Walker P L Jr, Rusinko F Jr, & Austin L G. Gas reactions of carbon. In Advances in Catalysis (Eley D D, Selwood P W & Weisz P B, Eds) Vol 11, pp 133-221, Academic Press, New York (1959).
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Gasification of carbons by O_2, CO_2, H_2, and steam is considered. Equilibrium data are given, followed by consideration of rate expressions. Possible effects of mass transport of reactants and products in the pores of carbons on gasification rates are considered in depth.

Carbon Gasification is Ubiquitous

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The writing of this chapter had its origin at the 1954 Gordon Conference on Catalysis which I attended. Paul Weisz, a co-editor of "Advances in Catalysis" at the time, presented a fascinating lecture on the possible influence of diffusion of reactants into porous catalyst pellets on catalyst utilization, activity, and selectivity. We had been studying gasification of porous carbons in CO_2, particularly being interested in the role of active carbon surface sites and catalysts in determining gasification rates. It was imperative that rates were measured under conditions where they were controlled by the chemistry of the reaction, that is in the essential absence of mass transport limitations. Weisz's talk was just what the doctor ordered — a description of a way to measure experimentally rates of diffusion of gases in porous solids and the use of such data to test for possible diffusion limitations in reactions. Weisz kindly agreed to determine counter diffusion coefficients for the H_2/N_2 system in our porous graphite as a function of extent of carbon gasified. The diffusion coefficient (D_{eff}) increased sharply with carbon gasification [D_{eff} proportional to $(\text{porosity})^2$]. We were able to convert the H_2/N_2 data to relevant diffusion data for the CO_2/CO system.

In the mid-1950's there was much interest developing in carbon gasification in such diverse fields as: gas-cooled nuclear reactors, electric arc furnaces, production of activated carbons, nose cones for rockets, coal gasification, and removal of carbon from spent catalyst pellets. Consequently, Weisz invited us to prepare a chapter for "Advances in Catalysis" considering

broadly the subject of carbon interaction with reactive gases. Initially I had reservations since the subject matter seemed somewhat remote from that in the typical chapter appearing in the series. Weisz emphasized though that much of the subject matter in the series was concerned with heterogeneous gas-solid reactions and that such a chapter would broaden the horizons of the series. So my graduate students, Austin and Rusinko, and I proceeded; and I understand that the 1959 chapter has been one of the most cited in the entire series.

The chapter formed the basis for our thinking and research on carbons over the next 30 years. Some references to key papers can be cited. In 1963, I co-authored the first paper on using oxygen chemisorption to measure the fraction of the total surface area of carbons which participates in their gasification by O_2.[1] We gave meaning to the term "active sites." In 1968, our chapter considered catalysis of carbon gasification by inorganic constituents, which are always present (more or less) at carbon crystallite boundaries.[2] In 1976, we showed that some gaseous impurities can act as strong inhibitors to carbon gasification — for example, H_2 inhibiting gasification in CO_2.[3] In 1983, we showed that the fundamentals of gas-carbon reactions could be used to understand the gasification of complex materials like lignite coal chars.[4] Finally, there is much interest today in carbon molecular sieves. Carbon gasification can play a key role in determining the pore size in these materials and, hence, their effectiveness in separating molecules of particular sizes.[5]

1. **Laine N R, Vastola F J & Walker P L Jr.** The importance of active surface area in the carbon-oxygen reaction. *J. Phys. Chem.* 67:2030-2034, 1963.

2. **Walker P L Jr, Shelef M & Anderson R A.** Catalysis of carbon gasification. In *Chemistry and Physics of Carbon* (Walker P L Jr, ed.) Vol 4, M. Dekker, New York, 1968, pp. 287-383.

3. **Biederman D L, Miles A J, Vastola F J & Walker P L Jr.** Carbon-carbon dioxide reaction: kinetics at low pressures and hydrogen inhibition. *Carbon* 14:351-356, 1976.

4. **Radovic L R, Walker P L Jr & Jenkins R G.** Importance of catalyst dispersion in the gasification of lignite chars. *J. Catalysis* 82:382-394, 1983.

5. **Verma S K & Walker P L Jr.** Alteration of molecular sieving properties of microporous carbons by heat treatment and carbon gasification. *Carbon* 28:175-184, 1990.

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June 4, 1990

Dr. James A. Mears
Senior Editor Manager
Institute for Scientific Information
3501 Market Street
Philadelphia, Pennsylvania 19104

Dear Dr. Mears:

Thanks you for inviting me to prepare a brief commentary on our Advances in Catalysis paper. The commentary is enclosed.

I regret that we were not able to use the floppy disk. I am returning it.

Yours truly,

Philip L. Walker, Jr.
Professor Emeritus

PLW:kc

Enclosures (5)