

Preparation of Nitrogen Enriched Pitches from Diazanaphthalenes by The Aid of AlCl₃

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1. INTRODUCTION

The present authors have reported in a previous paper syntheses of nitrogen enriched pitches and their derived cokes from isoquinoline as well as quinoline, using AlCl₃ as catalyst for their oligomeric condensation[1-2]. We have suggested that nitrogen enriched pitch can be a precursor for the activated carbon fibers with very basic surface.

In this study, structure and properties of pitches with more nitrogen prepared catalytically from diazanaphthalenes(quinoxaline, quinazoline, phthalazine) by aid of AlCl₃ were studied to clarify how different nitrogen location of diaza- naphthalene in the α - α ' (quinoxaline), α - β ' (quinazoline) and β - β ' (phthalazine) positions of the naphthalene ring influences on their condensation reaction, the nitrogen content of pitches, optical textures of pitches and its cokes, elimination rate of nitrogen in the carbonization, and basicity of the resultant cokes.

2. EXPERIMENTAL

Diazanaphthalenes, quinoxaline, quinazoline, phthalazine, and AlCl₃ in the present study were commercially available from ALDRICH.

Synthesis of pitch was carried out in a 100ml Pyrex flask under nitrogen atmosphere and reflux conditions at 240 °C for 2hr in presence of 0.1 molar ratio of AlCl₃ and 280 °C for 4hr in presence of 0.5 molar ratio of AlCl₃. After the reaction, the product was washed by 0.1N aq. HCl and methanol to remove AlCl₃ and the unreacted starting monomer.

Benzene soluble fraction(BS) from the pitches was analyzed with ¹H-NMR(VARIAN XL-400), ¹³C-NMR (VARIAN VL-400) and JEOL-DX 303 mass spectrometer. The whole pitches were analyzed with solid ¹³C-NMR (VARIAN XL-400, CP/MAS unit) and FT-IR(JIR-03F). The softening point of the pitch was defined by TMA (Seiko-TMA 120).

The quinoxaline(QXP), quinazoline(QZP) and phthalazine (PTP) pitches were carbonized at 600 °C for 1hr under nitrogen flow at a heating rate of 10 °C/min. The carbon product was further heat- treated at 900 °C and 1200 °C for 1hr under argon flow. Basicity of carbons obtained at 600 °C was determined by the back titration.

3. RESULTS AND DISCUSSION

3.1 Yields and properties of synthesized pitches

Table 1 summarizes the yields and some properties of all isotropic pitches prepared for diazanaphthalenes. The yields and softening points of the pitches ranged from 56 ~ 66wt.% and 165 ~ 254 °C, respectively, with 0.1 molar ratio AlCl₃ at 240 °C for 2hr. The lower softening point of the pitches reflected their solubilities in benzene and pyridine which ranged from 65% to 30% and 100% to 43%, respectively.

The atomic ratio of H/C and N/C of the pitches ranged from 0.60 to 0.67, respectively. Small ratios of the H/C with QXP1 and N/C with PTP1 are noted, indicating the dehydrogenation reactivity and C-N bond breakage of the respective substrates.

More AlCl₃(0.5 molar ratio) at higher temperature(280 °C)

for a longer reaction time(4hr) increased significantly the pitch yields of all substrates in the range of 68wt.% to 74wt.%. The pitches, basically pyridine insoluble exhibited no fusibility any more, reflecting very low solubility in benzene regardless of the substrates. The pitches suffered severe dehydrogenation, exhibiting H/C ratio of 0.61 to 0.57.

3.2 Structural characteristics of pitches

¹H-NMR spectra of BSs in the diazanaphthalene pitches are shown in Figure 1. The ¹H-NMR spectra of QXP1 exhibited intense peaks at 1.8~2.2 and 2.6~3.0 ppm which are ascribed to naphthenic β - hydrogen and α - hydrogen, respectively. In contrast, no resonance peak ascribed to the naphthenic structure was found in the spectrum of BS's in the other pitches. QXP2, QZP1 and PTP1 showed similar peaks at 0.8~0.1, 1.2~1.4 and 1.6~1.8 ppm which are ascribed to methylene or aliphatic groups. The BSs of QZP2 and PTP2 exhibited no resonance or much weaker peaks ascribed to methylene groups, respectively, indicating more dehydrogenation and condensation at the higher reaction temperature.

