THE INFLUENCE OF PARTIAL PRESSURE IN THE CHEMICAL VAPOR DEPOSITION OF PYROCARBON FROM C₁- TO C₆-HYDROCARBONS

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Introduction

This paper is a supplement of another paper in this conference which is concerned with the influence of residence time in the chemical vapor deposition of pyrocarbon from C_1- to C_6-hydrocarbons [1]. The experimental conditions were the same as those used in [1]. The influence of initial partial pressure of hydrocarbons was studied at 0,11 and 0,33 s residence time [2 - 5]. Results at 0,33 s will be presented which, however, does not mean a decisive lack of information.

Results and Discussion

Figures 1 to 3 show steady-state pyrocarbon deposition rates related to the surface area of the substrate as a function of normalized initial partial pressure p_i^{in*}; normalized means that the given partial pressures correspond to C_1. With ethylene, propylene and 1,3-butadiene the rates show an exponential increase with increasing initial partial pressure (Figure 1). The rate increases are based on the following empirically determined eq. (1) :

$$\dot{n}_{C\infty} = m \cdot p_i^{in*} + n \cdot (p_i^{in*})^2 \qquad (1)$$

At low initial partial pressures used in the experiments the rates of heterogeneous pyrocarbon deposition reactions should be determined by chemisorption and thus by first order kinetics, because saturation adsorption plays no role (see results with methane, Figure 4). Consequently, the empirically determined eq. (1) has to be ascribed to homogeneous simultaneous reactions in the gas-phase in which decisive pyrocarbon forming species are formed. Analysis of partial pressures of the product gases showed the same correlation (eq. (1)) between benzene partial pressure and initial partial pressure of the hydrocarbons, a result which supports the above suggestion.

Results with acetylene are given by the upper curve in Figure 2; they can be described by eq. (2):

$$\dot{n}_{C\infty} = m \cdot p_i^{in*} + n \cdot (p_i^{in*})^3 \qquad (2)$$

This correlation indicates simultaneous first and third order formal reactions determining benzene and thus pyrocarbon formation. A third order reaction in benzene formation can be explained by a pre-equilibrium between acetylene and vinylacetylene (eq.(3)).

$$2\,C_2H_2 = C_4H_4 \qquad (3)$$

The lower curve of Figure 2 was obtained with 4 kPa hydrogen in the feed gas and at a residence time of 0.11 s. This curve, like that of ethylene, is composed of simultaneous first and second order reactions. The chemical background of these reactions is presented elsewhere [3].

Results with benzene show a linear correlation between steady-state deposition rates and benzene initial partial pressures (Figure 3). This correlation indicates a direct pyrocarbon formation without formation of intermediates as stated in [1].

The influence of methane initial partial pressure was studied at 1100°C up to much higher partial pressures. At low initial partial pressures an exponential increase of steady-state deposition rate was found, too. At high partial pressures the rates tend to approach a limiting value, although the benzene partial pressures still increase exponentially [5]. These results suggest that the limited increase of the deposition rate is caused by a saturation adsorption of C_6-species at free active sites at the growing pyrocarbon surface.

Based on active site theory the following rate equation was derived (eq. (4)) [3].

$$\dot{n}_{C\infty} = \frac{c \cdot (k_1 \cdot p_{HC} + k_2 \cdot p_{HC}^2 + k_3 \cdot p_{HC}^3)}{1 + \dfrac{\sum k_{ads,H_2}}{\sum k_{des,H_2}} \cdot p_{H_2} + \dfrac{(k_1 \cdot p_{HC} + k_2 \cdot p_{HC}^2 + k_3 \cdot p_{HC}^3)}{\sum k_{des,H_2}}}$$

$$(4)$$

c = total concentration of active sites, k_i = rate constants, p_{HC} = initial partial pressure of hydrocarbon; $c \cdot k_1 \cdot p_{HC}$ means the rate of chemisorption of a species formed in the gas-phase in a first order formal reaction, $c \cdot k_2 \cdot p_{HC}^2$ that of species formed in the gas-phase in a second order reaction. The curve shown in Figure 4 was obtained by simulation with eq. (4).

Conclusions

Pyrocarbon deposition kinetics have to be treated as complex heterogeneous reactions superimposed by complex homogeneous gas-phase reactions. The surface area of the substrate or the concentration of active sites, c , respectively, have a tremendous influence on both deposition kinetics and structures of pyrocarbons. Details will be presented in a forthcoming paper [6].

