Hydrogenation Mechanism of Coal Tar Pitch for Carbon Fiber (Part 2) Hydrogen Transfer Mechanism from Tetralin to Coal Tar Pitch for High Performance Carbon Fiber Using Tritium Tracer Method

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Behavior of hydrogen in hydrogenation of the coal tar pitch for high performance carbon fiber with tetralin was investigated in temperature range of 410 to 470°C for 60 min using tritium tracer technique to elucidate the mechanism of hydrogen transfer. The amount of tritium transferred from tetralin to the pitch increased with rise in reaction temperature while the amount of hydrogen added from tetralin to the pitch was kept at almost constant value in temperature range of 410 to 470°C. At 410°C, the THFIS fraction decreased from 13.6 wt% to 5 wt% of the raw pitch, which was kept constant independent of the reaction temperature. HIS-BS fraction, increasing with rise in temperature from 410 to 450°C, was the main product at 450°C. Tetralin solvent began to decompose at 470°C and substantial hydrogen exchange reaction proceeded between pitch and tetralin.

1. Introduction

A number of attempts have been made to develop the utilization of heavy carbon resources. Among them, much attention has been focused on the utility of pitch and coal liquid and others as a raw material for a carbon fiber^{1)~3)}. Generally, it has been well-known that hydrogenation of pitch could be one of the important and effective methods to make a precursor for mesophase pitch⁴⁾, which gives a high performance carbon fiber (HPCF)^{5)~7)}. Yamada and others have reported that carbonaceous mesophases were prepared from vacuum-distillation residual oils by pyrolysis at 420°C and extraction of pitches formed with quinoline to obtain insoluble beads. The mesophase beads were hydrogenated in the presence of 1,2,3,4-tetrahydroquinoline to give a soluble component containing optically anisotropic micrograins⁸⁾. There have been few examples, however, of hydrogen mobility of coal tar pitch being quantitatively investigated in hydrogenation of pitch. We have already reported on the quantitative estimation of hydrogen transfer in the hydrogenation of coals^{9),10)} and coal liquids¹¹⁾ using a tritium tracer method. Further, we have

recently investigated the hydrogenation of coal tar pitch for HPCF, with tritium labelled gaseous hydrogen to estimate hydrogen mobility in pitch¹²⁾.

In the present paper, the coal tar pitch for HPCF was hydrogenated by tritium labelled tetralin. We report here completely different results from those of hydrogenation of pitch using gaseous hydrogen.

2. Experimental Section

2.1 Materials

The coal tar pitch for high performance carbon fiber was the same as that presented in previous paper¹²⁾ and its elemental analysis results were C, 92.3; H, 4.9; N, 1.0; O (diff.), 1.8 wt%. Hydrogen distributions of coal tar pitch by ¹H NMR spectroscopy and its composition by solvent fractionation were cited in previous paper¹²⁾. Tetralin obtained from commercial sources (extra pure grade) was used without further purification. Tritium labelled tetralin was added to unlabelled tetralin, and the initial concentration of tritium in solvent was controlled at 50,000 dpm/g.

2.2 Procedure of Hydrogenation Reaction with Tritium Labelled Tetralin

The hydrogenation reaction was conducted by tritium labelled tetralin without catalyst. Coal tar pitch (60 g) and tritium labelled tetralin (120 g)

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Fig. 1 Flow Sheet of Hydrogenated Treatment

were charged into a 500 ml autoclave having titan inside tube equipped with a stirrer assembly. The atmosphere inside of the autoclave was replaced with nitrogen (1 atm).

The autoclave was heated at a rate of 10°C/min, and held at temperature of 410, 430, 450 or 470°C for 60 min. After the reaction, the gaseous product was analyzed by g.c. using a Unibeads A column. The mixture of liquid and solid products was separated by filtration, distillation and extraction, as shown in Fig. 1. The filtration residue was separated into THF-soluble and insoluble materials (THFIS) by extraction. The filtrate and THF extract were separated by distillation: naphtha (under 200°C), solvent (200–220°C), light oil (220–350°C), and distillation residue (>350°C). Naphtha, solvent and light oil were analyzed by g.c. using an OV-17 column. Then the distillation residue was separated by Soxhlet extraction into hexane-soluble materials (HS), hexane-insoluble but benzene soluble (HS-B), and benzene-insoluble but THF-soluble materials (BIS).

2.3 Radioactivity Measurement

Specific activities of ^3H contained in these products were measured with a liquid scintillation counter. Colorless or light colored products were measured directly by dissolving them in the scintillator; but colored liquids, solids and gaseous products were oxidized to H_2O to avoid color quenching.