Solid ¹³C-NMR spectra of the diazanaphthalene pitches are illustrated in Figure 2. Carbon adjacent to nitrogen atom in aromatic ring was observed as a shoulder peak in the spectra of QXP1, while the spectra of QZP1 and PTP1 clearly exhibited the peak assigned to such an aromatic carbon. Percentage of such carbons in aromatic ring against total aromatic carbons calculated from solid ¹³C-NMR spectra was 23~24% for QXP1,2 and 18~19% for QZP1,2 and 10~11% for PTP1, respectively, reflecting the stability of diaza ring during the condensation.

Figure 3 illustrates FD-MS spectra of the BS fractions in QXP1, QZP1 and PTP1. The molecular weight of the constituents in the QXP1 distributed from m/z 112 to 1383 with the maximum abundance at m/z 386 and 514 which are ascribed to the trimers and tetramers. It is noted that the distribution was more continuous than those of QZP1 and PTP1, suggesting a series in the number of naphthenic hydrogens in the constituent molecules of QXP1. The molecular weight of the maximum abundance of QXP1 was certainly larger than that of QZP1 and PTP1.

3.3 Carbonization properties of diazanaphthalene pitches

Optical textures of the cokes obtained from QXP1, QZP1 and PTP1 at 600 °C are summarized in Table 2. QXP1 produced flow domain anisotropic texture while both QZP1 and PTP1 formed complete isotropic texture.

N/C values of the cokes obtained from diazanaphthalene pitches are shown in Figure 4. The nitrogen in QXP and QZP decreased more rapidly in the temperature range of 600 ~ 1200 °C than that in PTP, although much more nitrogen remained in the coke from QXP and QZP. PTP lost its major nitrogen at its preparation, while less in the temperature range of 300 ~ 900 °C.

Basicities measured by the titration and the content of nitrogen in cokes at 600 °C are summarized in Table 2. Cokes produced from QXP1, QZP1 and PTP1 carried basicity of 0.115, 0.275 and 0.280mmol/g, respectively, although much less nitrogen remained in the coke from QZP1 and PTP1. The location of nitrogen atom in the condensed ring may be computed for the basicity.

REFERENCES

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2. K.H. An, Y. Korai and I. Mochida, Extended Abstracts for Carbon'94 Conf., 18(1994).

Table 1. Some properties of diazaphthalene pitches.

Pitch	Yield (wt%)	S.P. (°C)	C.V. (wt%)	Elemental Analyses(wt%)					Solubility(wt%)		
				C	H	N	H/C	N/C	BS	BI-PS	PI
QXP1	56	253.5	79	74.06	3.72	19.41	0.603	0.225	30	13	57
QXP2	68	N.F.	84	72.88	3.70	18.19	0.609	0.214	17	19	64
QZP1	61	180.7	74	73.82	4.12	18.16	0.670	0.211	61	39	0
QZP2	74	N.F.	81	70.10	3.63	16.13	0.621	0.197	5	35	60
PTP1	66	164.7	66	82.64	4.40	9.39	0.639	0.097	65	35	0
PTP2	71	N.F.	82	81.94	3.90	8.94	0.572	0.094	22	19	59

S.P.:softening point, C.V.:carbon value at 600°C. BS:benzene soluble, BI-PS:benzene insoluble-pyridine soluble, PI:pyridine insoluble, N.F.:no fusion

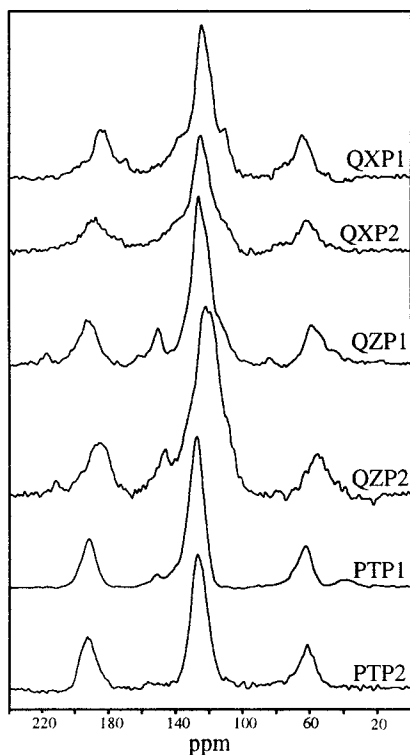


Fig. 2 The Solid ¹³C-NMR spectra of fractions in diazaphthalene pitches.

