water vapour release decreased readily with the time, CO_2 and CO evolutions persisted further. This behaviour was attributed to the pyrolysis of labile oxygenated groups [8].

An important change in the trend of thermograms corresponding to the oxidation reaction was observed, especially at high oxygen coverage, when the oxygen admission was preceded by a pyrolysis period of 16 h at 423 K. Figure 6 shows that a rapid process (part A of curve III) is superimposed on the slow process (curves I, II and part B of curve III). The slow process is very likely connected to the dehydrogenation reaction and the rapid processis interpreted as resulting from an oxygen chemisorption located on radical sites formed and accumulated during the pyrolysis period at 423 K. It is interesting to note that a such behaviour has already been observed with other carbonaceous materials [12] as char and activated carbon [13]. In the presence of water vapour, radical sites are not destroyed after several hours of contact showing that water can play a protective role against oxygen reaction.

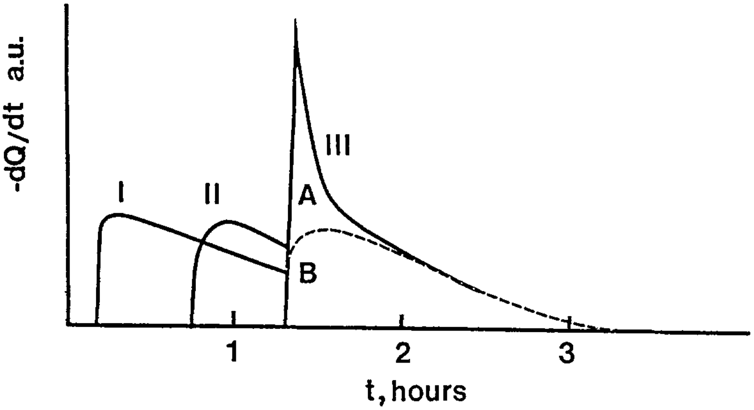

Fig. 6 Evidence of radical site regeneration at 423 K. Thermoanalytical curves I, and II correspond to the addition of equal successive doses of oxygen. Thermoanalytical curve III corresponds to the addition of a third equal oxygen dose preceded by a 16 h pyrolysis period

Conclusion

At 423 K the low temperature oxidation of coal consists of a dual mechanism. The main reaction is a dehydrogenation reaction evolving mainly water vapour and leaving generally less than 50% of the reacted oxygen attached on the surface. The side reaction is an oxygen chemisorption located on radical sites formed by pyrolysis of labile oxygenated groups. If these groups are peroxides, hydroperoxides or related compounds, they are expected to play a significant role in the weathering of coal.

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Zusammenfassung — Kalorimetrie kombiniert mit Gaschromatographie ermöglichte die Messung der Reaktionswärme mit Sauerstoff in Funktion der Sauerstoffbedeckung für drei französische Kohlen im Bereich von subbituminös bis semi-anthrazitisch. Bei niedriger Sauerstoffbedeckung verhält sich die Enthalpie komplex, was auf Chemisorption an radikalischen Zentren zurückgeführt wird, die während der Vorbehandlung durch Ausgasen gebildet und angereichert werden. Im Bereich höherer Bedeckung wird die Enthalpie unabhängig vom Sauerstoffbedeckungsgrad und hängt vorwiegend mit der Entfernung von Wasserstoff in Form von Wasserdampf zusammen. Bei geringer Bedeckung werden die Enthalpiemessungen in ausgeprägtem Masse durch die Ausgasungs-Vorbehandlung beeinflusst. Daher ist es im allgemeinen nur im Bereich hoher Sauerstoffbedeckung möglich, Enthalpiemessungen an unterschiedlich vorbehandelten Proben sinnvoll zu vergleichen.