

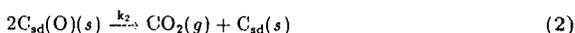
DESORPTION TURNOVER NUMBERS FOR THE CARBON-OXYGEN REACTION

Joseph M. Ranish
General Electric Company
Cleveland, OH 44112

Philip L. Walker, Jr.
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

For graphitic carbons reacting with O_2 , it is well established that the C atoms in the gasification products originate from the active surface, the (111) and (101) planes [1,2,3,4,5,6]. Even when the basal plane is gasified, it is gasified at defects which expose C atoms in these planes [7]. The gasified atoms are produced via either or both of the reactions below depending upon the reaction conditions.



The 'sd' subscript (strongly desorbing) in reactions 1 and 2 is used to show that only part of the active surface, the part comprised of C_{sd} surface atoms, is able to form the $C_{sd}(O)$ surface complex which is the precursor to the desorbed products. The rest of the surface oxygen complex is stable [8,9]. The fraction of the active surface which can form unstable surface oxides increases with increasing temperature. Because it is difficult to separate primary product CO or CO_2 from that produced by secondary reactions, a net desorption turnover number for C gasification, TON_C , will be used. It is defined in Equation (3) below as the atoms of C gasified per unit time per O atom of surface complex and incorporates the two more fundamental constants from reactions 1 and 2 above.

$$TON_C = k_1 + k_2[C_{sd}(O)] \quad (3)$$

Square brackets, [], denote species activities. Equation (4) shows that TON_C is the slope of the C gasification rate versus $[C_{sd}(O)]$ plot.

$$C \text{ gasification rate} = TON_C [C_{sd}(O)] \quad (4)$$

To the extent that the steady state primary product CO/ CO_2 ratio is large, the gasification rate will be a more linear function of the unstable surface oxide concentration and the TON_C will better approximate k_1 .

Although low temperature O_2 chemisorption techniques have been used to measure the active surface [8,10,11], the part of the active surface actually measured and its relationship to the part involved in the gasification, the covered strongly desorbing part, is not always clear. Aside from an in situ spectroscopic examination of the surface which, as yet, is undeveloped, a better way to estimate the surface involved in gasification may be to cool down a gasifying sample in O_2 and then measure the surface O content. At the instant of cooldown, the surface oxides consist

of stable and unstable types. As the temperature decreases, more of the unstable surface oxides become stable. Some of the unstable surface oxides desorb but should be replaced because the activation energies for adsorption and migration of O species are smaller than the activation energy for desorption [12,13,14]. The replacement of recently desorbed surface oxide would be less complete as the kinetics become less dominated by the desorption step. This limits the technique to low temperature, high O₂ pressure gasification. The cooled sample then contains oxygen originating from both the stable and unstable surface oxides. This oxygen can be recovered as CO and CO₂ by heating the surface oxides to about 1240 K [8].

The technique described above was used to study the gasification of a spectroscopic purity graphite powder in various pressures of O₂ at temperatures low enough so that the observed gasification rates were clearly chemically controlled. The results demonstrate a relationship between the gasification rate and the amount of surface oxide collected immediately after gasification. The relationship may be interpreted in terms of stable and unstable surface oxide and yields an estimate for the TON_C. This estimate is compared to global turnover numbers from the literature. The comparisons dramatize the importance of active site coverage in clarifying the role of active surface in gasification.

EXPERIMENTAL

Reactivity and linear programmed thermal desorption (LPTD) runs were performed in the same computer interfaced high pressure flow reactor. Gasification or desorption products were quantified by CO and CO₂ nondispersed infrared detectors and a mass flowmeter. Hydrocarbon free O₂ of >99.99% purity with a reported moisture content < 3 ppm was used for the reactivity studies. Ultra high purity Ar (>99.999%), passed through a Zr alloy gettering furnace to lower H₂O and O₂ levels to < 0.1 ppm, was used for the LPTD runs. The carbon studied was Union Carbide SP-1 spectroscopic purity graphite powder which had a total impurity content of < 0.1 ppm. It was supported unconsolidated in the reactor on high purity alumina or quartz trays or on sapphire disks.

