

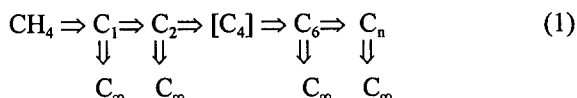
# DEPOSITION OF PYROLYTIC CARBON FROM METHANE AND METHANE-HYDROGEN MIXTURES AT VARIOUS SUBSTRATE SURFACE AREA/REACTOR VOLUME RATIOS

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## Introduction

Carbon deposition from light hydrocarbons is a homogeneous-heterogeneous process in which homogeneous gas phase reactions are competing with heterogeneous surface or deposition reactions [1]. Gas phase reactions are favored by a high reactor volume as compared to the substrate surface area, surface reactions in the inverse case. Gas phase reactions of methane are composed of complex consecutive reactions by formation of (1) C<sub>2</sub>-hydrocarbon species, (2) aromatic and (3) polyaromatic hydrocarbon species [2]. These species with increasing number of carbon atoms show increasing carbon deposition rates [1], (eq. (1)):



At a low substrate surface area/reactor volume ratio, [A<sub>S</sub>/V<sub>R</sub>], high surface related deposition rates may be expected; consumption of C<sub>1</sub> and C<sub>2</sub> species in deposition reactions will be low and aromatic (C<sub>6</sub>) and polynuclear aromatic hydrocarbons (C<sub>n</sub>), i. e. hydrocarbon species showing strongly increasing deposition rates, are rapidly formed. The inverse situation exists at a high [A<sub>S</sub>/V<sub>R</sub>]-ratio.

This hypothesis was experimentally investigated using deposition devices with [A<sub>S</sub>/V<sub>R</sub>]-ratios of 1.8, 10, 20, 40 and 80 cm<sup>-1</sup>. Methane and methane hydrogen mixtures were simultaneously studied. Hydrogen is a strong inhibitor of the overall deposition process, but the surface reactions are preferentially inhibited.

## Experimental

The deposition apparatus was described recently [1]. The deposition space is formed by an alumina ceramic tube, 22 mm in diameter and 20 mm in height. The gas flows from the bottom to the top. The tube exhibits a [A<sub>S</sub>/V<sub>R</sub>]-ratio of 1.8 cm<sup>-1</sup>. Channel structures with 25, 100, 400 and 1100 channels per square inch were fitted in the tube to increase

the [A<sub>S</sub>/V<sub>R</sub>]-ratio to 10, 20, 40 and 80 cm<sup>-1</sup>. Steady-state deposition rates at various residence times were determined from the mass increase of the deposition device as a function of deposition time.

The experiments were performed at a total pressure of 100 kPa and a temperature of 1100 °C. Methane was studied at a partial pressure of 10 kPa, the methane-hydrogen mixture at p<sub>CH<sub>4</sub></sub> = 17.5 kPa and p<sub>H<sub>2</sub></sub> = 2.5 kPa. Argon was used as diluent gas. The residence time was varied by the volume flow.

## Results

Deposition rates as a function of residence time are presented in Fig. 1 (a) (methane) and (b) (methane-hydrogen mixture). The rates increase with increasing residence time at all [A<sub>S</sub>/V<sub>R</sub>]-ratios and increasing [A<sub>S</sub>/V<sub>R</sub>]-ratios at all residence times. Decreasing rates at the highest [A<sub>S</sub>/V<sub>R</sub>]-ratio and high residence times are caused by a depletion of reactive species of the gas phase.

The rates given in Fig. 1 are production capacities depending on the reactor volume. By fitting the channels structures in the tube the reactor volume is lowered. Thus, the rates can not be compared directly. Volume and surface related rates are obtained from the following eqs. (2) - (5):

### Production capacity

$$\dot{n}_{\text{C}_\infty} = c_{\text{C}_\infty} \cdot \dot{V} \quad (2)$$

### Fictitious carbon concentration

$$c_{\text{C}_\infty} = \dot{n}_{\text{C}_\infty} / \dot{V} \quad (3)$$

### Volume related rate

$$dc_{\text{C}_\infty} / d\tau = d[\dot{n}_{\text{C}_\infty} / \dot{V}] / d\tau \quad (4)$$

### Surface related rate

$$\{dc_{\text{C}_\infty} / d\tau\} \cdot [A_S/V_R]^{-1} = \{d[\dot{n}_{\text{C}_\infty} / \dot{V}] / d\tau\} \cdot [A_S/V_R]^{-1} \quad (5)$$

Rates according to eqs. (4) and (5) are presented in Figs. 2 and 3, respectively. Volume related rates increase and

surface related rates decrease if the  $[A_S/V_R]$ -ratio is increased. This result implies that surface related rates are not constant because the deposition rates depend on the surface area/volume ratio in a complex manner, and any kinetics can be determined by changing this ratio. It is termed as a third parameter of chemical vapor deposition besides temperature and pressure or partial pressure. A more detailed treatment of this subject will be presented in forthcoming papers.

