

CHEMISTRY AND KINETICS OF PYROCARBON DEPOSITION IN THE LOW TEMPERATURE REGIME

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INTRODUCTION

Pyrocarbon is a structural material. For this reason it is not surprising that studies of pyrocarbon deposition were mainly focussed on correlations between the deposition conditions and the structures of the deposited carbons [1, 2]. Kinetics of the pyrocarbon deposition were studied with numerous hydrocarbons, but kinetic parameters were calculated by the over-simplified assumption of first order reactions [3]. Mass transport effects and the role of nucleation have also been considered [4]. On the contrary, the knowledges about the chemistry and kinetics of the reactions occurring (i) in the gas phase and (ii) on the surface of the growing pyrocarbon are poor; this also holds for hydrogen inhibition.

For improving and optimization of the total process understanding of the chemistry and kinetics of all reactions is essential. Experiments to these problems were performed with CH_4 , C_2H_4 , C_2H_2 , C_3H_6 , and C_6H_6 . These hydrocarbons were selected on the basis of thermodynamic calculations which showed that pyrocarbon deposition in the low temperature regime should occur via C_2 -hydrocarbons, benzene and polynuclear aromatics as the decisive growth species.

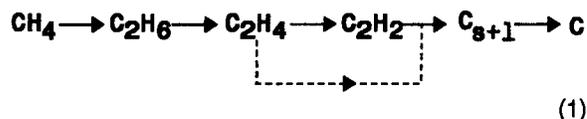
EXPERIMENTAL

For studying the deposition reactions a vertical tubular reactor with conical nozzles at the entrance and the exit was developed. The product gases were analyzed by on line gas chromatography. The amount of condensable products was determined by a carbon mass balance. Reaction temperature, partial pressure and residence time were varied, but results on the influence of the residence time τ at 1000°C will mainly be presented; it was varied between 0.1 and 1 s. In the case of the extremely unreactive CH_4 a temperature of 1100°C was used.

RESULTS

The results with CH_4 showed an exponential increase of the deposition rate with τ . The main reaction products were H_2 , C_2H_2 and condensable

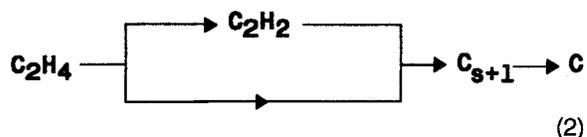
products, for which the abbreviation $\text{C}_{\text{s}+1}$ will be used. For both C_2H_2 and $\text{C}_{\text{s}+1}$ a clear incubation period exists at short reaction times. Therefore, the following reaction sequence may be assumed:



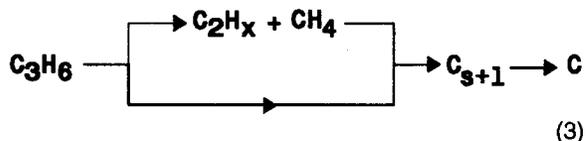
The concentration of C_2H_6 and C_2H_4 were found to be extremely low; these compounds are immediately converted to C_2H_2 and $\text{C}_{\text{s}+1}$.

With C_2H_4 and C_2H_2 , an exponential increase of the deposition rate with τ was found, too; with C_2H_4 , the main reaction products are H_2 , C_2H_2 , $\text{C}_{\text{s}+1}$ and CH_4 (very small amounts). With C_2H_2 , only H_2 and condensable products were detected. An incubation period exists for none of the gases.

Starting with C_2H_4 the following reaction sequence can be postulated:

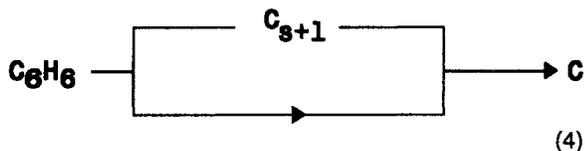


With C_3H_6 no influence of the residence time on the deposition rate up to 0.5 s was found, which is remarkable. At high residence time, the deposition rate increases. Main reaction products are H_2 , $\text{C}_{\text{s}+1}$, which are formed in much higher yields than C_2H_4 , C_2H_2 and CH_4 . C_3H_6 is completely decomposed already at 0.2 s. No incubation period was found for any of the product gases. C_2H_4 and CH_4 exhibit a maximum concentration at very short residence time, C_2H_2 at medium residence time. The following parallel reactions can be assumed to occur:



On the basis of these reactions, the constant deposition rate can be explained.