Graphite samples were loaded into the reactor, given a LPTD, then gasified to 20% burn-off at 840±3 K at a fixed O₂ pressure. After cooling in O₂, the surface oxide was collected with another LPTD. Once loaded into the reactor, the sample was not exposed to ambient air until the final LPTD was finished. LPTD's were performed from ca. 300 K to 1234 K at 5 K/min. Full details are given elsewhere [15].

RESULTS AND DISCUSSION

Gasification proceeds through three stages as noted before [16,17]. All samples were burnt-off to 20% to be within the range of steady state gasification. Figure 1 illustrates that, when the reaction conditions are kept constant, the gasification rate exhibits more variability at low sample weights and decreases with increasing sample weight. A mass transfer calculation following the procedure in reference [19] for the case most limited by O₂ transfer yields a value of $\phi^2\eta = 0.0032$ which is safely below the 0.1 upper limit for chemical control. ($\phi^2\eta$ is roughly the ratio of the actual O₂ consumption rate to the mass transfer limited O₂ supply rate.) Therefore, O₂ mass transfer limitation is not causing the decrease in gasification rate with increasing sample weight. For the largest weight samples, CO inhibition can explain the slight gasification rate decreases [18]. For the smaller weight samples, however, the decrease in rate with sample weight appears to be due to the influence of extrinsic catalysis. This view is supported by the higher CO₂/CO

ratio in the product gas for these samples as well as microscopic examinations of the burnt graphite powder which reveal that the smaller weight, higher reactivity samples exhibit a much higher incidence of flakes with roughened edges and channels. The gasification rates were not significantly influenced by changing the sample support materials.

A typical LPTD profile obtained after 20% burn-off in 2.3 MPa O₂ at 837 K is illustrated in Figure 2. All LPTD profiles were similar and differed mainly in the evolution rates and total amounts but little in the rate-temperature profile. Most of the gas recovered during LPTD was CO. It is likely that the similarity in LPTD profiles is due at least partly to very rapid surface oxide migration or rearrangement.

Figure 3 illustrates the relationship between the steady state gasification rate and the surface oxide collected afterwards expressed in terms of total O collected. Because a vertical temperature gradient existed at the highest O₂ pressure, 3.5 MPa, the sample temperature during gasification at this pressure could be as high as 851 K. Regardless of whether the rate differences among the samples are caused by sample size (catalysis) or O₂ pressure differences the data follow the same trend. A least squares linear fit to the data shows that 5.5 μmole O/g of the surface oxide is stable. The excess is unstable and has a TON_C of 0.043 s⁻¹. The absence of significant curvature in Figure 3 implies that the TON_C closely approximates k₁.

This turnover number is compared with other more global turnover numbers from the literature in Figure 4. In Figure 4, the right hand vertical scale is in units appropriate for turnover numbers, the left hand vertical scale is in units appropriate for edge recession rates. Where necessary, reactivities in Figure 4 were extrapolated to 1.3 KPa using an O₂ reaction order of 0.5. The literature global turnover numbers are the gasification rates divided by the total active surface areas, i.e. C atoms gasified per unit time divided by C atoms exposed at edges of basal planes. These global turnover numbers may be obtained directly from microscopic observations of the recession rates of pits in the basal plane [5,20,21,22,25] or of the recession rates of unwet catalyst channels at points far from the catalyst particle [23,24]. They may also be obtained by dividing the gasification rate by the amount of chemisorbed O [8]. The chemisorption conditions must be chosen with care. Low temperature chemisorption may suffer from failure to saturate the entire active surface due to kinetic limitations. At higher temperatures, significant fractions of the active surface will be C_{ad} type and unable to retain surface oxide. Since active surface coverages are not known for the literature global turnover numbers, they cannot be converted into TON_{CS}, however they do represent the lower limits to the TON_{CS}. The scatter in the data in Figure 4 is probably due to variable coverages of active surface caused by variable degrees of catalysis, since the data were normalized for O₂ pressure. The upper line in Figure 4 is constructed using data having the lowest reported O₂ reaction order of 0.3 [21] and thus the highest active surface coverage. This line should more closely approximate the TON_C.

ACKNOWLEDGEMENTS

This research was performed at The Pennsylvania State University and was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy on Contract No. DE-AC02-79ER 10488.

