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Mechanism of Thermal Dehydrogenation of Hydrotreated Pitch Using Tritium Tracer

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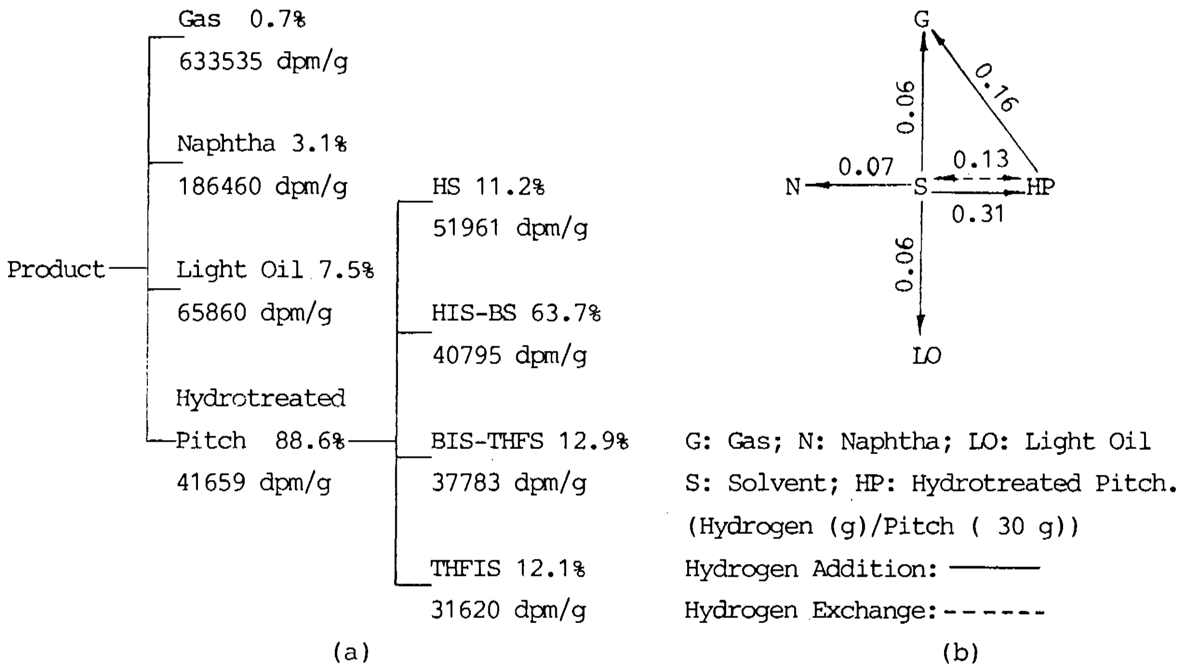
Behavior of hydrogen during the heat treatment of the tritiated coal tar pitch for high performance carbon fiber (HPCF) was investigated under nitrogen atmosphere by using a tritium as a tracer of hydrogen atoms. It was found that the reactions of carbon-carbon bond cleavage and the evaporation of volatile components were end up at about 600 °C. The dehydrogenation of polynuclear aromatic rings are sustained up to 1000 °C.

Recently, much attention has been focused on the upgrading of coal tar or petroleum pitch in order to manufacture HPCF from pitches. The hydrotreatment of pitch has been used to increase the fluidity of pitch, so as to easily produce the mesophase in the following heat treatment process.[1)] However, mechanisms of such processes as hydrogenation and carbonization of pitches, especially hydrogen movement in pitches, have not yet been clarified. In the present communication, we wish to deal with the mechanism of thermal dehydrogenation of the hydrotreated pitch by the use of tritium as a tracer of hydrogen atoms.

The pitch used in this study was the coal tar pitch which was supplied from Nitto Boseki Co.Ltd. Its elemental analysis was C, 91.5; H, 4.7; N, 1.3; O(diff.), 2.5wt%. The tritium labelled tetralin was prepared with the method described in the previous paper.[2)] The initial radioactivity in tetralin was 222521 dpm/g. The pitch and tritiated tetralin were put into 350 ml autoclave. The hydrotreatment reaction for coal tar pitch was carried out at 450 °C for 2 h. Products was separated into gas, naphtha, light oil and residual pitch by the distillation and a vacuum distillation. The residual pitch (the initial radioactivities were 41659 dpm/g) was used as a raw material for the following heat treatment.

