

ORGANIC IRON COMPOUNDS AS CATALYST PRECURSORS OF AN
IRON CATALYZED LIQUID-PHASE PYROLYSIS OF HYDROCARBONS:
I. ANTHRACENE PYROLYSIS.

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INTRODUCTION

The paper is concerned with the liquid-phase pyrolysis of anthracene catalyzed by iron clusters. The clusters are formed in situ by decomposition of organic iron compounds such as ferrocene, iron benzoate or iron naphthoate. These compounds are soluble in the liquid hydrocarbon and decomposed by formation of elemental iron during heating up to pyrolysis temperature [1-3]. The influence of the iron precursor material was studied with iron benzoate and ferrocene, which are decomposed at very different temperatures, namely below 300°C and above 400°C. Anthracene was used as a sulfur free aromatic model hydrocarbon to exclude a poisoning of iron by sulfur.

EXPERIMENTAL

Anthracene with a purity > 99% was mixed with the iron compounds in such amounts as to give an iron content of 1.5%. Pyrolysis studies were performed in an autoclave (without stirring) at an argon pressure of 1 MPa. Ferrocene was procured from Chemische Werke Pluto, Germany, and iron benzoate was synthesized from benzoic acid and iron-(III)-chloride [3]. The pyrolysis products were analyzed by determination of the tetrahydrofuran insoluble content with the Soxhlet technique (THF-IS), and the coke yield (CY). Formation of iron clusters was analyzed by X-ray diffraction.

RESULTS

Pyrolysis experiments were performed (1) at 464°C (iron benzoate) and at 486°C (pure anthracene, ferrocene, iron benzoate) by variation of reaction time, and (2) to check the onset of catalysis at a reaction time of 5h by variation of reaction temperature. The results of the first set of experiments are shown in Figs. 1a and b. Pure anthracene is very

unreactive even at 486°C. The extended incubation period reveals that THF insoluble products can only be formed in a series of consecutive reactions. To a first view the results with ferrocene are disappointing. However, the X-ray studies showed that the delayed formation of THF-IS as compared to iron benzoate is a consequence of its high stability. The onset of catalysis occurs about 3 to 4h before iron can be detected by X-rays. The real effect of iron clusters follows from the results with iron benzoate. A semi coke like material is already formed after 2h at 486°C or 5h at 464°C. This follows from both the THF-IS and CY values.

More impressive are the results found in the second series of experiments shown in Figs. 2a and b. The catalyzed reaction starts at about 408°C and a semi coke like material is already formed at 444°C. A product with 100% THF-IS was never obtained, a result which is ascribed to an encapsulation of the iron clusters by high molecular weight material.

Figs. 3a and b show examples of X-ray diffraction patterns. Peaks of α -iron at 2θ angles of about 45°, 65° and 82° can be detected. The peak at a 2θ angle of about 26° results from the basal plane (002) reflection of the carbon lattice. Further small peaks result from unreacted anthracene which confirm the hypothesis of limited catalyst activity by catalyst encapsulation.

SUMMARY

The model experiments with anthracene have shown that iron clusters formed by decomposition of a thermally sufficiently instable iron compound such as iron benzoate are catalytically extremely effective. This catalytic effect is based on an acceleration of dehydrogenation reactions which are known to be not only the initial but also the rate limiting step in pyrolysis reactions [4,5]. The effect of the same iron compounds in the pyrolysis of

pitch will be presented in another paper of this conference [6].

ACKNOWLEDGEMENT

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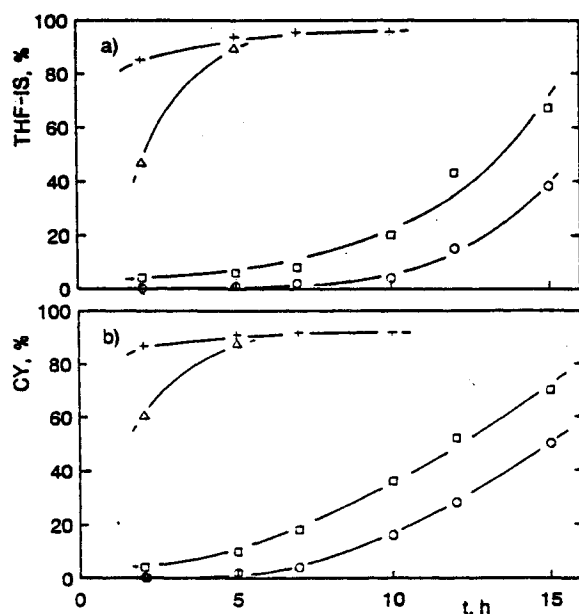


Fig. 1. Tetrahydrofuran-insoluble, THF-IS, (a) and coke yield, CY, (b) of the pyrolysis products at 464°C and 486°C in dependence on reaction time; O, pure anthracene (486°C); □, 5% ferrocene (486°C); Δ, 9,4% iron benzoate (464°C); +, 9,4% iron benzoate (486°C).

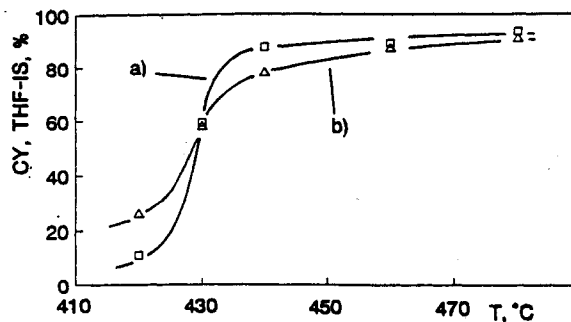


Fig. 2. Tetrahydrofuran-insoluble, THF-IS, (a) and coke yield, CY, (b) of the pyrolysis products obtained with 9,4% iron benzoate in dependence on reaction temperature (5 hours reaction time).

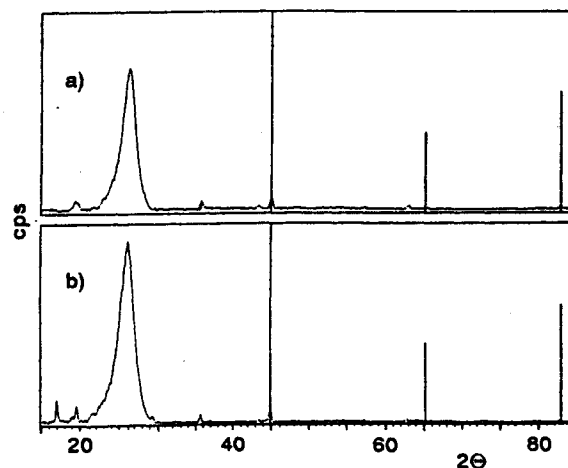


Fig. 3. X-ray diffraction patterns of pyrolysis products from anthracene obtained with 9,4% iron benzoate; (a) after 5h at 444°C, (b) after 7h at 486°C.