

A TEMPERATURE-PROGRAMMED DESORPTION STUDY OF SURFACE OXYGEN COMPLEXES FORMED ON CARBONS FROM ATOMIC OXYGEN

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Introduction

A knowledge of the properties of surface oxygen complexes on carbons is important, not only for an understanding of their role in gasification reactions (Ref. 1) but also in determining the surface chemistry e.g. adsorptive properties, of the carbon (Ref. 2). A recent approach adopted by Marsh and co-workers (Refs. 3 to 6) involves the use of atomic oxygen to form surface oxygen complexes. This has the advantage that relatively large amounts of surface complex, approaching monolayer coverage (Ref. 3), are formed even at room temperature and below. In one study using atomic oxygen (Ref. 5), a linear-programmed increase in temperature was used to investigate the decomposition of the surface complex formed by the sequential adsorption of ^{16}O and ^{18}O atoms at 195 K. The isotopic content of the desorbed products (CO and CO_2) indicated that at some time during either their formation or decomposition the surface oxygen complexes were mobile over the carbon surface. This led Marsh and Foord (Ref. 6) to suggest a unified hypothesis (Ref. 6) explaining variations in the CO/CO_2 ratio in the products of the gasification reaction between carbons and oxygen. The desorption of CO_2 was considered to be governed by the likelihood of collision-interactions between mobile chemisorbed oxygen atoms (i.e. the surface oxygen complexes). Hence, increasing the concentration of surface oxygen complex or its mobility over the surface should result in an increased chance of collision-interaction and so a lower CO/CO_2 ratio should be found. Factors such as an increase in reaction temperature, a lower oxygen pressure, the presence of micropores in the carbon and the presence of surface imperfections would all be predicted to either lower the concentration of surface complex or impede its mobility. While the results of Foord (Ref. 5) confirm the identification of factors which impede surface complex mobility (e.g. the presence of microporosity, or increasing the extent of surface imperfection by lowering the HTT of the carbon) they do not indicate whether complex mobility occurs immediately following the initial interaction of an oxygen atom with the carbon surface, or immediately prior to desorption (the latter case is necessary for complex mobility to influence the CO/CO_2 ratio). The present study is concerned with a more detailed study of selected carbon samples in order to investigate further this possible relationship between surface oxygen complex mobility and reaction product ratio.

Experimental

The preparation of graphitizing carbons from polyvinyl acetate (PVA) is described elsewhere (Ref. 7). Surface oxygen complex was formed by adsorption, at 195 K, of oxygen atoms prepared by a microwave discharge in (40 Pa) 0.3 torr of oxygen with a power adsorption of 55 watts. The sample, previously

outgassed at 1175 K, was situated approximately 150 mm from the discharge zone. ^{16}O was adsorbed first for 30 minutes followed by ^{18}O for 2 hours. This gave a surface approximately equally covered by each isotope. The surface oxygen complex was decomposed by linear programmed heating from room temperature to 1175 K. The decomposition products were continuously pumped away (maintaining a vacuum over the sample of better than 133 Pa (10^{-6} torr) and analyzed by a mass spectrometer (Micromass 6).

Results and Discussion

The results to be discussed are those from two experiments performed on samples of a PVA carbon, HTT 1200 K. The experiments were identical except for the linear desorption heating rate which was 4.8 K min^{-1} in one experiment and 12 K min^{-1} in the other. The isotopic ratio in the desorbed carbon monoxide is plotted as a function of desorption temperature in Figure 1. That the CO is initially rich in the oxygen isotope that was adsorbed last indicates that some mobility of complex to the available sites of highest heat of adsorption has occurred immediately following the initial adsorption step (i.e. leading to a last-on, first-off process on desorption). Since the desorption of surface oxygen complex is a kinetically activated process, increasing the desorption heating rate will have the effect of increasing the amount of unstable complex (or mobile complex if mobility is a prerequisite of desorption) present on the surface at a particular desorption temperature. As shown in Figure 1 this also displaces the isotopic ratio curve to higher temperatures (as an increasing contribution from low temperature desorption is carried over to higher temperatures by a faster heating rate) although one is not able to conclude from this whether complex mobility immediately prior to desorption is occurring.

However, if the surface oxygen complex is mobile immediately prior to desorption, the increased chance of collision-interaction due to the higher concentration of mobile species present at the higher heating rate should, according to the hypothesis outlined earlier, lead to a lower CO/CO_2 ratio. That this is not the case is shown in Figure 2. One is led therefore to the conclusion, either that surface complex mobility does not play a part in governing reaction product ratio, or perhaps more likely that once adsorbed on a particular surface site the complex does not become mobile again before desorption. Carbon dioxide is then formed by the reaction between adjacent surface complexes.

Although these studies of adsorption and desorption processes related to surface oxygen complexes on carbons do help our understanding of their reaction with molecular oxygen, the latter reaction must always be considered as a dynamic changing (perhaps non-equilibrium) system so that the detail of the separate studies of complexes may not be directly applicable.

References

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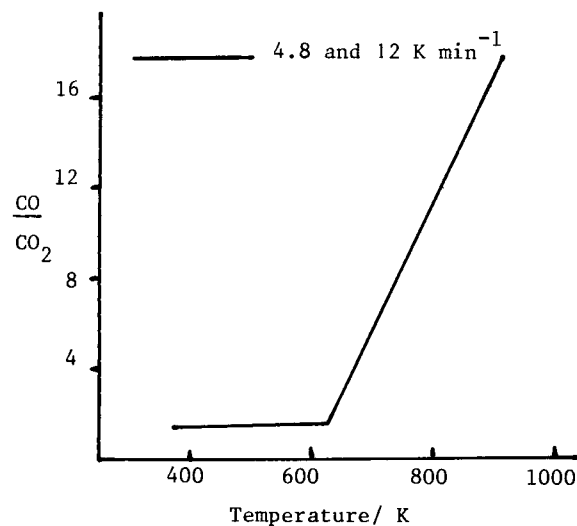


Figure 2. (Not drawn accurately to scale).

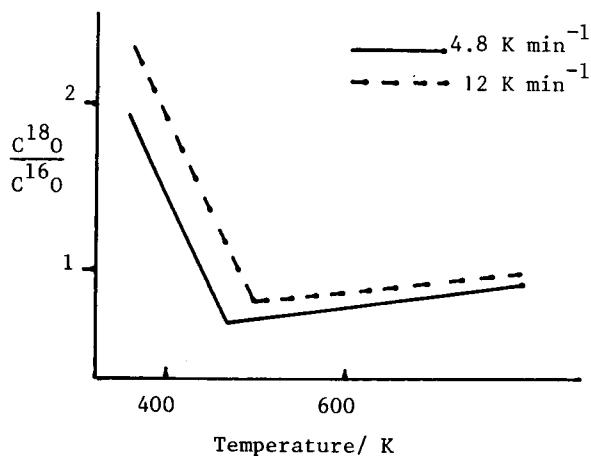


Figure 1. (Not drawn accurately to scale)