Heat treatment of the hydrotreated pitch was carried out in a thermobalance. The pitch 0.05 g was packed into quarts basket and was heated from room temperature to 1000 °C at a constant rate (12 °C/min) under an atmosphere of nitrogen. After the heat treatment, the weight, radioactivity and C, H, N ratio were measured. Radioactivities in products were measured by the same procedures in previous paper.[3)]



G: Gas; N: Naphtha; LO: Light Oil
S: Solvent; HP: Hydrotreated Pitch.
(Hydrogen (g)/Pitch (30 g))
Hydrogen Addition: ———
Hydrogen Exchange: ------

Scheme 1. Mass and hydrogen balances after hydrotreating for pitch.
HS: Hexane soluble; HIS-BS: Hexane insoluble-benzene soluble; BIS-THFS: Benzene insoluble-tetrahydrofuran soluble; THFIS: Tetrahydrofuran insoluble.

The mass and hydrogen balances after the hydrotreating reaction of the pitch is shown in Scheme 1. The product and tritium distributions are summarized in Scheme 1-(a). HIS-BS fraction, a main product, was 63.7% of the hydrotreated pitch and the formation of THFIS was inhibited to 12.1% even at 450 °C. Tritium was introduced from tetralin into every fraction of products. As shown in Scheme 1-(b), hydrogenation of pitch proceeded along with hydrogen addition and exchange reaction. The amounts of added and exchange hydrogens were calculated from the amount of tritium transferred from the solvent to the reaction products as described in the previous paper.[4)] The amount of hydrogen added from solvent to pitch was 0.31 g. The amount of hydrogen exchanged between pitch and solvent was 0.13 g, which was smaller than that of

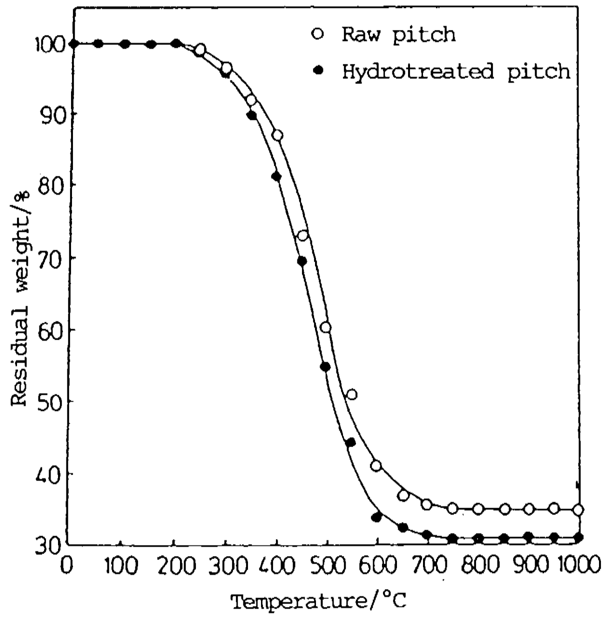


Fig. 1. Non-isothermal TG curves for raw and hydrotreated pitches at heating rate of 12 °C/min.

hydrogen added. The hydrotreatment of pitch by solvent was thought to proceed by a radical mechanism as in the hydrotreatment of petroleum heavy oil$^{5)}$ or liquefaction of coal.$^{6)}$ Hydrogen would be used to stabilize radicals produced by pyrolysis of pitch. Lighter fractions such as gas, naphtha and light oil were formed by hydrogen addition into radicals produced by pyrolysis of branched chain in aromatics. Considerable amounts of tritium were contained in the heavier fractions such as BIS-THFS and THFIS of pitch, which indicates that substantial hydrogen exchange reaction occurred.

