

LETTERS TO THE EDITOR

Fundamental rate constants for carbon gasification by oxygen

(Received 1 May 1980)

Recently, Lewis and Simons compared a large collection of experimental rates for gasification of porous and non-porous carbons by oxygen with those they predict from a transport model and basic chemical model for the oxidation of porous carbon char [1]. To make this comparison, it is necessary to specify values for the physical constants of the chars (i.e. porosity and surface area) and fundamental rate constants for carbon gasification by oxygen. They present physical constants for the chars based on previous considerations of a mechanistic model to describe the structure of coal chars [2, 3]. They suggest values for the rate constants of carbon gasification after analyzing literature data for reaction of oxygen with a wide variety of carbonaceous solids ranging from char to pyrolytic graphite. From the success which they feel they have in using their models to predict laboratory data for the oxidation of porous coal chars, they conclude that the basic carbon-oxygen rate is the same for all chars from all ranks of coal.

For the oxygen transfer (adsorption) step in the carbon-oxygen reaction [that is, they give $C + O_2 \rightarrow C(O_2)$] Lewis and Simons [1] use the rate constant

$$k_1 = 900 \exp(-19,000/T) \text{ gm C/cm}^2 \text{ sec atm O}_2 \quad (1)$$

where cm^2 represents the total available surface area of the char. They recognize that the fundamental area to be used is active surface areas (ASA) and not total surface area (TSA). In fact, they find that modeling results for the oxidation of petroleum coke do not agree with modeling results for the oxidation of coal chars and suggest that petroleum coke may possess 6 times as many active sites per unit total area as do typical coal chars.

Despite the great importance of the carbon-oxygen reaction, essentially nothing has been done on the obtaining of fundamental rate constants based on ASA. The author is only familiar with the studies of Laine, *et al.* on the oxidation of graphitized carbon black over the temperature range 848–948 K [4]. In this study, the graphitized black, which initially has a very low ASA, was oxidized to various levels of burn-off up to 35%. ASA, as measured by oxygen chemisorption at 573 K, increased over 18-fold as a result of this burn-off; but TSA, as measured by the physical adsorption of N_2 at 77 K, increased less than 2-fold. Laine *et al.* then followed the gasification of these samples in O_2 at low pressures (6.5×10^{-2} Pa) using a mass spectrometer to follow the depletion of O_2 , the formation of CO and CO_2 , and, by difference, the formation of a stable carbon-oxygen surface complex as a function of time. Good kinetic data could be obtained using this approach for each burn-off (ASA) level, while the samples underwent negligible additional burn-off or change in ASA. The rates of carbon gasification and oxygen depletion were found to be given by equations of similar form:

$$\text{Rate} = (k)(C_{O_2})(\text{ASA})(1 - \theta) \quad (2)$$

where $k = k_C$, the rate constant for carbon gasification or k_{O_2} , the rate constant for O_2 depletion, C_{O_2} = concentration of O_2 , $(1 - \theta)$ = fraction of ASA unoccupied by a stable carbon-oxygen complex.

From the form of this equation it is clear that, at the low pressures used, the rate controlling step in carbon gasification

was the oxygen-transfer step. Both k_C and k_{O_2} , based on ASA, were found to be essentially independent of carbon burn-off. The rate constants based on TSA were found to continuously increase with increasing carbon burn-off; i.e. they were not acceptable rate constants.

Laine *et al.* expressed rate constants in their paper in units of $1/\text{sec m}^2$. However, more convenient units for k_{O_2} are cm^2/sec . That is, the rate in molecules O_2 reacting per sec can be calculated from:

$$\text{Rate} = (k_{O_2}, \text{cm}^2/\text{sec})(C_{O_2}, \text{molecules/cc})(\text{ASA}, \text{cm}^2)(1 - \theta) \quad (3)$$

The rate constants in the Laine *et al.* paper can be converted to units of cm^2/sec by multiplying them by the reactor volume, that is $15,500 \text{ cm}^3$.

Within experimental accuracy, Laine *et al.* [4] report an activation energy for the adsorption step which agrees with that given by Lewis and Simons [1], that is 158 kJ/mole. Rate constants, in units of cm^2/sec , for the adsorption step are then:

$$k_{O_2} = 1.2 \times 10^7 \exp(-19,000/T)$$

and

$$k_1 = 5.5 \times 10^6 \exp(-19,000/T).$$

Since Lewis and Simons state that their low temperature (700 K) value of k_1 may be as much as a factor of five too low [1], the agreement found between k_{O_2} and k_1 is excellent. It would be expected that k_1 would be less than k_{O_2} , since it is based on an estimate of available TSA and not ASA.

Studies are continuing in this laboratory to measure fundamental rate constants for the carbon-oxygen reaction for carbonaceous solids of varying crystallinity.

Acknowledgements—Research on the measurement of fundamental rate constants for carbon gasification is supported by the U.S. Department of Energy on Contract No. DE-AC02-79ER10488. The author appreciates the helpful comments of Dr. Girard Simons on the manuscript.

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