### References

- [1] Hüttinger KJ. CVD in hot wall reactors. Adv. Mater. CVD 1998;4(4):157-158.
- [2] Antes J, Hu ZJ, Zhang WG, Hüttinger KJ. Chemistry and kinetics of chemical vapor deposition of pyrocarbon-VII. Carbon 1999; 37: in press.

*Acknowledgement*-This study was performed in the Collaborative Research Center 551. Financial support by the DFG is gratefully acknowledged.

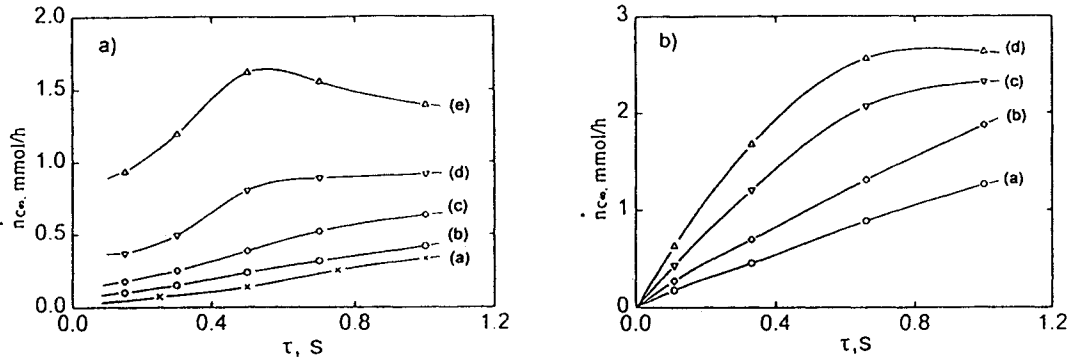


Fig.1 Deposition rates as a function of residence time, a) methane (20kPa), at  $A_S/V_R$  ratios of 1.8(a), 10(b), 20(c), 40(d),  $80\text{cm}^{-1}$ (e); b) methane-hydrogen mixture (17.5-2.5kPa), 10(a), 20(b), 40(c),  $80\text{cm}^{-1}$ (d).

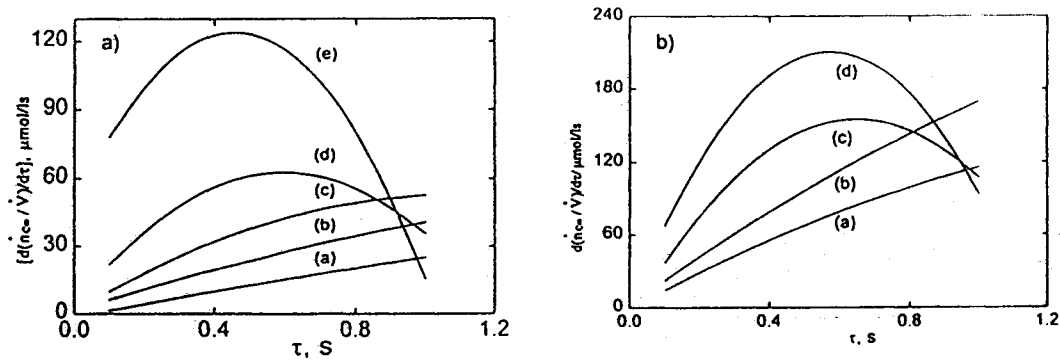


Fig.2 Volume related deposition rates; a) and b) see Fig. 1.

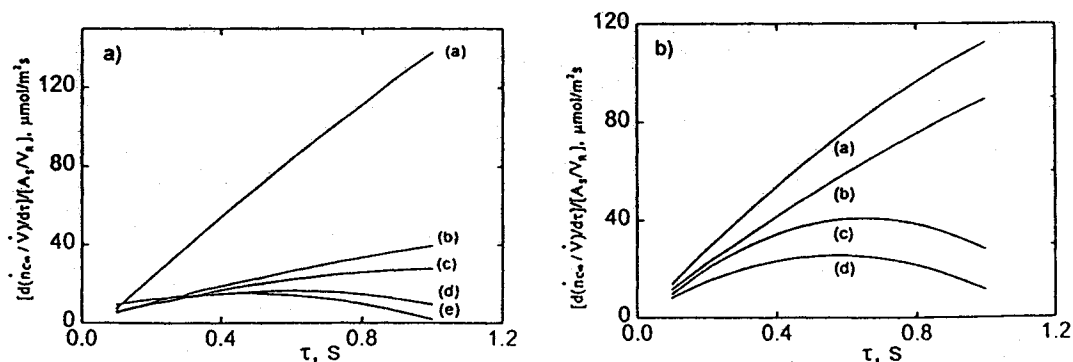


Fig.3 Surface related deposition rates; a) and b) see Fig. 1.