

Gasification of Carbon by Carbon Dioxide.Kinetic, Adsorption and ESR considerations.

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Carbons (prepared from pure polyfurfuryl alcohol) have been activated by carbon dioxide. Properties of these carbons are compared with those of carbons prepared from polyfurfuryl alcohol containing known quantities of catalytic impurities. In an attempt to obtain an even distribution of impurity throughout the bulk of the carbon (not possible by addition of colloidal metal or soluble salt to the carbon surface) the impurity, iron or nickel, was added as a soluble salt to the purified monomer (furfuryl alcohol) which was then polymerised. An atomic distribution of impurity was hoped for. However, during the carbonisation and activation processes migration and coalescence of these impurities occurred to produce granules identifiable by X-ray diffraction. Rates of gasification by carbon dioxide and carbon dioxide/carbon monoxide mixtures of pure and impure carbons prepared from furfuryl alcohol were measured using a semi-micro vacuum balance. Temperatures of activation were varied to obtain comparable rates of gasification. Activation was continued to about 25% burn-off. The effects upon developed pore structure, of presence of catalyst, of reaction temperature and of presence of carbon monoxide have been assessed. Dependence of rate of gasification upon gas flow and specimen particle size were noted. There was a marked reduction in catalytic activity as activation proceeded in pure carbon dioxide. The presence of carbon monoxide in the gas phase did not appear to affect the initial stages of the catalysed gasification of carbon containing iron. The development of porosity was followed by adsorption of nitrogen (77°K) and carbon monoxide (195°K). The isotherms were interpreted in terms of obedience to the Dubinin theory of pore filling. The pure carbon, on activation, gradually developed a bimodal distribution of micropores. No hysteresis phenomena were observed. Carbons, containing iron and nickel, on activation gave smaller total pore volumes (at comparable burn-offs) and a trimodal distribution of pore-size. Some hysteresis was observable (nitrogen at 77°K) indicating that the third distribution lay in the transitional pore-size range. Electron microscopy confirmed this and also showed the existence of granules of catalyst. The pores in this latter distribution were developed in the initial stages of activation and their volume ($\text{cm}^3 \text{ cm}^{-3}$) remained approximately constant during activation. It thus appears that activation of the impure carbons, in the initial stages, occurs in the immediate vicinity of the catalyst particles producing pores in the transitional pore-size range. However, with the subsequent reduction in catalytic effectiveness, activation proceeded by the normal uncatalysed reaction producing the second microporous distribution. The effect of carbon monoxide in the gas stream was to produce a carbon with a greater micropore volume than one prepared in pure carbon dioxide to the same burn-off. Results are discussed in terms of diffusion of reacting gases into the porous network. Recent ESR investigations of carbon gasification have been almost entirely restricted to considerations of oxygen chemisorption on surfaces and subsequent outgassing involving very low percentage burn-offs. In this present study, ESR has been used to follow gasification up to 85% burn-off in an attempt to note any selective oxidation of components of carbon structure (e.g. single layers as opposed to disordered carbon). This could possibly show up in measurements of free spin concentration, line-width, and temperature dependence of free spin concentration.

Two series of experiments were made. First, pure carbons were activated in CO_2 to selected burn-offs, treated with hydrogen to remove surface oxide and then examined. Activation proceeded at constant spin concentration per gram and constant line-width. Second, carbons were activated in CO_2 , treated with hydrogen, reactivated etc. A progressive increase in free spin concentration occurred ($12-15 \times 10^{17} \text{ spin g}^{-1}$) to about 60% burn-off with a decreasing line-width (3.35-1.55 gauss at 82% B.O.). Chemisorbed hydrogen appears therefore to influence gasification mechanisms. All carbons had comparable temperature dependence properties. It was interesting to observe that carbon monoxide was as effective as hydrogen in the removal of surface oxide and the restoration of free spin concentration. The surface sites left on removal of surface oxide by the carbon monoxide did not chemisorb oxygen, subsequently added at room temperature and then evacuated, in a way which affected spin concentration.