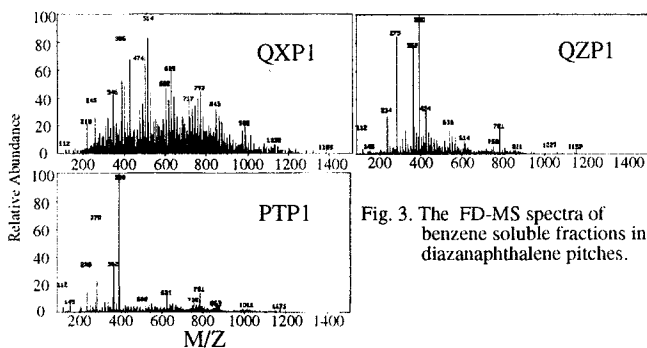


Fig. 3. The FD-MS spectra of benzene soluble fractions in diazaphthalene pitches.

Table 2. Basicities calculated from the titration curves of diazaphthalene cokes heat-treated at 600°C for 1hr.

Cokes	N/C at 600°C	N.P (meq/g)	Basicity (meq/g)	Optical texture
QXP1	0.205	0.385	0.115	anisotropic
QZP1	0.163	0.225	0.275	isotropic
PTP1	0.074	0.220	0.280	isotropic

N.P. : amount of 0.1N NaOH necessary for adjusting for neutralizing point(meq/g)

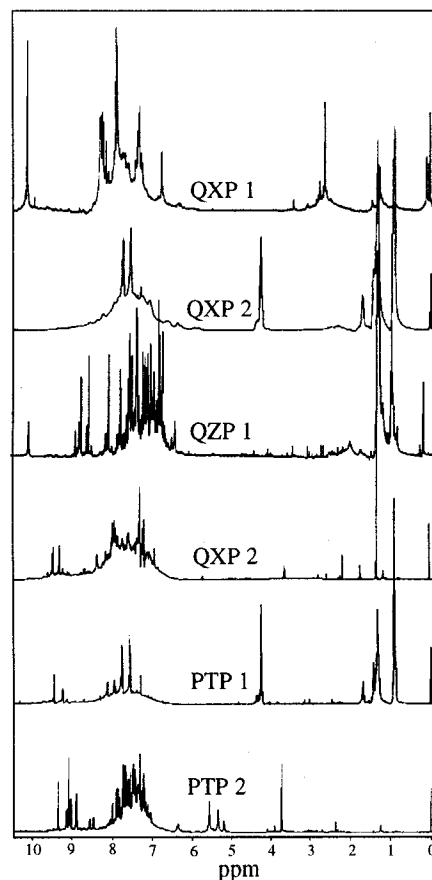


Fig.1. The ¹H-NMR spectra of benzene soluble fractions in diazaphthalene pitches.

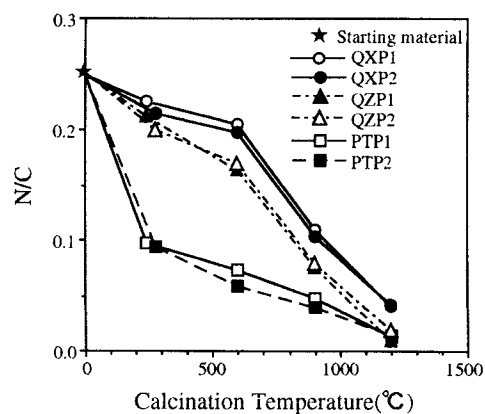


Fig.4. Variation of N/C ratio of diazaphthalene pitches dependence on carbonization temperature.