Complications introduced from gasification-induced densification of disordered carbons

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Disordered carbons are those having small crystallite size, poor crystallite alignment, and some degree of cross-linking between crystallites. Such carbons contain significant amounts of microporosity in open and closed pores. These carbons serve as precursors for the production of commercial activated carbons upon their gasification with CO_2 or steam. Gasification which removes carbon atoms from the interior of the particle results in the enlargement of open micropores and the opening up of closed micropores. The success of the activation depends, among other things, upon the fraction of carbon bum-off which occurs inside the particle compared to outside the particle. Obviously, bum-off outside the particle does not result in development of new porosity but only in reduction in particle size. As discussed at length by Walker, et. al [1], the amounts of internal and external carbon gasification depend upon the balance between the intrinsic gasification rate (kinetically or chemically controlled) and the diffusion rate of reactants into the carbon particle. The higher the kinetically controlled reaction rate relative to the diffusion rate, the greater the fraction of the total gasification which occurs externally.

It is, therefore, understood why workers are interested in determining the fractions of external and internal carbon gasification upon activation. Recently two such studies have appeared in this journal [2, 3]. Figueiredo, et al. studied the activation of coconut char (carbonized at 850°C) upon gasification in CO_2, [2]. Ryu, et al. studied the activation of carbon fibers (heated to <1000°C) upon gasification in steam [3]. Both sets of workers measured the decrease in particle or fiber volume as gasification proceeded. They then assumed that *all* the decrease in particle or fiber volume was due to removal of carbon atoms from the exterior surface. They then calculated the fractions of gasification which were external and internal.

Unfortunately, the assumption that the loss in volume is due only to the gasification of carbon atoms from the exterior surface is not necessarily correct. Hurt, et al. [4] reported that kinetically limited gasification of 1000°C char does not occur at constant particle diameter, as is widely assumed, but is accompanied by gasification-induced particle shrinkage. They conclude that "the phenomenon of gasification-induced carbon densification makes measurements of particle size or density unreliable tests for determining the fraction of gasification occurring on the exterior surface of the particle". Ignoring particle densification could lead to the calculation of fractional external gasification which is too high. More recently, Easler, et al. [5] also report gasification-induced densification of 870°C form coke reacted in CO_2.

The correctness of the assumption that loss of particle volume is only due to removal of carbon atoms from the exterior of the particle is expected to depend upon the carbon structure. Disordered carbons are expected to show more or less gasification induced densification. However, highly ordered carbons of large crystallite size, high crystallite alignment, and little cross-linking are not expected to show significant densification as a result of carbon gasification.

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