References

- [1] J. A. Hedley, *Nature*, **188**, 44 (1960)

- [2] I. M. Dawson, E. A. C. Follett, and D. M. Donaldson, Proc. Eur. Reg. Conf. on Electron Microscopy, Delft 1960, Vol. I, p. 337
- [3] G. R. Hennig, J. Chim. Phys., 58, 12 (1961)
- [4] I. M. Dawson and E. A. C. Follett, Proc. Roy Soc., A274, 386 (1963)
- [5] E. L. Evans and J. M. Thomas, Proc. of Third Conference on Carbon and Graphite London 1970, p. 3, Soc. Chem. Ind., London (1971)
- [6] J. R. Fryer, Proc. Third Conf. on Industrial Carbon and Graphite, p. 246, Soc. Chem. Ind., London (1971)
- [7] C. Wong, R. T. Yang, and B. L. Halpern, J. Chem. Phys., 78(6), 3325 (1983)
- [8] N. R. Laine, F. J. Vastola, and P. L. Walker, Jr., J. Phys. Chem., 67, 2030 (1963)
- [9] P. L. Walker, Jr., F. J. Vastola, and P. J. Hart in *Fundamentals of Gas-Surface Reactions*, (H. Saltsburg, J. N. Smith, Jr., and M. Rodgers -Eds.), p. 307, Academic Press, NY (1967)
- [10] E. M. Suuberg, J. M. Calo, and M. Wojtowicz, ACS Div. Fuel Chem. Prep., 31 (3), 186 (1986)
- [11] L. R. Radovic, P. L. Walker, Jr., and R. G. Jenkins, Fuel, 62, 849 (1983)
- [12] J. Nagle and R. F. Strickland-Constable, Proc. of the Fifth Conf. on Carbon, Vol 1, p. 154, Pergamon Press, NY (1962)
- [13] J. Dollimore, C. M. Freedman, and B. H. Harrison, Carbon, 8, 587 (1970)
- [14] P. R. Olander, W. Siekhaus, R. Jones, and J. A. Schwartz, J. Chem. Phys., 57, 408 (1972)
- [15] J. M. Ranish, Ph. D. Thesis, The Pennsylvania State University, (1984)
- [16] P. Magne and X. Duval, Bull. Soc. Chem., France, 5, 1585 (1971)
- [17] D. J. Allardice and P. L. Walker, Jr., Carbon, 8, 375 (1970)
- [18] J. M. Ranish and P. L. Walker, Jr., Carbon, 24, 109 (1986)
- [19] P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin in *Advances in Catalysis*, Vol. XI (D. D. Eley, P. W. Selwood, and P. B. Weisz -Eds.), p. 133, Academic Press, NY (1959)
- [20] G. R. Hennig in *Chemistry and Physics of Carbon*, Vol. 2, (P. L. Walker, Jr.-Ed.), p. 1, Marcel Dekker, NY (1966)
- [21] J. M. Thomas in *Chemistry and Physics of Carbon*, Vol. 1, (P. L. Walker, Jr.-Ed.), p. 121, Marcel Dekker, NY (1965)
- [22] R. T. Yang and C. J. Wong, J. Chem. Phys., 75(9), 4471 (1981)
- [23] R. T. K. Baker and P. S. Harris, Carbon, 11, 25 (1973)
- [24] R. T. K. Baker and J. J. Chludzinsky, Jr., Carbon, 19, 75 (1981)
- [25] J. J. Baker, Ph. D. Thesis, The Pennsylvania State University (1970)