References

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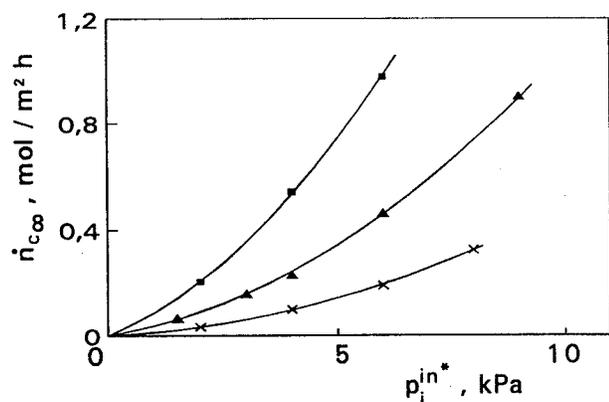6. Becker, A. and Hüttinger, K.J., *Carbon*, 1997, submitted.

Figure 2. Steady-state pyrocarbon deposition rates with acetylene as a function of normalized initial partial pressure at 1000°C and 0.33 s residence time (■) and by addition of 4 kPa hydrogen at 1000°C and 0.11 s residence time (▲).

Figure 3. Steady-state pyrocarbon deposition rates as a function of benzene initial partial pressure at 1000°C and 0.33 s residence time.

Figure 1. Steady-state pyrocarbon deposition rates with ethylene (X), propylene (▲) and 1,3-butadiene (■) as a function of normalized hydrocarbon initial partial pressure at 1000°C and 0.33 s residence time.
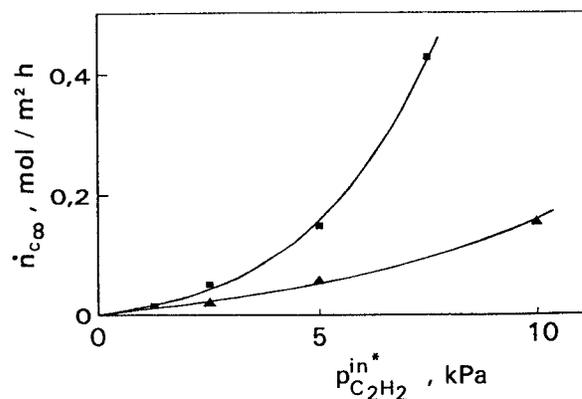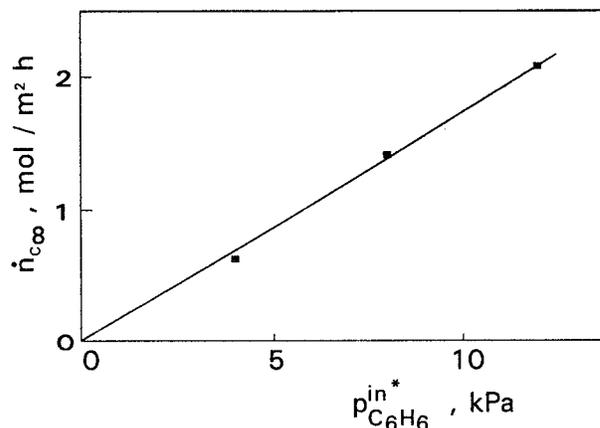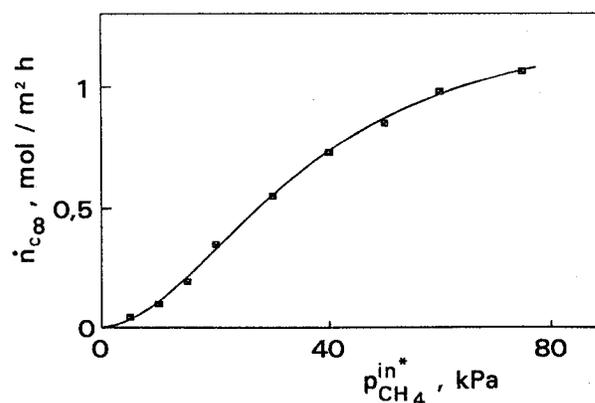

Figure 4. Steady-state pyrocarbon deposition rates as a function of methane initial partial pressure at 1100°C and 0.33 s residence time.