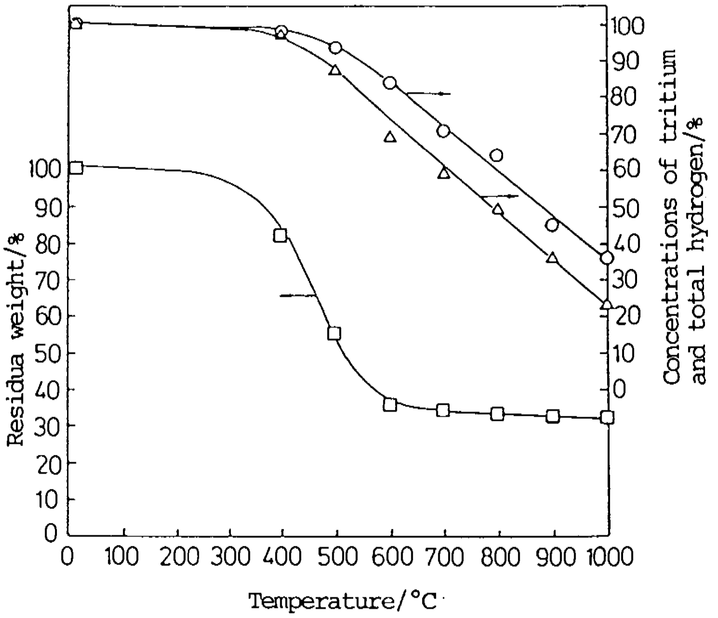


Fig. 2. Weight loss and change in tritium and total hydrogen concentrations with temperature in pyrolysis of tritiated pitch.
(The initial total hydrogen content in pitch was 5.14 wt%, and the initial tritium content was 45214 dpm/g. The experimental points were plotted on the basis of these initial values.)
○ Tritium △ Total hydrogen □ Weight

The features of the heat treatment of the raw and hydrotreated pitches were compared by non-isothermal TGA, and the results are shown in Fig. 1. The TG curves of both pitches are nearly similar, but the weight loss of the hydrotreated pitch in the final stage was more than that of the unhydrotreated pitch. It seems that the difference of weight loss is mainly due to the disparity in distillation range of raw and hydrotreated pitches. The amount of light fraction in the hydrotreated pitch is higher than that in unhydrotreated pitch. Therefore, the considerable differences on the features in the heat treatment can not be seen from the non-isothermal TG.

An important phenomenon could be found in Fig. 2, in which the pyrolysis of the tritiated pitch was performed from room temperature to 1000 °C. The amounts of tritium and hydrogen in pitch decreased with a rise in temperature from 400 °C to 1000 °C. The rate of decrease of hydrogen in the pitch was faster than that of tritium in the range of 400 °C to 600 °C, in which the rate of weight loss of pitch was fastest. The rates of decrease of tritium and hydrogen in pitch became same over 600 °C, in which the weight loss of pitch could be scarcely seen. The difference of concentration of tritium and hydrogen in pitch was formed in the range of 400 °C to 600 °C. This result indicates that hydrogen, which was not tritiated in preparation of tritiated pitch, was released in this temperature range, and can be explained as follows. Saturated hydrocarbons and branched chains in aromatics would be difficult to be tritiated, since tritium was introduced from tritiated tetralin to pitch without catalyst in preparation of the tritiated pitch. Pitch has such saturated hydrocarbon and branched chains in aromatics which would be released by pyrolysis in the range of 400 °C to 600 °C. The remarkable weight loss in the range of 400 °C to 600 °C supports this suggestion. Since the difference between tritium and hydrogen contents was kept constant over 600 °C, it was likely that all hydrogens, which was not tritiated, were released up to 600 °C. Further, since the weight loss could not be seen over 600 °C, it was thought that only tritiated hydrogens attached to aromatics were released and that the carbonization reaction of pitch was proceeding at this temperature range.

Table 1. Elemental analysis after heat treatments of the hydrotreated pitch

Heat treatment	Elemental composition/%				
temp /°C	C	H	N	O(diff.)	H/C
none	92.78	5.14	1.23	0.84	0.055
400	93.35	4.97	1.22	0.45	0.053
500	93.65	4.46	1.16	0.73	0.048
600	94.73	3.57	0.92	0.78	0.038
700	94.57	3.03	0.96	1.44	0.032
800	94.69	2.53	0.97	1.81	0.027
900	95.25	1.87	0.92	1.95	0.020
1000	97.27	1.20	0.88	0.65	0.009

In commercial production, spinning of pitch is usually performed in the range from 350 °C to 400 °C,[7] in which the primary process is the removal of smaller molecules and the formation of small mesophase spheroid.[1] When the pitches are heat-treated at higher temperatures, they undergo a series of physical and chemical transformations to form an infusible hydrocarbon polymer designated as coke. The conversion of pitch to coke generally involves an intermediate liquid crystalline state designated as mesophase pitch.[8] As the coke are heated to about 1000 °C, the removal of residual hydrogen and some of the substituent heteroatoms produces a disordered carbon substantially free from hydrogen. In addition, the molecular weight of pitch increases when it transforms to coke as a result of both polymerization of aromatic molecules and distillation of smaller molecules.[9] As presented in Table 1, the ratio of H/C was decreased from 0.055 to 0.009, and the nitrogen and the oxygen were decreased from 1.23 and 0.84 (%) to 0.88 and 0.65 (%) respectively, with a rise from room temperature to 1000 °C. In our case, heat-treatment of pitch would also proceed in a same way as described above.

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