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INTRODUCTION

There are very few issues in the carbon-oxygen reaction that have not been investigated thoroughly. There are more than a few, however, that are not well understood [1]. One issue that falls into both categories is the dependence of the CO/CO₂ ratio on the surface chemistry and structure of the carbon.

Arthur [2] proposed an empirical relationship for the temperature dependence of the CO/CO₂ ratio in the form $CO/CO_2 = A \exp(-E/RT)$. The absolute values of A and E vary in a broad range and depend on oxygen pressure and type of carbon. Marsh [3] and Foord [4] have found for PVDC carbons that the CO/CO₂ ratio decreases as the heat treatment temperature of carbon increases. They explained this fact by the increasing mobility of surface oxygen complexes for ordered carbons. Yang and Wong [5] also emphasized the importance of oxygen mobility on the basal plane.

The objective of this ongoing work is to study in detail the influence of carbon structure and carbon surface chemistry on the distribution of products between CO and CO₂. In addition to clarifying this important practical issue, its investigation is an important guide in the formulation of necessary and sufficient mechanistic steps in the carbon-oxygen reaction.

EXPERIMENTAL

Several samples with different extents of crystalline order were prepared by carbonization of cellulose (C) and petroleum pitch (P) at temperatures between 1000 and 2500 °C. Their degree of crystallinity was analyzed by x-ray diffraction (XRD). The results are summarized in Table I. (Sample SP-1 is SP-1 graphite.)

The CO/CO₂ ratio, reactivity and reactive surface area measurements were done using a commercial transient kinetics (TK) apparatus (SSITKA 2000, Altamira Instruments, Inc.). The samples were oxidized until 25% burnoff in a flow of 20% O₂ in helium (1 atm). The products were analyzed by a mass spectrometer. The reactive surface area (RSA) was measured by the method

described in [6]. The total surface area (TSA) was measured by CO₂ adsorption at 0 °C using the Dubinin-Polanyi approach.

Table I. Average crystallite dimensions of carbons.

Sample	d ₀₀₂ , Å	L _c , Å	L _a , Å
C1000	4.27	10.8	35.5
C25000	3.56	22.0	72.6
P1000	3.63	16.3	54.5
P2500	3.35	171.4	116.7
SP-1	3.35	392	638

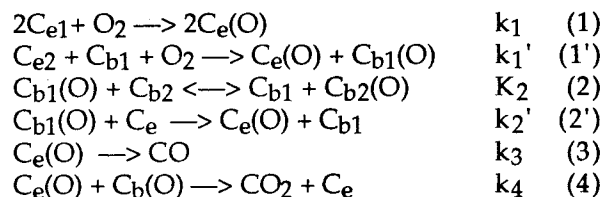
RESULTS

The dependence of the CO/CO₂ ratio on the type of carbon and temperature at P_{O₂}=0.2 atm is shown in Figure 1. For all reaction temperatures the CO/CO₂ ratio indeed obeys an Arrhenius expression [2] and is lower for carbons with a higher extent of graphitic order.

Figure 2 represents the dependence of the CO/CO₂ ratio on the crystalline order (L_a) of different carbon samples. There is a very strong dependence of the product ratio on the crystallite size. As the carbon becomes more graphitic, L_a (and L_c) increases and the CO/CO₂ ratio decreases.

DISCUSSION

In order to account for the results in Figures 1 and 2, as well as for some other recent proposals [7], the following reaction mechanism is proposed:



Due to geometric constraints, O₂ is also assumed to adsorb dissociatively on adjacent C_e (e.g., zig-zag) and C_{b1} sites (reaction (1')); C_e(O) is an edge carbon-oxygen surface complex and C_b(O) is a mobile carbon-oxygen complex on the basal plane. Step 2 represents surface diffusion, which appears to control the formation of CO₂.

It follows from reactions (3) and (4) that

$$\frac{\text{CO}}{\text{CO}_2} = \frac{k_3}{k_4[\text{C}_b(\text{O})]} \quad (5)$$

i.e., the CO/CO₂ ratio is inversely proportional to the concentration of stable carbon-oxygen surface complexes on the basal plane.

