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Dehydrogenation of Hydroaromatic Components in Coal-Derived Hydrocarbons for Structural Analysis

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Synopsis. The dehydrogenation technique was evaluated by using several cyclic hydrocarbons, and was successfully used to convert hydroaromatic components in coal-derived nonpolar fractions into the corresponding aromatic compounds.

Detailed analyses of coal-derived liquids are required for the development of coal liquefaction and utilization. Since coal-derived liquids include many hydrogenated homologues of polyfused aromatic compounds, dehydrogenation must be a useful pretreatment for structural analyses.[1-3)]

The purpose of this work was to evaluate the dehydrogenation technique by using several cyclic hydrocarbons and to apply this technique to the dehydrogenation of coal-derived hydrocarbons.

Experimental

The standard hydroaromatic mixture was produced from the hydrogenation of 1-methylnaphthalene, fluorene, phenanthrene, fluoranthene, and pyrene over a presulfided Ni-Mo/Al_2O_3 catalyst at 375 °C for 1 h. Their conversions were 91, 12, 74, 92, and 68%, respectively. Anthracene and 1,1′-binaphthyl were individually hydrogenated under the same conditions and the conversions were 99% for anthracene and 100% for 1,1′-binaphthyl. Other organic compounds were used as received.

Two samples derived from coal were used in this work. Sample A was a nonpolar fraction in the 280—450 °C middle distillate, which was produced from Wandoan coal in tetralin at 450 °C for 1 h. Sample B was a nonpolar fraction separated from the 250—400 °C middle distillate, which was produced by the further hydrocracking of Wandoan coal-derived asphaltene over a presulfided Ni-Mo/Al_2O_3 catalyst at 375 °C for 2 h.

200 mg of a 5%-Pt/Al_2O_3 catalyst was placed in the three-necked flask(20 cm×2 cm, Fig. 1) and activated at 350 °C for 1 h in a H_2 stream. 500 mg of a sample was dropped and treated at 325 °C for 1 h in a H_2/N_2 (1:1) stream. The temperature was controlled at the outer wall of the flask and the inner temperature was also determined. The product was cooled to room temperature in a N_2 stream, and analyzed by using a capillary GC and GC/MS.

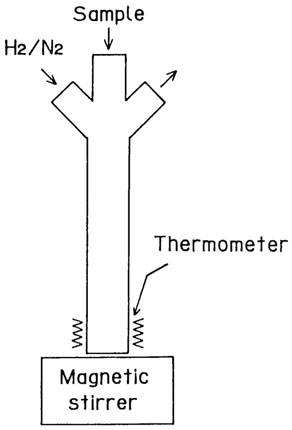

Fig. 1. Reaction apparatus for dehydrogenation.

Results and Discussion

Chromatograms of the standard hydroaromatic mixture and the dehydrogenated product (Fig. 2) showed that the dehydrogenation proceeded satisfactorily. The hydroaromatic components were converted over 90% into the corresponding aromatic compounds (Table 1). The set temperature was 325 °C but the real reaction temperature was 275 °C because the reaction system contained lower-boiling-point compounds, such as hydrogenated 1-methylnaphthalenes and 1-methylnaphthalene (bp 242 °C).

Cyclohexylbenzene, dodecylcyclohexane, hydrogenated anthracene, and hydrogenated 1,1′-binaphthyl were added to the standard mixture individually and dehydrogenated under the same conditions. The hydroaromatic components in the standard mixture were dehydrogenated sufficiently in all experiments, and hydrogenated 1,1′-binaphthyl was dehydrogenated over 95%. However, conversions of the other cyclic hydrocarbons were not sufficient (65% for cyclohexylbenzene, 72% for hydrogenated anthracene and 49% for dodecylcyclohexane). The dehydrogenation of their compounds might require a higher temperature than 275 °C. An attempt was again made to dehydrogenate a mixture of hydrogenated anthracene and dodecylcyclohexane at 325 °C (inner temperature 310 °C).

