This Week’s Citation Classic

Walker P L, Rusinko F & Austin L G. Gas reactions of carbon.
[Fuel Science Department, Pennsylvania State University, University Park, PA]

Gasification of carbons by O₂, CO₂, H₂ 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. [The SCITM indicates that this paper has been cited in more than 450 publications.]

Carbon Gasification Is Ubiquitous

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The writing of this paper had its origin at the 1954 Gordon Conference on Catalysis, which I attended. Paul Weisz, a coeditor 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 CO₂, 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 H₂/N₂ system in our porous graphite as a function of extent of carbon gasified. The diffusion coefficient \(D_{\text{eff}}\) increased sharply with carbon gasification [\(D_{\text{eff}}\) proportional to (porosity)²]. We were able to convert the H₂/N₂ data to relevant diffusion data for the CO₂/CO system.

In the mid-1950s 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 paper 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 paper would broaden the horizons of the series. So my graduate students, Austin and Rusinko, and I proceeded; and I understand that the 1959 paper has been one of the most cited in the entire series.

The paper formed the basis for our thinking and research on carbons during the next 30 years. Some references to key papers can be cited. In 1963 I coauthored the first paper on using oxygen chemisorption to measure the fraction of the total surface area of carbons that participates in their gasification by O₂.¹ We gave meaning to the term “active sites.” In 1968 our paper 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, H₂ inhibiting gasification in CO₂.³ 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

   (Cited 200 times.)
5. Verna S K & Walker P L. Alteration of molecular sieving properties of microporous carbons by heat treatment and

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