Because oxygen first adsorbs on the edges and then spreads over the basal plane by surface diffusion, [C_b(O)] should be proportional to the parameter η, which we determine as follows:

$$\eta = \frac{\text{number of edge sites}}{\text{number of sites on basal plane}} \quad (6)$$

Assuming for simplicity that the carbon crystallite is a cube, η can be estimated as follows:

$$\eta \sim \frac{4L_a L_c}{2(L_a)^2} = \frac{2L_c}{L_a} \quad (7)$$

The ratio L_c/L_a typically increases with increasing extent of carbon graphitization [8] (see also Table II). Therefore, one may expect the CO/CO₂ ratio to be lower for more ordered carbons. This is confirmed by experimental data in Figures 1 and 2.

Keeping in mind that in an "inert gas flush" (or transient kinetics) experiment in O₂ [5,6] C_b(O) may represent a significant fraction of the RSA, [C_b(O)] can also be estimated as follows:

$$[\text{C}_b(\text{O})] \sim \text{RSA}/\text{TSA} \quad (8)$$

Values for η, RSA/TSA and the CO/CO₂ ratio for different carbons are given in Table II. For all samples the CO/CO₂ ratio is indeed seen to be inversely proportional to η and RSA/TSA.

SUMMARY

It was found experimentally that the CO/CO₂ ratio decreases as the crystalline order of the carbon increases. A mechanism of the carbon-oxygen reaction is proposed, in accordance with which the CO/CO₂ ratio is inversely proportional to the concentration of oxygen on the basal plane. It is hypothesized that the size of a carbon crystallite determines the CO/CO₂ ratio, because [C_b(O)] depends on the relative contributions of edge and basal plane sites to the C/O₂ reaction.

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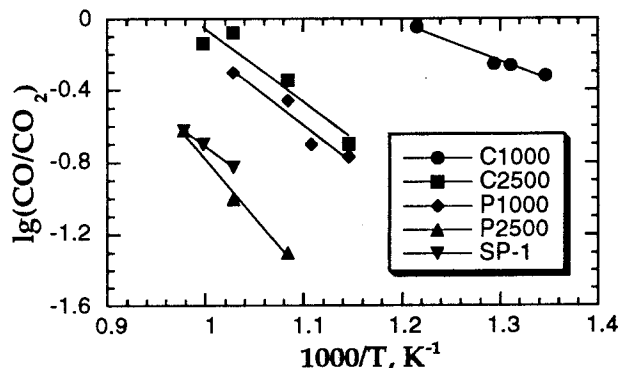


Figure 1. Dependence of the CO/CO₂ ratio on temperature and carbon structure.

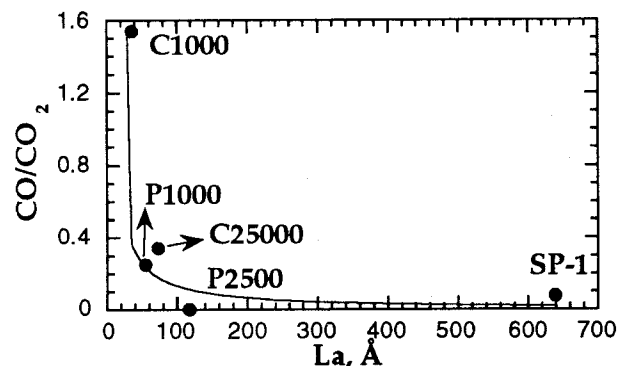


Figure 2. Dependence of the CO/CO₂ ratio on the size of crystallites (T=630 °C).

Table II. Dependence of the CO/CO₂ ratio on parameter η and RSA/TSA ratio (T=630 °C).

Sample	η	RSA/TSA, mgC/m ²	CO/CO ₂	Rate, gC/gC/h
C1000	0.57	0.05	1.54	21.7
C2500	0.60	-	0.34	0.04
P1000	0.60	1.27	0.25	2.6
SP-1	1.23	2.11	0.08	0.03
P2500	2.93	-	0.04	0.02