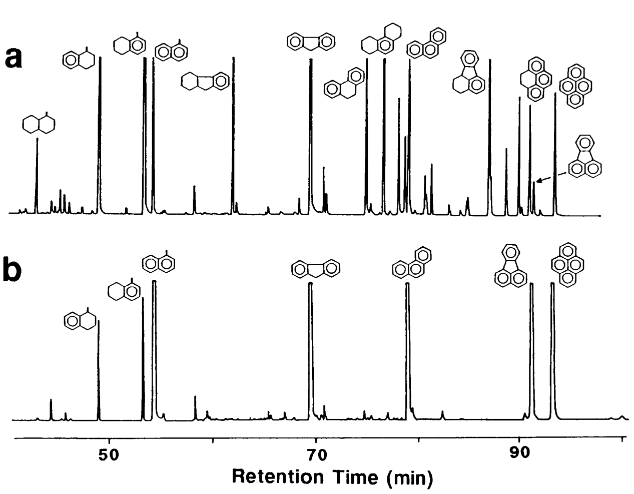

Fig. 2. Gas chromatograms of standard hydroaromatic mixture(a) and the dehydrogenated product(b).

Table 1. Dehydrogenation of Standard Hydroaromatic Mixture

Aromatic compound	Content of aromatic compound/%[a]						
	Feed[c]	Additive[b]					
		none	O1	O2	O3	S	N
1-Methylnaphthalene	9	94	93	94	93	28	76
Fluorene	88	100	100	100	100	97	98
Phenanthrene	26	98	96	97	99	78	94
Fluoranthene	8	100	100	100	99	100	99
Pyrene	32	100	99	99	99	99	99

325 °C, 1 h, Each additive is 5 wt% of the standard mixture. a) in the corresponding homologues. b) O1: dibenzofuran, O2: 1,1′-biphenyl-2-ol, O3: anthrone, S: dibenzothiophene, N: benzo[*h*]quinoline. c) The composition of each hydrogenated homologues is; 10H(decahydro-) 2%, 4H 89% for 1-methylnaphthalene, 6H 12% for fluorene, 12H 1%, 8H 40%, 4H 14%, 2H 19% for phenanthrene, 10H 28%, 4H 64% for fluoranthene, 10H 9%, 6H 36%, 2H 23% for pyrene.

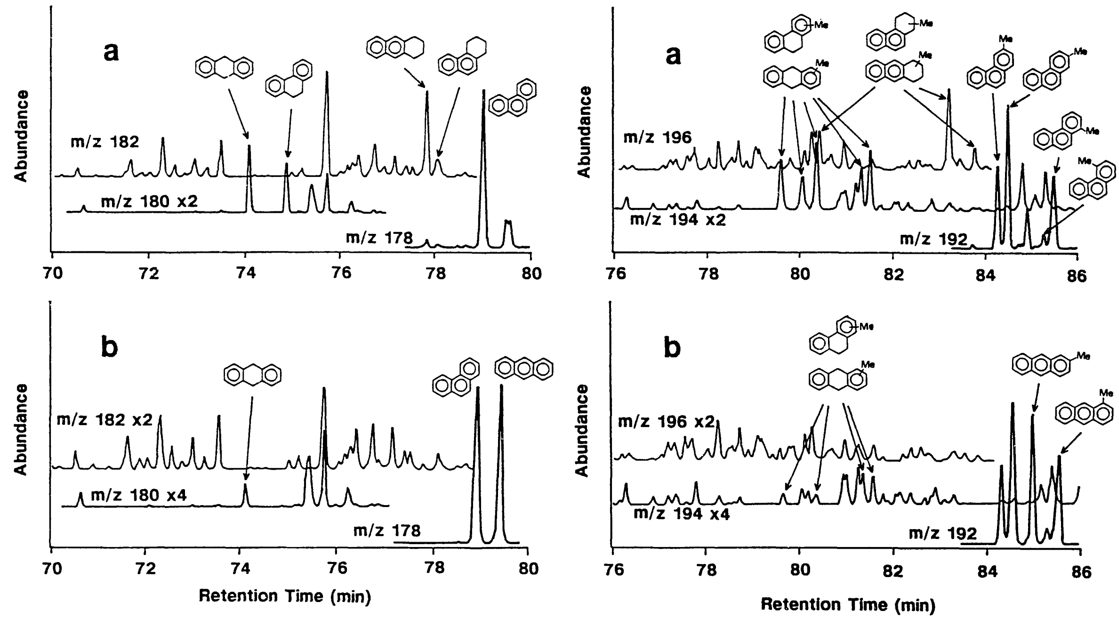

Fig. 3. Single ion chromatograms of *m/z* 178, 180, 182 and *m/z* 192, 194, 196 for Sample A, coal-derived nonpolar distillate(a), and the dehydrogenated product(b).