With C_6H_6 the deposition rate decreases up to about 0.5 s, but then it increases. Main reaction products are H_2 and $\text{C}_{\text{s}+1}$. The following reaction sequence can be postulated:



The decreasing deposition rate can be explained by the consumption of C_6H_6 , the increase of the deposition rate at high residence time by the preformation of polynuclear aromatics in the gas phase.

A summary of the results is presented in Fig. 1. It shows the specific deposition rate (related on the surface of the substrate), normalized to 1 mol C in dependence of τ . It can be recognized that the deposition rate strongly depends on the precursor only at short residence time. With increasing residence time, when the influence of thermodynamic equilibria are of progressive influence, the influence of the hydrocarbon is diminished more and more. Thermodynamic calculations favour formation of polynuclear aromatics; they should be the precursor or growth species of pyrocarbon. For underlining this conclusion the fictitious carbon concentration \dot{n}_C/\dot{V} is plotted in Fig. 2 in dependence of the concentration of C_2 -hydrocarbons (dotted line) and the concentration of condensable products (full lines). The correlation of \dot{n}_C/\dot{V} with the concentration of C_2 -hydrocarbons shows decreasing carbon yields with increasing concentration of these hydrocarbons, a result which is not logical. The inverse dependency can be observed with the concentration of condensable products. The correlation between \dot{n}_C/\dot{V} and the concentration of condensable products is specific to the hydrocarbon. This should be a consequence of the different compositions of the condensable products formed. The analysis of those will be performed in future studies.

SUMMARY

It is shown that pyrocarbon deposition in the low temperature regime is controlled by the intermediate formation of condensable products, in other words aromatics and polynuclear aromatics.

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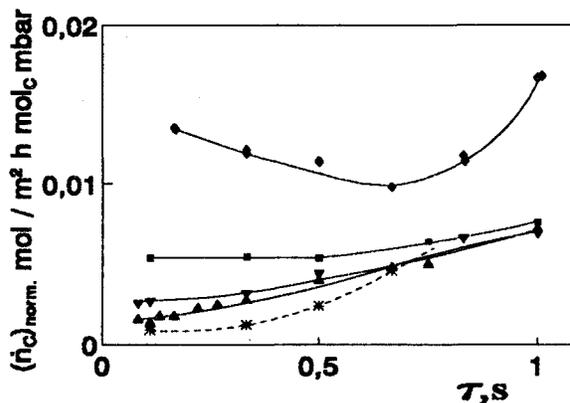


Fig. (1): Dependence of the specific normalized deposition rate on the residence time, (*) CH_4 (1100°C); (Δ) C_2H_4 , (∇) C_2H_2 , (\blacksquare) C_3H_6 , (\blacklozenge) C_6H_6 (1000°C).

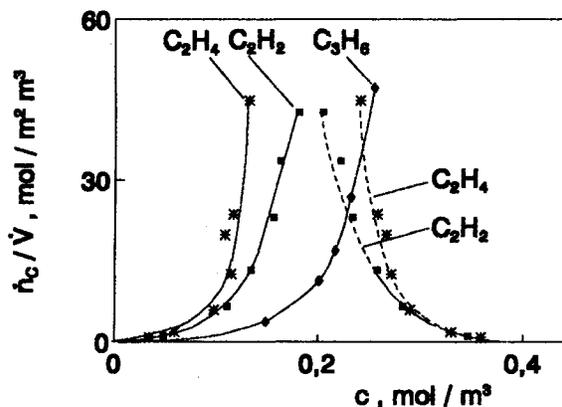


Fig. (2): Correlation between \dot{n}_C/\dot{V} and (i) the concentration of C_2 -hydrocarbons (dotted line) and (ii) the concentration of condensable products (full lines) in the product gas.