The amounts of hydrogen added and exchanged were estimated as follows: The amount of

hydrogen added from tetralin to pitch was calculated from the amounts of naphthalene, decalin and gaseous hydrogens produced on the basis of Eq. (1). The amounts of hydrogen exchanged between pitch and tetralin were calculated by subtracting the amount of hydrogen, which was added to pitch from tetralin, from the amount of hydrogen corresponding to the amount of tritium transferred to pitch on the basis of Eq. (2). The amounts of hydrogen transfers from solvent and pitch to gas phase were also calculated on the basis of Eqs. (3) and (4), in which it was assumed that radioactivities in gas phase were derived from gaseous hydrogen.

$$H_{\text{ad}} = 4N - H_{\text{S} \rightarrow \text{G}} \quad (1)$$

$$H_{\text{ex}} = \frac{H_{\text{int}} \times R_{\text{pitch}}}{R_{\text{total}}} - H_{\text{ad}} \quad (2)$$

$$H_{\text{S} \rightarrow \text{G}} = \frac{H_{\text{int}} \times R_{\text{gas}}}{R_{\text{total}}} \quad (3)$$

$$H_{\text{P} \rightarrow \text{G}} = H_{\text{gas}} - H_{\text{S} \rightarrow \text{G}} \quad (4)$$

N	: the amount of naphthalene formed	[mol]
H_{ad}	: the amount of hydrogen added from solvent to coaltar pitch	[g]
H_{ex}	: the amount of hydrogen exchanged between solvent and coal tar pitch	[g]
H_{int}	: the initial amount of hydrogen in solvent	[g]
$H_{\text{S} \rightarrow \text{G}}$	: the amount of hydrogen transferred from solvent to gas phase	[g]
$H_{\text{P} \rightarrow \text{G}}$	: the amount of hydrogen transferred from pitch to gas phase	[g]
H_{gas}	: the amount of gaseous hydrogen in gas phase after reaction	[g]
R_{total}	: total radioactivity	[dpm]
R_{pitch}	: radioactivity in pitch products	[dpm]
R_{gas}	: radioactivity in gas phase	[dpm]

3. Results and Discussion

The coal tar pitch for high performance carbon fiber (HPCF) was hydrogenated by a tritium labelled tetralin in the temperature range of 410 to 470°C. The distributions of products at each reaction temperature are shown in Fig. 2. The THFIS fraction in the raw coal tar pitch was 13.6 wt%. In the temperature range of 410 to 470°C, the THFIS fractions were about 5 wt% and did not change with rise in temperature. The distillation residue, including HS, HS-B and BIS fractions, was more than 80% in the temperature

Fig. 2 Distributions of Products (Symbols on a left vertical line represent raw pitch.)

range of 410 to 450°C. In comparison with the case of the raw material, the HIS-BS fraction decreased and the HS fraction increased at 410°C. Light oil was formed at 410°C while the BIS fraction did not change significantly. These show that the distillation residue fraction could be hydrogenated by tetralin solvent at temperature higher than 400°C in contrast with recent results which we obtained in the reaction of coal tar pitch with molecular hydrogen where polycondensation proceeded substantially¹²⁾. With rise in temperature from 410 to 450°C, the HIS-BS fraction increased and the HS fraction decreased. These clearly show that the condensation of HS fraction would proceed to yield HIS-BS fraction in this temperature range. At 450°C, HIS-BS reached the maximum, about 70 wt%. In order to make good carbon fiber from a pitch, one should hydrogenate the pitch to increase HIS-BS fraction. In the present case, therefore, the best raw material to make good carbon fiber was obtained at 450°C. On the other hand, the hydrocracking of coal tar pitch by tetralin also proceeded to increase gas and naphtha fractions with a rise in temperature from 410 to 470°C and to decrease BIS fraction at 470°C.

The distribution of recovered solvent after the reaction is shown in Fig. 3. The amounts of naphthalene and methylindan formed increased with rise in temperature while the amount of decalin formed slightly increased. At 470°C, about 10% of tetralin decomposed to naphtha fraction.

The distribution of tritium concentration in

Fig. 3 Distribution of Recovered Solvent

Fig. 4 Distributions of Tritium Concentration in Products

products is shown in Fig. 4. The tritium concentration in naphtha fraction was 30,000–45,000 dpm/g greater than those in other fractions, in the temperature range of 410 to 470°C. This indicated that the decomposition of tetralin to the naphtha fraction would proceed even at lower temperatures. The tritium concentrations in fractions other than naphtha increased with an increase in temperature.

