

# KINETICS OF PYROLYTIC CARBON DEPOSITION AT HIGH TEMPERATURES AND LOW PRESSURES

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The kinetics of carbon deposition by heterogeneous decomposition of carbon containing gases on carbon surfaces has been studied at temperatures between 1000 and 2000°C. The possibility of gas phase reactions has been eliminated by the use of sufficiently low gas pressures. Experiments have been carried out with a molecular flow of gas passing over an electrically heated carbon filament, the reaction products being continuously analyzed with a mass spectrometer. Different reactants have been used for comparison, including hydrocarbons (methane, ethane, ethylene, acetylene, allene, diacetylene, benzene, naphthalene, anthracene) and  $C_3O_2$  and  $C_6N_4$  (carbon-halogen compounds decompose without carbon deposition). Decomposition of hydrocarbons evolves almost exclusively hydrogen.

Methane and ethane decompose very slowly and a carbon deposit can barely be detected. Rates of decomposition of other hydrocarbons are about a thousand times faster, and surprisingly are not very different: at 1400°C, the collision yields, i. e., the ratios of number of reacting molecules to number of impinging molecules on the surface, range between  $10^{-4}$  and  $10^{-5}$ . The effect of temperature on reaction rates is remarkably similar for all these carbon deposition reactions: the rate increases with temperature up to a maximum at about 1400°C, and then decreases from this temperature to about 1900°C. The occurrence of a maximum in reaction rate followed by a negative temperature coefficient is of course quite unusual for chemical reactions. Surface area determinations by means of physical adsorption have shown that it is not due to a change in the roughness factor of the surface of deposited carbon, which remains approximately constant at a value of about 3.5. It is not due either to a variation of the accommodation coefficient of reactant molecules, which also remains approximately constant.

This unusual change of reaction rate with temperature is however akin to that observed previously in all carbon gasification reactions under comparable temperature and pressure conditions. It had then been shown that upon temperature changes, stationary reaction rates were not obtained immediately, but through transient rates, decreasing or increasing, following respectively an increase or decrease of temperature. A detailed experimental investigation of these transient effects (which are also observed upon pressure changes) has led to the conclusion that the (small) reactive part of the surface is increased by gasification of the solid, but the new reactive sites so created can be destroyed by thermal healing; this latter effect predominates at higher temperatures and is responsible for the negative temperature coefficient.

It is remarkable and significant that qualitatively similar transient effects are observed in carbon deposition reactions. The question which arouses immediately is: are the reaction sites reactive in gasification reactions also active in decomposition reactions with carbon deposition? There is effectively a good correlation between the reactivities of a carbon surface with respect to both gasification and deposition. A surface enriched with reactive sites by a gasifying reactant under proper conditions, will temporarily show an enhanced activity with respect to deposition reactions. Even more significant is the following experiment: if two reactants (at different partial pressures), one gasifying and the other depositing carbon, are made to react simultaneously with a carbon surface, the faster reaction rate will determine the stationary concentration of reactive sites and impose the rate of the other reaction.