

ROLE OF CARBON-OXYGEN COMPLEXES IN THE CO/CO₂ RATIO DURING CARBON OXIDATION

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Introduction

The carbon-oxygen reaction selectivity, i.e., the CO/CO₂ ratio in the reaction products, is one of the insufficiently investigated issues in the area of carbon reactivity. Analysis of the literature [1] shows that there is no agreement regarding experimental values of the CO/CO₂ ratios from the data of different authors. This analysis also shows that the CO/CO₂ ratio depends not only on temperature and oxygen pressure, but also on the structure of the carbon material being oxidized. This means that not only carbon reactivity, but also the ratio of reaction products is a structure-sensitive parameter. The purpose of this paper is to demonstrate the fundamental dependence of the CO/CO₂ ratio on surface concentrations of stable and reactive C(O) complexes.

Experimental

Carbon samples were prepared from petroleum pitch A-240 (P1000) and cellulose (C1000) precursors by carbonization at 1000 °C. Reaction rates and CO/CO₂ ratios were measured using a mass spectrometer (SSITKA, Altamira Instruments). The reactive surface area (RSA) was measured according to the procedure described elsewhere [2]. The total surface area was measured by CO₂ adsorption at 0 °C.

Results and Discussion

The essential features of the reaction mechanism of carbon oxidation can be represented as follows:



This leads to the following expression for the CO/CO₂ ratio:

$$\frac{CO}{CO_2} = \frac{k_2}{k_3[C(O)]} \quad (4)$$

In the above expression, [C(O)] is the surface concentration of reactive intermediates (number of complexes per unit area). It can be estimated as a ratio of RSA (mg of reactive C/g of total C) to TSA (m² of total area/g of total C).

Reactive Carbon-Oxygen Complexes

Figure 1 presents the CO/CO₂ ratio dependence on the RSA/TSA ratio for different carbon samples. The main conclusion from this figure is that, in agreement with the conventional reaction mechanism and Equation

4, the CO/CO₂ ratio is inversely proportional to the surface coverage with reactive complexes. In other words, as the surface coverage increases, so does the rate of CO₂ formation, and the CO/CO₂ ratio decreases. This is in agreement with the data of other authors [3,4].

The next interesting conclusion from Figure 1 is that the carbon samples with higher HTT and with larger crystallite sizes have a higher RSA/TSA ratio and, therefore, a higher surface coverage with reactive C(O) complexes. This result may be confusing, since it is generally believed that more graphitic carbons have lower surface oxygen coverages.

A likely resolution of this apparent contradiction is based on the dynamic relationship between the concentration of reactive and stable carbon-oxygen complexes. If the surface is already occupied by stable complexes, the number of active sites available for the formation of reactive complexes decreases and, therefore, the concentration of reactive complexes also decreases. (This consideration is in accord with the earlier finding that stable complexes temporarily inhibit oxidation [2,5].) As will be shown below, more graphitic carbons indeed have a lower concentration of stable carbon-oxygen complexes. They thus have a higher concentration of reactive complexes, and therefore a lower CO/CO₂ ratio in the products of carbon oxidation.

Oxygen Content from Elemental Analysis

One of the measures of stable carbon-oxygen complexes on the carbon surface is the oxygen content obtained from elemental analysis. As it will be shown below, the oxygen that exists on the surface before the onset of oxidation does not take a very active part in the formation of gaseous products and it may be considered as stable surface oxygen.

Table 1 shows the CO/CO₂ ratios, the RSA/TSA ratios, as well as the elemental oxygen content of different carbons. The CO/CO₂ ratio and RSA data refer to the reaction temperature of 630 °C and 25% burnoff level. The TSA and oxygen content correspond to the initial unoxidized condition of the carbons.

It follows from Table 1 that, as the heat treatment temperature of carbon sample and the extent of its graphitization increases, the oxygen content decreases, as expected. But the RSA/TSA ratio increases (as is also shown in Figure 1), and the CO/CO₂ ratio decreases. These results are in agreement with the logic chain constructed above: more ordered carbons → lower oxygen content → lower surface coverage with stable complexes → higher surface coverage with reactive

C(O) complexes (assuming that the total concentration of active sites is constant) → lower CO/CO₂ ratio in the products of oxidation.

