

THE INFLUENCE OF RESIDENCE TIME IN THE CHEMICAL VAPOR DEPOSITION OF PYROCARBON FROM C₁ - TO C₆ - HYDROCARBONS

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Introduction

Earlier investigations on pyrocarbon deposition were mainly focused on the structure and properties of the pyrocarbons or correlations between deposition conditions and structures, but such correlation are only valid for a given experimental set-up [1]. Pyrocarbon deposition, *i.e.* pyrocarbon deposition rates and resulting structures, are determined by complex heterogeneous deposition reactions which are superimposed by complex homogeneous gas-phase reactions. This paper describes results on the influence on residence time with C₁ - to C₆-hydrocarbons; the influence of initial partial pressure will be the subject of another paper presented at this conference [2].

Experimental

Deposition studies were performed at 1000°C, ambient pressure and equal hydrocarbon initial partial pressures of 4 kPa, if normalized to C₁. Due to its low reactivity, methane was studied at 1100°C and an initial partial pressure of 10 kPa. The deposition reactor equipped with on-line gas analysis has been described recently [3].

Results and Discussion

Figure 1 shows steady-state pyrocarbon deposition rates related to the surface area (13.8 cm²) of the deposition tube, made of high-density alumina ceramic. These rates are not influenced by boundary film diffusion [4]. A comparison of the rates at zero residence time shows increasing rates with increasing carbon content of the hydrocarbon, suggesting that one free active site is needed for chemisorption of one C_xH_y-species. The rate with acetylene is about two times as high as that of ethylene demonstrating the role of the C/H-ratio. Hydrogen blocks free active sites by formation of C_∞(H)-surface complexes. The inhibiting effect of hydrogen on pyrocarbon deposition from the hydrocarbons is presented in Figure 2; it

shows deposition rates obtained by addition of hydrogen related to the rate without hydrogen.

Methane, ethylene and acetylene show increasing deposition rates with increasing residence time (Figure 1); they form consecutive products with higher carbon content in homogeneous gas-phase reactions *i.e.* C₂-, C₄- and finally C₆-species, which are more active in pyrocarbon formation as mentioned above. The formation of C₂-, C₄- and C₆-intermediates was detected by gas-analysis. A simplified reaction scheme for methane is shown in Figure 3.

Propylene and 1,3-butadiene show nearly constant deposition rates up to about 0,5 s residence time, caused by superposition of several deposition reactions. The rate increase with propylene above 0,5 s residence time indicates progressive formation of higher hydrocarbons like benzene from decomposition products of propylene particularly from C₂-species. The rate decrease with 1,3-butadiene results from decreasing carbon contents in the gas-phase; too much carbon has been removed at lower residence times.

Removal of carbon from the gas-phase determines the rates with benzene. This hydrocarbon does not form intermediates, it forms pyrocarbon directly. Thus, the rate is maximum at zero residence time due to the maximum benzene partial pressure. Decreasing rates are caused by decreasing benzene partial pressures. It is obvious that these results are very important for chemical vapor infiltration.

Reaction schemes including both homogeneous gas-phase and heterogeneous pyrocarbon deposition reactions have been derived and used to simulate pyrocarbon deposition rates as shown in Figure 1 [3 - 5].

References

1. Benzinger, W., Becker, A. and Hüttinger, K.J., *Carbon*, 1996, 34, 957.
2. Becker, A. and Hüttinger, K.J., this conference.
3. Becker, A. and Hüttinger, K.J., *Carbon*, 1997, submitted.

4. Becker, A. and Hüttinger, K.J., *Carbon*, 1997, submitted.
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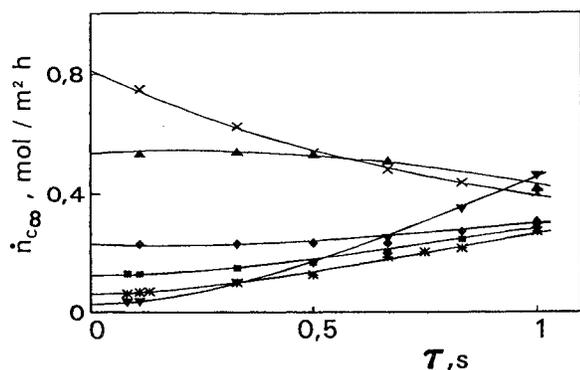


Figure 1. Steady-state pyrocarbon deposition rates as a function of residence time obtained with ethylene (*), acetylene (■), propylene (◆), butadiene (▲) and benzene (x) at 1000°C and 4 kPa normalized hydrocarbon initial partial pressure, and methane (▼) at 1100°C and 10 kPa initial partial pressure.

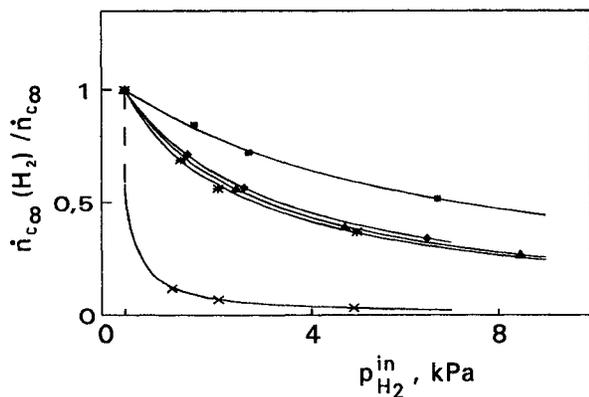


Figure 2. Steady-state pyrocarbon deposition rates related to the deposition rate obtained without hydrogen with ethylene (*), acetylene (■), propylene (◆), butadiene (▲) and benzene (x) as a function of hydrogen initial partial pressure at 1000°C, 4 kPa normalized hydrocarbon initial partial pressure and 0.33 s residence time.

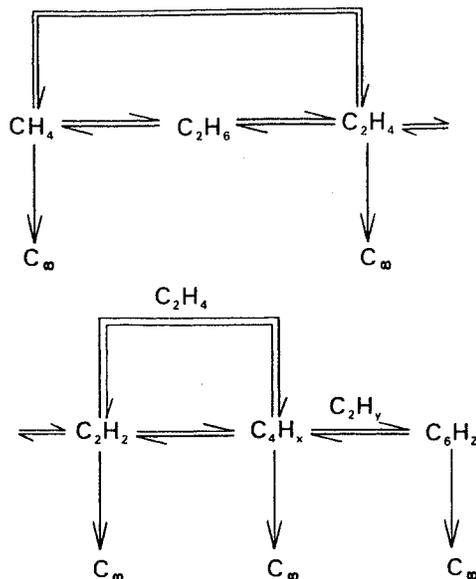


Figure 3. Simplified reaction scheme for pyrocarbon deposition from methane; C_{∞} means pyrocarbon.