IV - SURFACE COMPLEXES FORMED BY CONTACT WITH AIR ON SPHERON 6 TREATED AT HIGH TEMPERATURE

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We continued our studies on the surface complexes obtained by oxidation in air of Spheron 6 purified at around 1800°C in the presence of chlorine, or above 3000°C in an inert atmosphere. By heating the samples in a current of argon (12 $l.h^{-1}$) which then circulates in infra-red analysers, the concentrations of CO and CO_2 produced by the degradation of oxygenated complexes can be known at each moment. The carbon is heated to 900°C, by raising the temperature either continuously or in successive stages. The results are the same qualitatively whatever method of purification is employed; quantitatively they seem a little higher in the case of samples with a larger specific surface (purification at 1800°C), even when expressed in $\mu l.m^{-2}$.

In our earlier work we showed that a sample left in atmospheric air desorbs from 1 to 3 $\mu l.m^{-2}$ of CO and CO_2 (50 to 70 % CO). After oxidation at 620°C up to a weight loss of about 10 %, we observe a desorption of 25 to 30 $\mu l.m^{-2}$ (95 % CO, 5 % CO_2) on heating discontinuously by 100°C stages, most of the desorption taking place between 600 and 700°C. The addition of moisture to the combustion gas causes a slight increase in the volume of gas desorbed. It will be recalled that at 620°C it produces an apparent inhibition of the oxidation rate.

The main purpose of our present research is to determine the effect of a degassing at 900°C on the later behaviour of the sample in air. Two products were heated to 900°C in a current of argon :

- the first received no thermal oxidation

- the other was oxidised between 480°C and 620°C before treatment

Most of the samples prepared in this way were then left in contact with dry or damp air and a few placed in water, the temperature and exposure time being strictly defined. The samples were then degassed in a current of argon at temperatures rising continuously from 25°C to 900°C; since the duration of this operation can appreciably modify the quantity of oxygen degassed, we fixed it at 1 h 30 m.

A - Carbon blacks not subjected to thermal oxidation -

Carbon black simply treated at 900°C in a current of argon seems to react little with air or moisture. In fact the amounts of oxides resulting from the decomposition of complexes formed either by the action of damp or dry air during several days at 25°C, or by that of moisture-saturated argon, are hardly detectable.

B - Thermally oxidised carbon blacks -

The sample is thermally oxidised (480 to 620°C) by dry or damp air to between 10 and 35 % weight loss. All the oxygenated compounds are then eliminated by heating to 900°C in an inert atmosphere, after which the carbon black is exposed for periods varying between one hour and several days in the atmosphere under investigation.

a) Action of damp argon

Contact with damp argon during a 24 h. period leads to the formation of complexes between the water and the carbon. These complexes are decomposed by heat, giving about 1 $\mu l.m^{-2}$ of CO and CO_2. The maxima lie between 350 and 400°C for CO_2 and between

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600 and 700°C for CO.

b) Action of dry or damp air at 25°C

The quantities of CO and CO_2 produced by degradation of the complexes formed increase with exposure time and after a few months reach values close to those observed after thermal oxidation, i.e. about 30 $\mu l.m^{-2}$ according to the degree of corrosion. The CO_2 desorption temperature does not exceed 400°C, and CO is desorbed between 600 and 700°C.

c) Action of dry air above 25°C

If the temperature of the reaction with air is raised to between 150 and 300°C, we find that the CO_2 desorption maximum still lies between 350 and 400°C but that, in addition, a second maximum appears between 600 and 700°C. If the treatment is carried out at a temperature higher than 360°C the first maximum dwindles, leaving only the second. CO always desorbs chiefly between 600 and 700°C whatever the adsorption temperature; it constitutes about 90 % of the mixture.

A contact of 30 mn at about 300°C or 10 mn around 600°C leads to the same CO + CO_2 liberation (about 15 $\mu l.m^{-2}$).

d) Influence of treatments received by the sample on the reactivity at 25°C

Alternate degassings and exposures to dry air at 25°C appreciably lower the aptitude of a sample to form oxygenated complexes. This effect increases with the number of these cycles (20 % reduction for 4 cycles).

If an exposure to damp air is included in a series of experiments the reactivity drop is much greater still.

An oxidation at 620°C suffices to restore the sample to its initial state of reactivity.

CONCLUSION - Purified spheron 6 ($\theta \geqslant 1800$°C) thermally oxidised then degassed at 900°C becomes reactive at 25°C towards water and particularly oxygen, because of the creation of active sites. Some of the surface oxides thus formed decompose at low temperature (350-400°C). This reactivity is reduced if the sample is subjected to repeated oxidations (dry or damp air at 25°C) followed by degassings at 900°C. The latter treatment seems to inhibit a certain number of these sites and this action is still more marked in the presence of moisture.

B.R. PURI (1) has reported the formation of surface complexes by the action of oxygen or air at 25°C on sugar or coconut charcoals carbonised at a temperature between 350 and 400°C; these complexes decompose at low temperature.

M.M. DUBININ (2) has admitted the possibility in certain cases of a chemisorption of water on carbon blacks at 20 - 25°C.

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1) B.R. Puri, Proceeding of the fifth Conf. on Carbon, vol. 1, p. 165 (1962)

2) M.M. Dubinin, Chemistry and Physics of Carbon, vol. 2, p. 117 (1966)