Stable Carbon-Oxygen Complexes

Four experimental runs were performed in which the P1000 sample was first gasified (in a 20% mixture of O₂ in He) to 25% burnoff and then quickly cooled (in O₂). In the first run, a TPD was performed right after the cooling to remove all carbon-oxygen complexes. Then, a typical reaction run was performed at 600 °C. In the second experimental run, only a portion of the complexes was removed during TPD, i.e., TPD was performed only up to some intermediate temperature, allowing for some complexes to remain on the surface. Subsequently, a typical reaction run was performed at 600 °C. Similarly, during the third and fourth runs, different amounts of carbon-oxygen complexes were allowed to remain on the surface after TPD. The amount retained on the surface was calculated as

$$[C-O]_s = [C-O]_{total} - [C-O]_{TPD}$$

where $[C-O]_{total} = 0.38$ mmol/g (determined during the first run).

Therefore, four different samples with the same total surface area but different amounts of stable complexes were studied to determine their reactivities and CO/CO₂ ratios.

The reactivity data and the CO/CO₂ ratio profiles for these samples are shown in Figure 2. It can be seen that, as the coverage with stable complexes increases,

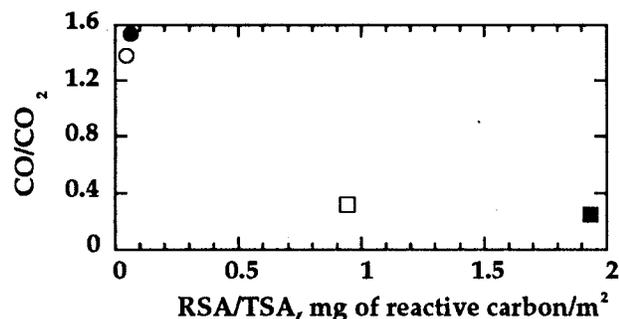


Figure 1. Relationship between the CO/CO₂ ratio and the RSA/TSA ratio. ○, C1000, 0.06 atm; ●, C1000, 0.2 atm; □, P1000, 0.06 atm; ■, P1000, 0.2 atm.

Table 1. CO/CO₂ ratios, RSA/TSA ratios, and wt% of oxygen for carbon samples (T = 630 °C).

Sample	P _{O₂} , atm	CO/CO ₂	RSA/TSA, mg reactive carbon/m ²	Wt% O*
C1000	0.06	1.38	0.045	3.34
C1000	0.2	1.54	0.063	3.34
P1000	0.06	0.32	0.937	0.07
P1000	0.2	0.25	1.935	0.07

*obtained from elemental analysis (by difference).

the reactivity generally decreases while the CO/CO₂ ratio increases monotonically. This important experimental fact is in agreement with the earlier speculation about the relationship between stable complexes, reactive intermediates and the CO/CO₂ ratio. Although direct measurements of the concentration of reactive intermediates were not performed yet, the fact that samples with less stable complexes are typically more reactive indicates that the same samples have a higher concentration of reactive C(O) complexes.

In summary, it was shown that the CO/CO₂ ratio is inversely proportional to the surface coverage with reactive C(O) intermediates. However, the CO/CO₂ ratio is directly proportional to the surface coverage with stable carbon-oxygen complexes.

References

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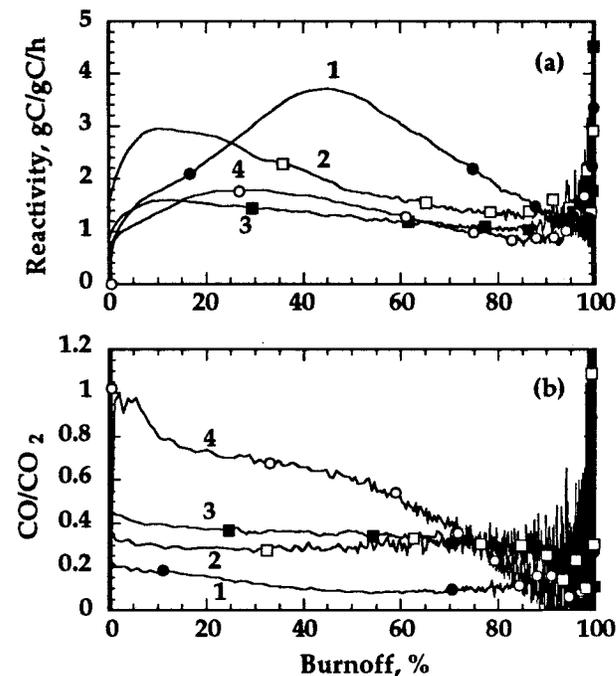


Figure 2. Reactivity (a) and CO/CO₂ ratio (b) of P1000 sample with different amounts of stable carbon-oxygen complexes on the surface: 1 - 0.0 mmol/g; 2 - 0.08 mmol/g; 3 - 0.25 mmol/g; 4 - 0.36 mmol/g.