

THE KINETICS OF THE CARBON-OXYGEN REACTION IN PYROLYTIC GRAPHITES AND ITS RELATION TO THE DEGREE OF ORIENTATION

J. de D. López-González, M. Rodríguez-Gallego, F. Rodríguez-Reinoso and L. Zurita-Herrera.

Departamento de Química Inorgánica. Facultad de Ciencias. Universidad de Granada. (Spain).

The carbon-oxygen reaction has been studied for many years, but the results found in the literature vary greatly depending on the materials used and the experimental conditions. The use of highly oriented pyrolytic graphite seems to be a good solution to this problem as it has been shown in previous papers (1,2), but even in this case there can be variations in experimental data according to the degree of orientation, grain size, and other characteristics of the pyrolytic graphite used. In order to find the influence that these variables may have on the kinetics of the carbon-oxygen reaction we are carrying out the study of the carbon-oxygen reaction on different highly oriented pyrolytic graphites kindly supplied by Dr. A. Moore, of The Union Carbide Corporation, Cleveland, Ohio.

Samples of about $15 \times 10 \times 1$ mm. were cut from the original specimens and the carbon-oxygen reaction was followed in a Cahn RG Electrobalance using an oxygen pressure of 50 Torr. The temperature range of the reactivity runs was from 650°C to 800°C, where the reaction rate was chemically controlled. In all cases the reaction presents a high initial reaction rate which gradually drops to a steady state value. There is not a great difference between the steady state values found at a given temperatures for the several graphites used, but the difference is large for the initial values of the reaction rates. The high initial reaction rates are not due to the attack on the basal planes of the graphites as it has been shown by reacting the samples again after cleavage of the basal surfaces of the previously oxidized samples; in this case the oxidation rate is practically constant and equal to the steady state rate of the first reaction. Consequently, the high initial reaction rate is due basically to the oxidation of the edge surfaces of the samples and the differences between the rates for the different samples of graphite studied must be attributed to differences in the reactivity of the edges of the materials.

The reactivity data have been used to determine the kinetics of the carbon-oxygen reaction in each kind of graphite. The Arrhenius plots of the oxidation rate (the steady state value) at the different temperatures for 50 Torr oxygen pressure, allows the calculation of the activation energy. The order of the reaction was

determined by using samples of identical dimensions at 750°C and in the oxygen pressure range from 20 to 120 Torr. The activation energy obtained for the different samples of graphite used ranges from 65 to 46 Kcal mole⁻¹ and the order of the reaction gave always values from 0.6 to 0.7, near the ideal value of 0.5 corresponding to the attack of two neighbouring carbon atoms by an oxygen atom.

In order to find a relationship between the experimental values for the activation energy and the crystalline perfection of the graphite used, we have carried out a qualitative determination of the degree of orientation (3) of the different graphites and the determination of their grain size (4). In the first case, the samples of graphite, prior to the reaction run, were positioned in an X-ray diffractometer with the layer plane surface normal to the plane of the incident beam; an automatic drive motor rotates the sample and the proportional counter records the variations of diffraction intensity at different angles. Once the diffractograms were obtained, the samples were oxidized with 50 Torr O₂ at 800°C for 8 hours and the diffraction experiment repeated, in order to see the variation in reflectance of the samples due to the oxidation.

The grain size of the graphites was determined by etching the graphite basal surfaces in molecular oxygen (50 Torr O₂ at 750°C for several short periods of time). Subsequent examination of the etched specimens under the optical microscope gave an estimate of the crystallite size. The sample of pyrolytic graphite with lower reflectance and larger crystallite size gave the lower value for the activation energy and, at the same time, this graphite shows the larger increase in reflectance after oxidation (it increases up to more than four times the original reflectance). On the other hand, the graphite with larger original reflectance and larger crystallite size gave the higher value for the activation energy, and very low increase in reflectance after oxidation.

The samples studied have been seven and we have found that for the intermediate samples there is not a so clear relationship between the values of activation energy and reflectance and crystallite size. This is the reason why at this moment a quantitative determination of the degree of orientation is being carried out, by

calculating the mosaic spread of the different graphites and oxidized samples.

It is hoped that a quantitative relationship may be given at the moment of the presentation of this paper.

REFERENCES

- (1) RODRIGUEZ-REINOSO, F., THROWER, P.A. and WALKER, P.L.Jr.; Carbon, 12, 63 (1974).
- (2) LOPEZ-GONZALEZ, J. de D., RODRIGUEZ-REINOSO, F. and ZURITA-HERRERA, L.; Anales de Quí mica. In press.
- (3) NAGLE, D.C.; Ph. D. Thesis. The Pennsylvania State University (1973).
- (4) RODRIGUEZ-REINOSO, F. and THROWER, P.A.; Carbon, 12, 269 (1974).