The distribution of C/H ratios in distillation residue, the THFIS fraction and the sum of these are shown in Fig. 5. The C/H ratio in distillation

○: Distillation residue and THFIS, △: Distillation residue, □: THFIS

Fig. 5 Distributions of C/H Ratios in Distillation Residue and THF Insoluble (A symbol on a left vertical line represents raw pitch.)

residue gradually decreased with rise in temperature from 410 to 470°C, which shows that hydrogen molecules in tetralin were captured by the distillation residue. Although C/H ratio in the THFIS fraction was about twice as high as that of the distillation residue, the C/H ratio of the distillation residue and the THFIS fraction was low since the yield of the distillation residue was much greater than that of the THFIS fraction.

The balance of hydrogen transfer among three compositions, pitch, solvent and gas phase, are illustrated in Fig. 6. The amounts of hydrogen added and exchanged are represented by a solid line and a dotted line, respectively. The hydrogen contents in three phases after the reaction are shown in parentheses. As shown in Fig. 6, the amount of hydrogen release from either pitch or solvent to gas phase, which was calculated on the basis of Eqs. (3) and (4), increased with rise in temperature and the polycondensation of pitch seemed to increase with rise in temperature. In fact, the HS fraction decreased and the HIS-BS fraction increased with rise in temperature as shown in Fig. 2. The yield of HIS-BS reached the maximum at 450°C. The amounts of hydrogen added from solvent to pitch were almost the same, however, and the amount of THFIS was kept constant in the temperature range of 410 to 470°C. In our previous paper on the hydrogenation of coal tar pitch with gaseous hydrogen¹²⁾, the polycondensation proceeded, substantially, to increase THFIS fraction with rise in temperature from 300 to 400°C and prolonged time. In the present

Fig. 6 Hydrogen Balance of Three Compositions (The amounts of hydrogen in each phase after the reaction are given in parentheses.)

hydrogenation of pitch with tetralin, on the contrary, the THFIS fraction was kept to a low value, even at 470°C. These results suggest that there would be particular sites in the pitch which accepted hydrogen of tetralin and that tetralin would inhibit the increase of THFIS. The amount of hydrogen exchange between pitch and solvent increased significantly at 470°C. Since the decomposition of tetralin proceeded substantially at 470°C, it strongly suggested that radicals generated on tetralin would be related to the exchange reaction between pitch and tetralin.

In conclusion, although the release of hydrogen from pitch increased with rise in temperature, the increase of THFIS fraction was inhibited in the presence of tetralin and the yield of HIS-BS attained the maximum at 450°C.

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要 旨

炭素繊維原料としてのコールタールピッチの水素化機構 (第 2 報) トリチウムトレーサー法を用いたテトラリンから高性能 炭素繊維用コールタールピッチへの水素移行機構

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高性能炭素繊維の原料となるコールタールピッチのテトラリンによる水素化反応機構をトリチウムトレーサー法により水素の挙動および溶媒分別により生成物分布を調べることに検討した。反応はコールタールピッチ 60 g, トリチウムでラベルしたテトラリン 120 g, 反応温度 410~470°C, 反応時間 1 時間の条件で行った。溶媒分別には, ヘキサン, ベンゼン, およびテトラヒドロフランを用いた (Fig. 1)。テトラリン中の水素のピッチへの付加量およびテトラリンとピッチとの水素交換量は Eqs. (1) および (2) により計算した。

トリチウムでラベルしたテトラリンの水素はコールタールピッチに移行した。Fig. 2 に生成物分布を示した。THFIS は原料ピッチ中に 13.6% 含まれているが 410°C で約 5% まで減少

した。これは反応温度を上げても変化せず, 470°C でもピッチの重縮合による THFIS の増加は観察されなかった。高性能炭素繊維原料となる HIS-BS は温度の上昇とともに増加し 450°C で最大となった。470°C では一部の溶媒が分解しナフサが生成した (Fig. 3)。生成物中のトリチウム濃度は反応温度の上昇とともに向上した (Fig. 4)。溶媒, ピッチ, 並びに気相に放出された水素間の水素移行収支は Fig. 6 より, ピッチ, 溶媒ともに気相への水素ガスの放出量が反応温度の上昇とともに増加した。一方, 溶媒からピッチへの水素付加量は温度によらずほぼ一定であった。このことは, ピッチ中にテトラリンの水素を受け入れる特定の場所があり, またテトラリンが THFIS の増加を抑制している可能性を示唆した。

Keywords

Tritium, Coal tar pitch, Tetralin, Hydrogenation, Carbon fiber