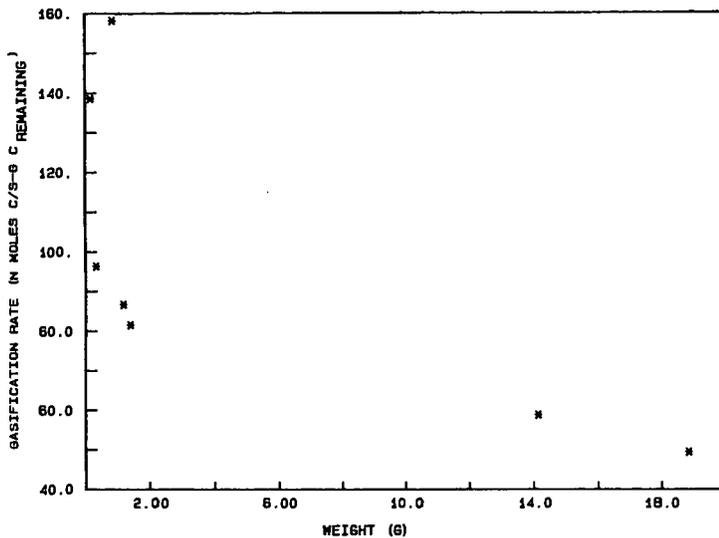


Figure 1: EFFECT OF INITIAL SAMPLE WEIGHT ON GASIFICATION RATE.
GASIFICATION AT 840 ± 3 K, 0.1 MPa O_2 , 20% BURN-OFF

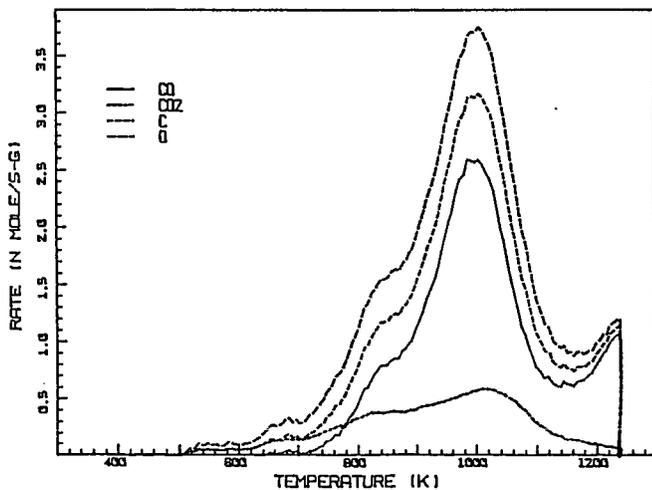


Figure 2: EVOLUTION RATES DURING LPTD AFTER GASIFICATION.
GASIFICATION TO 20 % BURN-OFF AT 837 K IN 2.3 MPa O_2

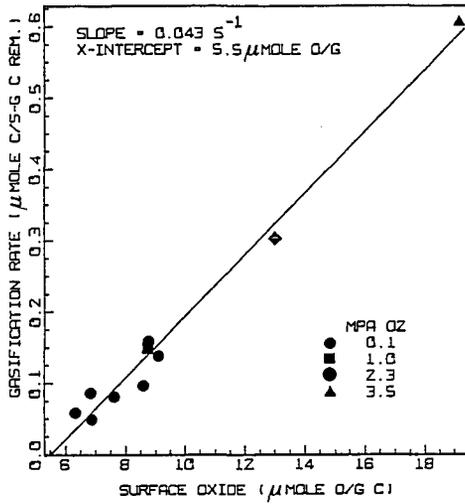


Figure 3: GASIFICATION RATE AT 20 % BURN-OFF, $840 \pm 3 \text{ K}$ VERSUS SURFACE OXIDE

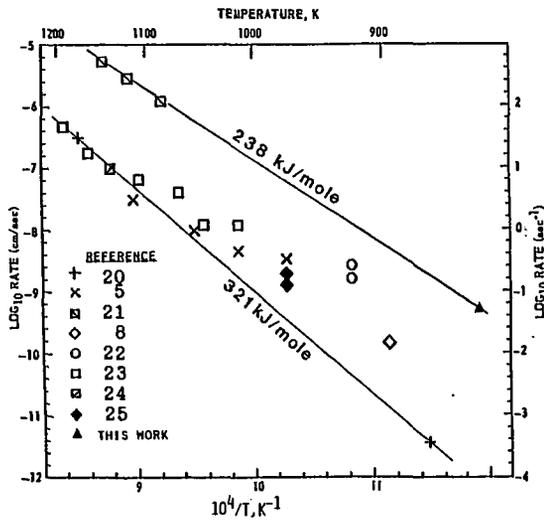


Figure 4: TURNOVER NUMBERS FOR THE CARBON-OXYGEN REACTION AT 1.3 KPA