

STUDY ON CO-CARBONIZATION OF AROMATIC HYDROCARBONS BY THE AID OF SUPERACID

C.Y.Wang, J.M.Zheng, X.Q.Ruan and C.T.Guo

Department of Chemical Engineering
Tianjin University, Tianjin 300072, P.R.China

INTRODUCTION

Excellent precursor mesophase pitches are demanded for making high performance pitch-based carbon fibers. The procedure proposed by Isao Mochida et al for the preparation of mesophase pitch from pure aromatic hydrocarbons by the aid of HF/BF₃, has been known as very significant^(1,2,3). This research is trying to extend the raw material range, using the same catalyst, and introduce specific groups purposely by means of co-carbonization, hoping to adjust the structure of mesophase molecules freely at the request of molecular design.

In the present study, alkylating reaction and co-carbonization were conducted by the aid of HF/BF₃ using naphthalene (C₁₀H₈) and anthracene (C₁₄H₁₀) as starting materials, bromoethane (CH₃CH₂Br) and tetralin (C₁₀H₁₂) as alkylating agent and co-carbonization agent. As a result, the number of alkyl and naphthenic groups on the obtained pitches were increased, thus the goal to adjust the structure of mesophase pitches was achieved.

EXPERIMENTAL

The samples of pitch were synthesized by co-carbonization from naphthalene and anthracene respectively with bromoethane and tetralin using HF/BF₃ as a catalyst. The reactions were carried out at the temperature ranging from 180~220 °C for 2.0~3hr, under 30~50 atm of autogenous pressure in an autoclave which is made of corrosion resistant alloy. After the reaction, HF/BF₃ and light fractions were distilled out. Their heat treatment conditions (HTC) are listed in Table 1.

The pitches were fractionated by extraction with hexane (H), benzene (B), and quinoline (Q). The BS fractions of pitch were analyzed with ¹H-NMR (BRUKER AC-P 200) in the solvent C₆D₆, using tetramethylsilane as an in-

ternal standard. FT-IR (Bio-Rad FTS 15/90) spectra of the whole pitch were also measured using the KBr disc procedure.

RESULTS AND DISCUSSION

General properties of the pitches prepared by carbonization and co-carbonization from naphthalene, anthracene and alkylating agents with the aid of HF/BF₃ are summarized in Table 2. NA1, AN1 and TNA possess higher solubilities and H/C ratios; this can be attributed to the results of co-carbonization. The highest quantity of QI fraction of AN2 is partially ascribed to the higher catalyst ratio.

It is obvious that NA1, AN1 and TNA show more intense peaks in the aliphatic hydrogens region of the ¹H-NMR spectra as shown in Fig.1. In more detail, NA1 and AN1 exhibit more intense peaks from 1.1 to 1.6 ppm and from 2.1 to 2.5 ppm than NA2, which are assigned to H_β and H_α of alkyl side chains. Oppositely, TNA exhibits a intense peak from 1.6~2.1 ppm, which is ascribed to rich naphthenic H_β. So it is suggested that NA1 and AN1 possess more alkyl side chains, and TNA carries more naphthenic groups. It can also be imagined that, as in the Kyukoshi method⁽⁴⁾, further heat treatment of TNA at about 450 °C for a short time will give an excellent mesophase pitch.

FT-IR spectra of pitches are illustrated in Fig.2. Absorption bands at 2920 cm⁻¹ (methylene/naphthenic C-H stretching) and 1380 cm⁻¹ (methyl C-H bending) in both NA1 and AN1 are more intense than in NA2 and AN2; it proves that the alkylating reactions were effective. TNA exhibits the most intense band at 2920 cm⁻¹, while the band at 1380 cm⁻¹ is very weak; it indicates that TNA carries rich naphthenic groups. On the other hand, the bands at 870 cm⁻¹ (isolated aromatic C-H bending) in NA1 and AN1 are more intense than in NA2, AN2 and TNA. This obviously indicates

more substituent groups on the aromatic nucleus of NA1 and AN1.