Anthracene and dodecylbenzene were produced over 95% from the corresponding hydroaromatic compounds. Therefore, if a sample does not contain relatively low-boiling-point components, the dehydrogenation will proceed sufficiently.

Coal-derived liquids contain some kinds of heteroaromatic compounds; each of the heteroaromatic compounds was added to a standard mixture and dehydrogenated individually (Table 1). The oxygen-containing compounds had little effect on the dehydrogenation, but dibenzothiophene depressed the conversion remarkably.

This dehydrogenation method was applied to structural analyses of coal-derived hydrocarbons. Sample A, coal-derived nonpolar distillate, was dehydrogenated and the product was analyzed by GC/MS. Figure 3 shows ion chromatograms of *m/z* 178, 180, 182 and *m/z* 192, 194, 196. Dihydro(2H)- and tetrahydro(4H)-phenanthrenes were converted to phenanthrene completely, and 2H/4H-anthracenes were sufficiently converted to anthracene, although a small amount of 2H-anthracene remained. Hydrogenated anthracene was one of the hydroaromatic compounds difficult to be dehydrogenated; therefore, the high conversion of 2H/4H-anthracenes implied that almost all hydroaromatic components in this sample were sufficiently converted to the corresponding aromatic compounds. The peaks unaffected by the dehydrogenation treatment were the other compound-types, such as fluorenes (*m/z* 180, 194) and acenaphthenes/dibenzofurans (*m/z* 182, 196).

Sample B, asphaltene-derived nonpolar distillate, contained much larger amounts of hydroaromatic compounds (Fig. 4a), and the assignment of each peak was more difficult due to a lack of authentic samples. However, the dehydrogenated product afforded a much simpler gas chromatogram (Fig. 4b), which consisted of aromatic compounds well-known to be

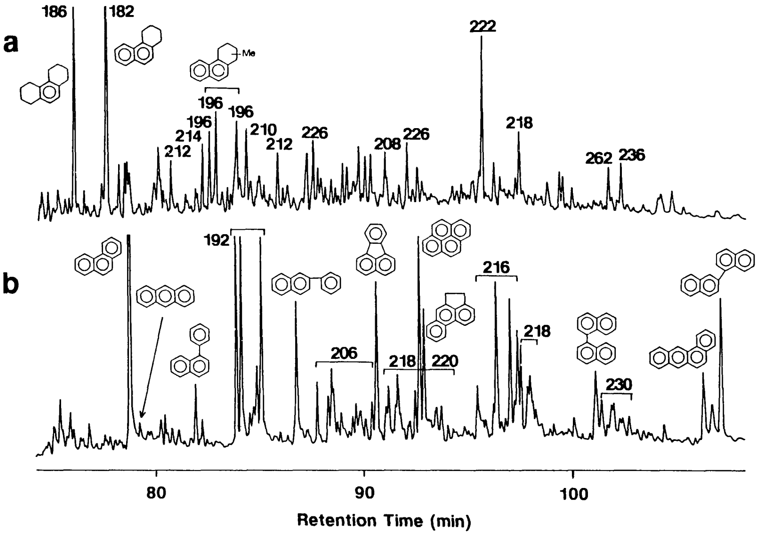

Fig. 4. Gas chromatograms of Sample B, asphaltene-derived nonpolar distillate(a), and the dehydrogenated product(b).

present in anthracene oil[4] such as phenanthrene, phenylnaphthalenes, fluoranthene, pyrene, benzacenaphthene, benz[*a*]anthracene, binaphthyls and their alkylated derivatives.

This work demonstrated that the dehydrogenation of hydroaromatic compounds proceeded sufficiently over a Pt/Al_2O_3 catalyst and that dehydrogenation is a very useful pretreatment for structural analyses of coal-derived hydrocarbons.

References

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