CONCLUSION

Co-carbonization by the aid of superacid is one of the effective methods to adjust the amount of alkyl and naphthenic groups in mesophase pitches.

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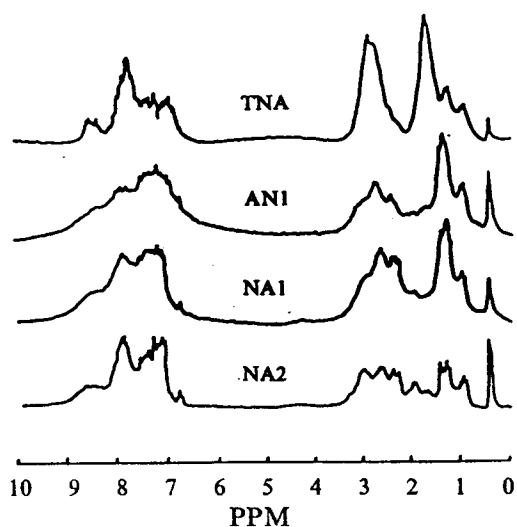


Fig.1. ¹H-NMR spectra of the BS fractions

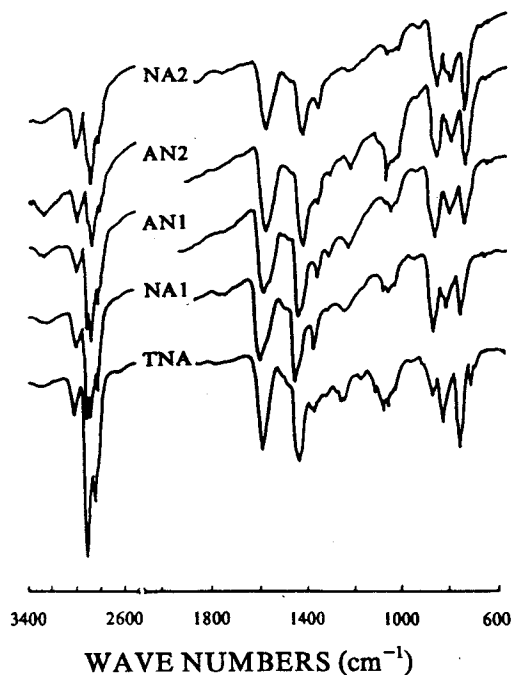


Fig.2. FT-IR spectra of pitches

Table 1. Preparation Conditions of pitch*

| Sample | Starting | Material | HTC (°C-h) | Yield (wt%) |
|--------|---|-----------|---------------|----------------|
| | Content | Mol ratio | | |
| NA1 | C ₁₀ H ₈ +CH ₃ CH ₂ Br | 1:1 | 220-3.0 | — |
| NA2 | C ₁₀ H ₈ | — | 220-3.0 | 78 |
| AN1 | C ₁₄ H ₁₀ +CH ₃ CH ₂ Br | 1:1 | 220-2.5 | — |
| AN2 | C ₁₄ H ₁₀ | — | 220-2.0 | 90 |
| TNA | C ₁₀ H ₈ +C ₁₀ H ₁₂ | 1:1 | 180-3.0 | 77 |

* The mol ratio of starting material, HF and BF₃ is 1 : 5 : 0.5

Table 2. Some properties of pitch prepared by co-carbonization

| Sample | S.P. (°C) | A.C. (vol%) | Solubility (wt%) | | | | H/C |
|--------|--------------|----------------|------------------|-------|-------|------|------|
| | | | HS | HI-BS | BI-QS | QI | |
| NA1 | 170 | 60 | 3.3 | 56.6 | 30.7 | 9.4 | 0.78 |
| NA2 | 195 | 90 | 5.2 | 29.9 | 38.7 | 26.2 | 0.69 |
| AN1 | 210 | 100 | 9.3 | 26.0 | 49.4 | 15.3 | 0.74 |
| AN2 | 280 | 100 | 3.1 | 4.1 | 16.6 | 76.2 | 0.65 |
| TNA | 80 | 0 | 8.2 | 85.5 | 6.3 | 0 | 0.91 |